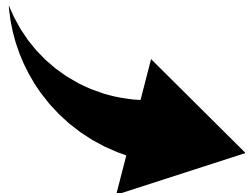


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# ARJUNA

*for*

## JEE

# CHEMISTRY

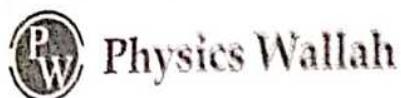
Full Course Study Material

XI

SOLUTIONS

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# PREFACE

A highly skilled professional team of Physics Wallah (PW) works arduously to ensure that the students receive the best content for the JEE exam.

From the beginning, the whole content team comprising Associate faculties, DTP operators, Proofreaders and others are involved in shaping the material to their best knowledge and experience to produce powerful content for the students.

Faculties have adopted a new style of presenting the content in easy-to-understand language and have provided the team with their guidance and supervision throughout the creation of this Study Material.

Physics Wallah (PW) strongly believes in conceptual and fun-based learning. PW provides highly exam-oriented content to bring quality and clarity to the students.

A plethora of **JEE Study Material** is available in the market but PW professionals are continuously working to provide the supreme Study Material for our **JEE** students.

This Study Material adopts a multi-faceted approach to master and understanding the concepts by having a rich diversity of questions asked in the examination and equip the students with the knowledge for the competitive exam.

The main objective of the study material is to provide a large number of quality problems with varying cognitive levels to facilitate the teaching-learning of concepts that are presented through the book.

It has become popular among aspirants because of its easy-to-understand language and clear illustrations with diagrams, mnemonics, flow charts and tables.

Students can benefit themselves by attempting the exercise given in this Study Material for the self-assessment and also mastering the basic techniques of problem-solving.

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Mastering the Physics Wallah (PW) study material curated by the PW team, the students can easily qualify for the exam with a Top Rank in the **JEE**.

In each chapter, for better understanding, questions have been classified according to the latest syllabus of **JEE**

- The nature and diversity of the questions help students to ace the examination
- Quality questions to strengthen the concept of the topic at the zenith level

## BOOK FEATURES

- Detailed theory with Train Your Brain and Concept Application Questions
- Short Notes & Solved Miscellaneous Examples
- Topicwise, Learning Plus & Advance Level MCQs covered in exercises
- Match the Column, Comprehension Based, Numerical Type and Multicorrect questions covered for complete practice.
- JEE Past Year Questions
- Elaborated Solutions



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# CHAPTER

# 1

# Some Basic Concepts of Chemistry

## Exercise-1 (Topicwise)

1. (a) All chemical compounds are found to have constant composition irrespective of their method of preparation and sources.
2. (c) Nitrogen equivalent weight is variable.
3. (a)  $\frac{1}{12}$  of C-12
4. (b) In chemical scale, the relative mass of the isotopic mixture of oxygen atoms ( $O^{16}$ ,  $O^{17}$ ,  $O^{18}$ ) is assumed to be equal to 16.00.
5. (b) 1 Mole of  $CH_4$  contains 4 mole of hydrogen atom i.e. 4g atom of hydrogen.
6. (a)  $\because 5.8L$  of gas has mass = 7.5 gm  
 $\therefore 22.4L$  of gas has mass =  $\frac{7.5}{5.8} \times 22.4 = 28.96$   
So molecular weight = 29  
So, molecular formula of compound is NO
7. (d)  $\because 17gm$   $NH_3$  contains  $6 \times 10^{23}$  molecules of  $NH_3$   
 $\therefore 4.25gm$   $NH_3$  contains =  $\frac{6 \times 10^{23}}{17} \times 4.25$   
 $\therefore$  No. of atoms =  $\frac{6 \times 10^{23} \times 4.25}{17} \times 4 = 6 \times 10^{23}$
8. (a)  $\because 1L$  of gas at S.T.P. weight 1.16g  
 $\therefore 22.4 L$  of gas at S.T.P. weight =  $22.4 \times 1.16 = 25.984 \approx 26$   
This molecular weight indicates that given compound is  $C_2H_2$ .
9. (a)  $6 \times 10^{23}$  molecules has mass = 18 gm  
1 molecules has mass =  $\frac{18}{6 \times 10^{23}} = 3 \times 10^{-23}$  gm  
 $= 3 \times 10^{-26}$ .
10. (a) 14 gm  $N^{3-}$  ions have =  $8N_A$  valence electrons  
4.2 gm of  $N^{3-}$  ions have =  $\frac{8N_A \times 4.2}{14} = 2.4N_A$
11. (b)  $\because 22400 ml$  at NTP has  $6.023 \times 10^{23}$  molecule  
 $\therefore 1 ml$  at NTP has =  $\frac{6.023 \times 10^{23}}{22400}$   
 $= 0.0002688 \times 10^{23} = 2.69 \times 10^{19}$ .

12. (b)  $\because 22400cc$  of gas at STP has molecules  
 $\therefore 1.12 \times 10^{-7}$  of gas at STP has  
 $\frac{6 \times 10^{23} \times 1.12 \times 10^{-7}}{22400} = .03 \times 10^{14} = 3 \times 10^{12}$ .
13. (a)  $\because 2.24L$  of gas has mass = 4.4gm  
 $\therefore 22.4L$  of gas has mass =  $\frac{4.4}{2.24} \times 22.4 = 44$   
So given gas is  $CO_2$  because  $CO_2$  has molecular mass = 44.
14. (a) 44g of  $CO_2$  has  $2 \times 6 \times 10^{23}$  atoms of oxygen  
4.4g of  $CO_2$  has =  $\frac{12 \times 10^{23}}{44} \times 4.4$   
 $= 1.2 \times 10^{23}$  atoms.
15. (c)  $\because 100gm$   $CaCO_3$  =  $6.023 \times 10^{23}$  molecules  
 $\therefore 10gm$  =  $CaCO_3 = \frac{6.023 \times 10^{23}}{100} \times 10$   
 $= 6.023 \times 10^{22}$  molecule  
1 molecule of  $CaCO_3$  = 50 protons  
 $6.023 \times 10^{22}$  molecule of  $CaCO_3$  =  $50 \times 6.023 \times 10^{22}$   
 $= 3.0115 \times 10^{24}$
16. (c) According to Avogadro's hypothesis equal volumes of all gases under similar conditions of temperature and pressure contains equal no. of molecules.
17. (d)  $d = \frac{M}{V}$  density, M = mass, V = volume  
Since  $d = 1$   
So,  $M = V$   
 $18gm = 18ml$   
 $18ml = N_A$  molecules ( $N_A$  = avogadro's no.)  
 $1000ml = \frac{N_A}{18} \times 1000 = 55.555 N_A$
18. (b) 2gm of oxygen contains atom =  $\frac{2}{16} = \frac{1}{8}$  mole  
also 4g of sulphur =  $\frac{4}{32} = \frac{1}{8}$  mole.
19. (a) 100 gm caffeine has 28.9 gm nitrogen  
194 gm caffeine has =  $\frac{28.9}{100} \times 194 = 56.06$  gm  
 $\therefore$  No. of atoms in caffeine =  $\frac{56.06}{14} \approx 4$ .

20. (a)  $\because$  40 gm NaOH contains 16 gm of oxygen  
 $\therefore$  100 gm of NaOH contains  $\frac{16}{40} \times 100 = 40\%$  oxygen.

21. (d) C = 24 gm, H = 4 gm, O = 32 gm  
 So, Molecular formula =  $C_2H_4O_2$   
 So, Empirical formula =  $CH_2O$   
 (Simplest formula).

22. (c) In  $Fe(CNS)_3 \cdot 3H_2O$

$$\% \text{ of } H_2O = \frac{3 \times 18}{284} \times 100 = 19\%$$

Element	At.wt	Mole	Ratio	Empirical formula
C = 86%	12	7.1	1	$CH_2$
H = 14%	1	14	2	Belongs to alkene

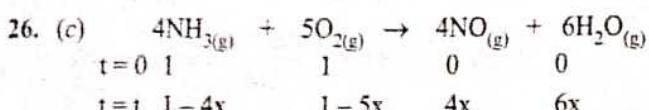
Element	%	At.wt.	Ratio
X	50	10	5
Y	50	20	2.5

Simplest formula =  $X_2Y$

$$25. (c) N = \frac{W(\text{gm}) \times 1000}{V \times \text{Eq.wt.}}$$

1500 ml of 0.1N HCl = 150 ml (N)

$$1 = \frac{W(\text{gm}) \times 1000}{150 \times 40}, W(\text{gm}) = \frac{150 \times 40}{1000} = 6 \text{ gm.}$$



Oxygen is limiting reagent

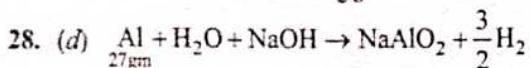
$$\text{So, } X = \frac{1}{5} = 0.2 \text{ all oxygen consumed}$$

$$\text{Left } NH_3 = 1 - 4 \times 0.2 = 0.2.$$

27. (c)  $\because$  100 gm Hb contain = 0.33 gm Fe

$$\therefore 67200 \text{ gm Hb} = \frac{67200 \times 0.33}{100} \text{ gm Fe.}$$

$$\text{gm atom of Fe} = \frac{672 \times 0.33}{56} = 4.$$

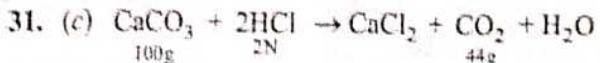


$$\frac{3}{2} \times 22.4 = 33.6 \text{ L}$$

29. (c) 0.1 M  $AgNO_3$  will react with 0.1 M  $NaCl$  to form 0.1 M  $NaNO_3$ . But as the volume is doubled, conc. of  $NO_3^- = \frac{0.1}{2} = 0.05 \text{ M}$

30. (b)  $Mg^{2+} \equiv H_2$

$$n = \frac{12 \text{ gm}}{24 \text{ gm}} = \frac{1}{2} \text{ mole of } H_2$$



100 g  $CaCO_3$  with 2 N HCl gives 44 g  $CO_2$

100 g with  $CaCO_3$  with 1 N HCl gives 22 g



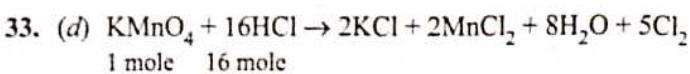
$$\text{moles of } I_2 = \frac{5}{127}$$

1 mole  $I_2$  reacts with 10 moles of  $HNO_3$

$$\frac{5}{127} \text{ moles of } I_2 \text{ reacts with} \rightarrow 10 \times \frac{5}{127}$$

$$= 0.393$$

$$\text{Wt. of } HNO_3 = 0.393 \times 63 \\ = 24.8 \text{ g}$$

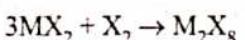
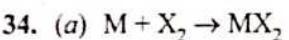


$$1 \text{ mole} \quad 16 \text{ mole}$$

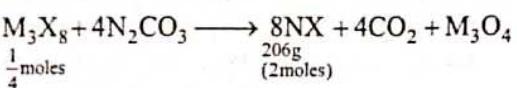
2 mole of  $KMnO_4$  produces 5 moles of  $Cl_2$

$$1 \text{ mole of } KMnO_4 \text{ will produce} \rightarrow \frac{5}{2} \text{ mole of } Cl_2$$

$$2.5 \text{ moles} \times 22.4 \\ = 56 \text{ litre of } Cl_2$$



$$\frac{3}{4} \text{ moles} \quad \frac{1}{4} \text{ moles}$$



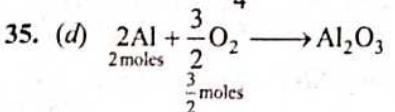
8 moles of NX produced by  $\rightarrow 1$  moles  $M_3X_8$

so, 2 moles of NX will be produced by  $\rightarrow \frac{1}{4}$  mole  $M_3X_8$

$\therefore \frac{1}{4}$  mole  $M_3X_8$  is produced by  $\rightarrow 3 \times \frac{1}{4}$  mole  $MX_2$

$\therefore \frac{3}{4}$  moles of  $MX_2$  is produced by  $\rightarrow \frac{3}{4}$  moles of M

$$\text{wt. of M} = \frac{3}{4} \times 56 = 42 \text{ g}$$



2 moles Al reacts with  $\rightarrow \frac{3}{2}$  moles of  $O_2$

$\therefore 1$  mole Al reacts with  $\rightarrow \frac{3}{4}$  moles of  $O_2$

$$\text{wt. of } O_2 = \frac{3}{4} \times 32 = 24 \text{ g}$$

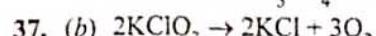
36. (d) Balanced eq<sup>n</sup>.



0.5 moles 0.2 moles

(L.R)

2 moles  $\text{Na}_3\text{PO}_4$  react with  $\rightarrow$  1 mole of  $\text{BaCl}_2$   
 $\therefore$  0.2 mole  $\text{Na}_3\text{PO}_4$  react with  $\rightarrow$  0.1 mole



3 moles of  $\text{O}_2$  is produced by = 2 moles of  $\text{KClO}_3$

$$\therefore \frac{1}{3} \text{ mole of } \text{O}_2 \text{ is produced by} = \frac{2}{3} \times \frac{1}{2} = \frac{1}{3} \text{ moles}$$

of  $\text{KClO}_3$



0.5 0.2 ?

(L.R)

1 mole of  $\text{Ca}(\text{OH})_2$  produce  $\rightarrow$  1 mole  $\text{CaSO}_4$   
 $\therefore$  0.2 mole of  $\text{Ca}(\text{OH})_2$  will produce  $\rightarrow$  0.2 mole  $\text{CaSO}_4$

39. (d)  $\text{H}_3\text{PO}_4$  is tribasic so N = 3 M =  $3 \times 1 = 3$

40. (c) Number of moles of NaOH

$$= \frac{\text{given mass of NaOH}}{\text{molar mass}} = \frac{10^{-3}}{40}$$

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in mL}} \times 1000$$

$$\text{Molarity} = \frac{10^{-3} \times 1000}{40 / 250} = 10^{-4} \text{ M}$$



1 mole of HCl is neutralized by 1 mole (40 g) of NaOH.

100 ml of 0.1N HCl corresponds to 0.01 moles.

Thus, 0.01 mole of HCl is neutralized by 0.01 mole (or 0.4 g) of NaOH.

42. (b) For hydrated oxalic acid,  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , molar mass is 126 g/mol.

$$\text{Equivalent weight} = \frac{M}{2} = 63$$

$$\text{Meq. of oxalic acid} = 500 \times 0.1 = 50$$

$$\frac{w}{E \times 1000} = 50$$

$$w = \frac{126}{2} \times 50 \times 1000 = 3.15 \text{ g}$$

Hence, mass of oxalic acid required is 3.15 g.

43. (c)  $M_{\text{H}_2\text{SO}_4} = 18\text{M} = 18$  mole of  $\text{H}_2\text{SO}_4$  in 1 litre solution  
density = 1.8 g/mL (given)

so, Mass of Sol<sup>n</sup> =  $1.8 \times 1000 = 1800 \text{ g}$

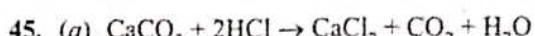
Mass of Solute =  $18 \times 98 = 1760$

$\therefore$  Mass of solvent =  $1800 - 1760$

= 36 g

$$\text{Molality} = \frac{18}{36(\text{g})} \times 1000 = 500 \text{ molal}$$

$$44. (c) \% \text{ w/w} = \frac{110 \times 10^{-3}}{100} = 0.11\%$$



0.02 0.05

L.R

1 mole of  $\text{CaCO}_3$  produce  $\rightarrow$  1 mole of  $\text{CO}_2$

So 0.02 mole  $\text{CaCO}_3$  will produce  $\rightarrow$  0.02 moles of  $\text{CO}_2$

Volume of  $\text{CO}_2$  evolved =  $0.02 \times 22.4$

$$= 0.448 \text{ L}$$



Dibasic acid NaOH

Here,

$$\text{N}_1 = \frac{w}{E} = \frac{0.16}{E}$$

$$\text{V}_1 = 1000$$

$$\text{N}_1 = \frac{1}{10}$$

$$\text{V}_2 = 25 \text{ mL}$$

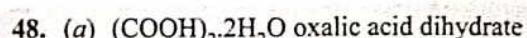
$$\frac{0.16}{E} \times 1000 = \frac{1}{10} \times 25$$

$$\frac{160}{E} = \frac{25}{10}$$

$$E = \frac{1600}{25} = 64$$

$$M = 2 \times E = 2 \times 64 = 128 \text{ g}$$

47. (a) One molal solution is one that contains one mole of a solute in 100g of the solvent.



$$\text{Molarity} = \frac{6.3}{126} \times \frac{1}{250} \times 1000 = 0.2 \text{ M}$$

No. of equivalents of oxalic acid = No. of equivalents of NaOH

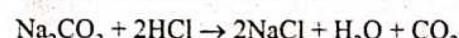
$$\text{N}_1\text{V}_1 = \text{N}_2\text{V}_2$$

$$0.2 \times 2 \times 10 = 0.1 \times \text{V}_2$$

$$0.4 \times 10 = 0.1 \times \text{V}_2$$

$$\text{V}_2 = 40 \text{ mL}$$

49. (c) Methyl orange indicator gives the end point corresponding to 100% of sodium carbonate.



$$20 \times x = 10 \times 0.1 + 5 \times 0.2 \times 2$$

$$x = 0.15 \text{ M}$$

50. (a) 2.5 mL of 0.1 M  $\text{H}_2\text{SO}_4$  = 2.5 mL of 0.2  $\text{NH}_2\text{SO}_4$

$$= \frac{1}{2} \text{ Na}_2\text{CO}_3 \text{ present in 10 mL of mixture}$$

So,

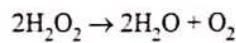
5 mL of 0.2 N  $\text{H}_2\text{SO}_4$  =  $\text{Na}_2\text{CO}_3$  present in 10 mL of mixture



$\equiv 5 \text{ mL of } 0.2 \text{ N Na}_2\text{CO}_3$   
 $\equiv \frac{0.2 \times 53}{1000} \times 5 = 0.053 \text{ g}$   
 Amount of  $\text{Na}_2\text{CO}_3 = \frac{0.053}{10} \times 1000 = 5.3 \text{ g/L of mixture}$   
 Between first and second end points,  
 $= 2.5 \text{ mL of } 0.2 \text{ M H}_2\text{SO}_4 \text{ used}$   
 $= 2.5 \text{ mL of } 0.4 \text{ N H}_2\text{SO}_4 \text{ used}$   
 $= 5 \text{ mL of } 0.2 \text{ N H}_2\text{SO}_4 \text{ used}$   
 $\equiv \frac{1}{2} \text{ Na}_2\text{CO}_3 + \text{NaHCO}_3 \text{ present in } 10 \text{ mL of mixture}$   
 $(5 - 2.5) \text{ mL } 0.2 \text{ N H}_2\text{SO}_4$   
 $\equiv \text{NaHCO}_3 \text{ present in } 10 \text{ mL of mixture}$   
 $\equiv 2.5 \text{ mL } 0.2 \text{ N NaHCO}_3$   
 $\equiv \frac{0.2 \times 84}{1000} \times 2.5 = 0.042 \text{ g}$   
 Amount of  $\text{NaHCO}_3 = \frac{0.042}{10} \times 1000$   
 $= 4.20 \text{ g/L of mixture.}$

51. (a)  $24 \text{ dm}^3 \rightarrow 1 \text{ mole of O}_2 \text{ gas.}$

$$3 \text{ dm}^3 \rightarrow \frac{3}{24} = \frac{1}{8} \text{ mole of O}_2 \text{ gas}$$



$$n_{\text{H}_2\text{O}_2} = 2 \times n_{\text{O}_2} = 2 \times \frac{1}{8} = \frac{1}{4} \text{ moles}$$

$$\therefore X \times 0.1 = 0.25$$

$$X = 2.5$$

## Exercise-2 (Learning Plus)

1. (c) In  $\text{Ca}_3(\text{PO}_4)_2$

$$\frac{\text{mole of Ca atom}}{\text{mole of O atom}} = \frac{3}{8}$$

$$\text{Mole of 'O' atom} = \frac{8}{3} (\text{mole of Ca atom})$$

$$\text{Mole of 'Ca' atom} = 3$$

2. (a)  $\text{H}_2\text{SO}_4 \quad \text{Al}_2(\text{SO}_4)_3$

$$\downarrow \quad \downarrow$$

$$32 \quad 3 \times 32$$

$$\text{so total molecular mass} = 98$$

$$\frac{1}{3} (\text{Al}_2(\text{SO}_4)_3)$$

$$\downarrow$$

$$\frac{1}{3} \times 342$$

$$\downarrow$$

$$114$$

$$\frac{98}{114} = 0.86$$

$$3. (c) (a) n = \frac{10 \times 1}{18} = 0.55$$

$$(b) n = 0.1 \times 5 = 0.5$$

$$(c) n = \frac{12}{48} \times 3 = 0.75$$

$$(d) n = \frac{N}{NA} = 0.2 \times 2 = 0.4$$

4. (a)  $3.9854 \times 10^{-23} \text{ g of element} = 1 \text{ atom.}$

$$1 \text{ g of element} = \frac{1}{3.9854 \times 10^{-23}}$$

$$= 2.509 \times 10^{22}$$

$$5. (c) (a) n = \frac{12}{12} = 1$$

$$(b) n = \frac{8}{16} = 0.5$$

$$(c) n = \frac{32}{32} = 1$$

$$(d) n = \frac{24}{24} = 1$$

$$6. (b) \text{ Moles of Mg}_3(\text{PO}_4)_2 = \frac{1}{8} \times 0.25 = 3.125 \times 10^{-2}$$

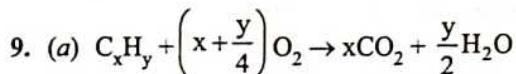
	C	H	O
Mass	24	8	32
Moles	24	8	32
	12	1	16
Ratio	2	8	2
Simple integer ratio	1	4	1
Hence empirical formula is $\text{CH}_4\text{O}$			

8. (a) X Y

$$\frac{75.8}{75} \quad \frac{24.2}{16}$$

$$1.01 \quad 1.5 \times 2$$

$$2 \quad 3$$



$$a \left( x + \frac{y}{4} \right) a \quad ax \quad \frac{ay}{2}$$

$$a + \left( x + \frac{y}{4} \right) a = 600 \quad \dots(i)$$

$$ax + a \frac{y}{2} = 700 \quad \dots(ii)$$

(i) divide by (ii)

$$7 + x = 5y/4$$

$$x < 5$$

put the value

$$\text{if } x = 3 \quad 10 = 5y/4 \quad y = 8$$

Ans. is  $\text{C}_3\text{H}_8$

10. (d) Mole fraction of  $H_2O = 1 - 0.25 = 0.75$

$$\frac{X_{C_2H_5OH}}{X_{C_2H_5OH} + X_{H_2O}} = \frac{n_{C_2H_5OH}}{n_{C_2H_5OH} + n_{H_2O}} \text{ or wt. \%}$$

$$= \frac{0.25 \times 46}{0.25 \times 46 + 0.75 \times 18} \times 100 = 46\%$$

11. (c)  $CO_2 = 132 \text{ g} = \frac{132}{44} \text{ mole} = 3 \text{ mole}$

$$H_2O = 54 \text{ g} = \frac{54}{18} \text{ mole} = 3 \text{ mole}$$

$\Rightarrow C$  atoms = 3 mole

H atoms = 6 mole

12. (a)  $Fe_2O_3 = \frac{2 \times 56}{3 \times 16} = \frac{7}{3}$

$$FeO = \frac{56}{16} = \frac{7}{2}$$

$$\therefore Fe_2O_3 : FeO = \frac{7}{3} \times \frac{7}{2} = 3 : 2$$

13. (a) Amount of butter =  $\frac{2 \times 10^{-3}}{5.5 \times 10^{-6}} = 363.6 \text{ gm}$

14. (b) According to question, atomic ratio of metal and oxide is 2:3

$\therefore$  formula =  $M_2O_3$

$$\% \text{ of Oxygen} = \frac{\text{Mass of Oxygen}}{\text{Mol. mass of oxide}} = \frac{30}{100}$$

$$= \frac{16 \times 3}{2M + (16 \times 3)} = \frac{30}{100}$$

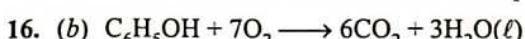
$$\text{or } M = \frac{160 - 48}{2} \\ = 56 \text{ g}$$

15. (a) 2 moles of  $SO_2$  will react with 1 mole of  $O_2$  to form 4 moles of  $SO_3$ . 8 moles of  $SO_2$  will react with 4 moles of  $O_2$  to form 8 moles of  $SO_3$ .

Hence,  $10 - 8 = 2$  moles of  $SO_2$

and  $15 - 4 = 11$  moles of  $O_2$

did not enter into the combination respectively.



30 ml

$6 \times 30 = 180 \text{ ml}$  of  $CO_2$  is produced

Volume used initially

$$= 30 + 210 = 240$$

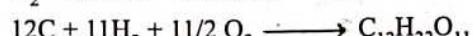
(for  $C_6H_5OH$ ) (for  $O_2$ )

change in volume =  $240 - 180 = 60 \text{ ml}$

17. (b)  $C = 84/12 = 7 \text{ mole}$

$H_2 = 12 \text{ g} = 6 \text{ mole}$

$O_2 = 56/22.4 = 5/2 \text{ mole}$



L.R. =  $O_2$

11/2 mole  $O_2$  produce 1 mole sucrose

5/2 mole  $O_2$  will form 5/11 mole sucrose

mass of sucrose =  $5/11 \times (\text{mol. mass})$

$$= 5/11 \times 342$$

$$= 155.45 \text{ g}$$

18. (a) Let volume is  $V \text{ ml}$



$$\text{mole } 0.2 \text{ V} \quad 40 \times 0.1$$

$$\text{moles of } H_2SO_4 \text{ remains} = 0.2 \text{ V} - \frac{40 \times 0.1}{2}$$

$$\frac{0.2V - \frac{40 \times 0.1}{2}}{V + 40} = \frac{6}{55} \text{ V} = 70 \text{ mL}$$

19. (a) 1 Mol of x will give =  $\frac{5}{2} = 2.5 \text{ mol of w}$

$$\text{But \% yield} = \frac{1.25}{2.5} \times 100 = 50\%$$

20. (a) Explanation :  $2 Ag + S \rightarrow Ag_2S$

$2 \times 108 \text{ g}$  of Ag reacts with 32 g of sulphur

$$10 \text{ g of Ag reacts with } \frac{32}{216} \times 10 = \frac{320}{216} > 1 \text{ g}$$

It means 'S' is limiting reagent

32 g of S reacts to form  $216 + 32 = 248 \text{ g of } Ag_2S$

$$1 \text{ g of S reacts to form} = \frac{248}{32} = 7.75 \text{ g}$$

Alternately

$$n_{eq} \text{ of Ag} = \frac{10}{108} = 0.0925 n_{eq} \text{ of S} = \frac{1}{16} = 0.0625$$

( $n_{eq}$  = number of equivalents)

Since  $n_{eq}$  of S is less than  $n_{eq}$  of Ag

$\Rightarrow 0.0625 \text{ eq of Ag will react with } 0.0625 \text{ eq of S to form } 0.0625 \text{ eq of } Ag_2S$

Hence, amount of  $Ag_2S = n_{eq} \times \text{Eq. wt. of } Ag_2S$

$$= 0.0625 \times 124 = 7.75 \text{ g}$$

21. (a) Molality =  $\frac{X_B}{X_A \times M_A} \times 1000$

$$m_B = 75 \text{ m}$$

$$m = \frac{M \times 1000}{d \times 1000 - M \times M_1}$$

$$M = 30$$

$$22. (a) NaOH = \frac{125ml \times 1 \times \frac{8}{100}}{40} \text{ mole} = 0.25 \text{ mole}$$

$$HCl = \frac{125 \times \frac{10}{100}}{36.5} = 0.34 \text{ mole}$$

HCl > NaOH

Acidic

23. (d)  $M = \frac{\% \text{ by weight} \times 10 \times d}{Mw_2} = \frac{36.5 \times 10 \times 1.2}{36.5} = 12 \text{ M}$

$$m = \frac{36.5 \times 1000}{36.5 \times (100 - 36.5)} = \frac{1000}{63.5} = 15.7 \text{ m}$$

24. (b) 1000 mL solution contain 2 mole of ethanol or  $1000 \times 1.025$  g solution contain 2 mole of ethanol  
wt. of solvent =  $1000 \times 1.025 - 2 \times 46$

$$m = \frac{2}{1000 \times 1.025 - 2 \times 46} \times 1000$$

$$m = \frac{2}{933} \times 1000 = 2.143$$

$$25. (c) \text{Molarity} = \frac{6.02 \times 10^{22}}{6.02 \times 10^{23}} \times \frac{1}{1/2} = 0.2$$

$$26. (b) \text{Let, } n_{H_2O} = n_{NaCl} = n \\ m = \frac{\text{Mole of solute}}{\text{wt. of solvent(kg)}} = \frac{n}{n \times 18} \times 1000 \\ = \frac{1}{18} \times 1000 = 55.55 \text{ m.}$$

27. (b)

(I) 50g of 40% (w/w) NaOH for 100 gm solution which means 60 gm of  $H_2O$  and 40 gm of NaOH and for 50 g solution has 20 gm NaOH.

(II) 50 ml of 50% (w/v) NaOH ( $d_{sol} = 1.2 \text{ g/ml}$ ) and for 100 ml of solution has 50 gm NaOH

$\therefore$  for 50 ml solution  
 $\Rightarrow 25 \text{ gm of NaOH.}$

$$(III) 50 \text{ g of } 15\text{M NaOH} (d_{sol} = 1 \text{ g/ml}) \\ d_{sol} = 1 \text{ g/ml, for 50 gm solution } \Rightarrow 50 \text{ ml solution} \\ \text{moles of NaOH} = M \times V \\ = 15 \times 0.05 = 0.75 \\ \text{Mass of NaOH} = 0.75 \times 40 \\ = 30 \text{ gm}$$

So mass in decreasing order is III > II > I.

28. (a) Mole fraction of A i.e.  $X_A = \frac{n_A}{\text{Total moles}}$

$$\text{So } X_{H_2O} = \frac{n_{H_2O}}{\text{Total moles}}$$

$$\text{Now } \frac{X_A}{X_{H_2O}} = \frac{n_A}{n_{H_2O}}$$

$$\text{and molality} = \frac{n_A \times 1000}{n_{H_2O} \times 18} = \frac{X_A \times 1000}{X_{H_2O} \times 18} \\ = \frac{0.2 \times 1000}{0.8 \times 18} = 13.9 \text{ Ans.}$$

$$29. (c) \text{Molarity} = \frac{98 \times 10 \times 1.84}{98} = 18.4 \text{ M}$$

$$\{ M = \frac{(\% w/w) \times (d) \times 10}{\text{Mol. mass of solute}} \} (d \text{ in g/ml.})$$

30. (b) Weight of KOH = 2.8 gram

Volume of solution = 100 ml

$$M = \frac{2.8 \times 1000}{56 \times 100} = \frac{28}{56} = 0.5 \text{ M}$$

31. (c) Molarity of  $Cl^- = 3$  (molarity of  $FeCl_3$ )

$$= 3 \left( \frac{M}{30} \right) = \frac{M}{10}$$

$$32. (a) M_1V_1 + M_2V_2$$

$$= M_R [V_1 + V_2]$$

$$1 \times 500 + 1 \times 500$$

$$= M_R [500 + 500]$$

$$M_R = 1$$

33. (b) Mole = M  $\times$  V

$$100 \times 10^{-3} = 0.8 \times V$$

$$V = 0.125$$

34. (d) Moles of  $Cl^-$  in 100 ml of solution

$$= \frac{2}{58.5} + \frac{4}{111} \times 2 + \frac{6}{53.5} = 0.2184$$

$$\text{Molarity of } Cl^- = \frac{0.2184}{100} \times 1000 = 2.184.$$

$$35. (d) \text{Conc. of cation} = \frac{400 + 300 + 200}{400} = \frac{900}{400} = 9/4$$

$$\text{Conc. of anion} = \frac{200 + 300 + 400}{400} = \frac{900}{400} = 9/4$$

$\therefore$  Ratio of the conc. = 1

$$36. (b) \text{No. of moles of } CO_2 \text{ in } 4.4 \text{ g } CO_2 = \frac{4.4}{44} = 0.1 \text{ mole}$$

$$\text{No. of moles of } H_2 \text{ gas in 2.24 liters at STP} = \frac{2.24}{22.4} = 0.1 \text{ mole}$$

$$\text{So total moles of } H_2 \text{ and } CO_2 \text{ gas are} = (0.1 + 0.1) = 0.2 \text{ moles}$$

$$\text{Total No. of molecules in the container} = 0.2 \times 6.022 \times 10^{23} = 1.2046 \times 10^{23}$$

37. (b) If percentage of A = 75.08, then percentage of B =  $(100 - 75.08) = 24.92$

Ratio in which A and B atoms are combining can be calculated as:

$$A : B = \frac{75.08}{75} : \frac{24.92}{16} = 1 : 1.5 = 2 : 3$$

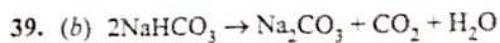
$\therefore$  Formula of the compound is  $A_2B_3$

38. (c)  $CaCO_3 \rightarrow CaO + CO_2$

10g of  $CaCO_3$  = 0.1 mole of  $CaCO_3$

0.1 mole of  $CaCO_3$  will produce  $\rightarrow$  0.1 mole of  $CaO$   
0.1 mole of  $CaO$  = 5.6g of  $CaO$

$$\% \text{ yield} = \frac{\text{Actual}}{\text{Theoretical}} \times 100 \\ = \frac{5}{5.6} \times 100 = 89\%$$



$$\text{Moles of CO}_2 = \frac{4.4}{44} = 0.1 \text{ moles}$$

Then moles of  $\text{NaHCO}_3$  will be 0.2 moles

$$\text{wt. of NaHCO}_3 = 0.2 \times 84 = 16.8 \text{ g}$$

$$\% \text{ purity} = \frac{16.8}{33.6} \times 100 = 50\%$$

40. (c) The atomic masses of nitrogen and oxygen are 14 and 16 g/mol respectively.

$$n_N = \frac{28}{14} = 2 \text{ moles}$$

$$n_O = \frac{80}{16} = 5 \text{ moles}$$

The mole ratio N : O = 2 : 5

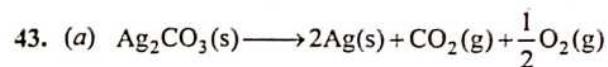
The formula of the compound is  $\text{N}_2\text{O}_5$ .

41. (a) No. of e<sup>-</sup> in 1 molecule of  $\text{CO}_2$  = 6 + 2(8) = 22

42. (c)  $\begin{array}{ccccc} & \text{O}_2 & & \text{N}_2 & \\ \text{Weight ratio} & 1 & & 4 & \\ \text{Moles ratio} & \frac{1}{32} & & \frac{4}{28} = \frac{1}{7} & \end{array}$

$$\text{Molecules ratio } \frac{1}{37} \text{ N}_A \quad \frac{1}{7} \text{ N}_A$$

Molecules ratio = 7 : 32

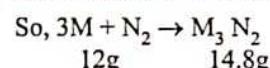


Molecular weight of  $\text{Ag}_2\text{CO}_3$  = 276 g

And, molecular weight of Ag =  $2 \times 108 = 216$  g  
276 g of  $\text{Ag}_2\text{CO}_3$  gives 216 g of Ag.

Therefore, 2.76 g of  $\text{Ag}_2\text{CO}_3$  on heating will give  
 $\frac{216}{276} \times 2.76 = 216$  g Ag as residue.

44. (c) Let the metal be M with atomic weight be X.



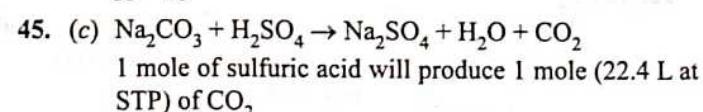
$$3x \rightarrow 3x + 28$$

So,

$$\frac{12}{3x} = \frac{14.8}{3x + 28}$$

$$\frac{12}{14.8} = \frac{3x}{3x + 28}$$

$$X = 40$$



100 mL (0.1 L) of 0.1 M  $\text{H}_2\text{SO}_4$  corresponds 0.01 mole  
Thus 0.01 mole of  $\text{H}_2\text{SO}_4$  will produce 0.01 moles of  $\text{CO}_2$   
0.01 moles of  $\text{CO}_2$  = 0.224 L of  $\text{CO}_2$

46. (c) To form one molecule of  $\text{X}_2\text{Y}_3$ , two atoms of X and three atoms of Y will be needed

It means  $36 \times 2 = 72$  amu and  $24 \times 3 = 72$  amu of Y will be needed to form 144 amu of  $\text{X}_2\text{Y}_3$ .

$$47. (a) \text{Moles of sugar} = \frac{1.71}{342} = \frac{1}{200} \text{ moles}$$

$$\text{No. of molecules} = \frac{1}{200} \times N_A$$

$$\text{No. of C-atoms} = 12 \times \frac{1}{200} \times N_A = 3.6 \times 10^{22}$$

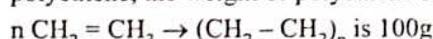
48. (a) The ratio among C : H : N is 38 : 8 : 16 : 45.2

$$\text{The molar ratio is } \frac{38.8}{12} : \frac{16}{1} : \frac{45.2}{14}$$

$$= 3.23 : 16 : 3.22 \\ = 1 : 5 : 1$$

Therefore the empirical formula of the compound would be  $[\text{CH}_3\text{NH}_2]$

49. (b) When 100g of Ethylene polymerises entirely to polyethylene, the weight of polyethylene formed as →



Because entire mass of ethylene is converted to polyethylene as there is no addition, elimination or condensation of simple molecules.

50. (c) Given,

Mass % = 98% i.e. 98 g of  $\text{H}_2\text{SO}_4$  is present in 100 g of the solution

$$\text{density} = 1.84 \text{ g/cc} = 1.84 \text{ g/mL}$$

$$\text{Hence volume} = \frac{100}{1.84} \text{ mL} = \frac{1}{18.4} \text{ L}$$

$$\text{given mass of H}_2\text{SO}_4 = 98 \text{ g}$$

$$n_{\text{H}_2\text{SO}_4} = \frac{98}{98} = 1$$

$$\text{Molarity} = \frac{1}{\frac{1}{18.4}} = 18.4 \text{ M}$$



### Exercise-3 (JEE Advanced Level)

1. (a,b,c)

$$\text{Mole of NH}_3 = 1.7 = 0.1$$

$$\text{Mole H atom} = 0.3$$

$$\text{Total atoms} = 0.4 \times 6.02 \times 10^{23} = 2.408 \times 10^{23}$$

$$\% \text{ H} = \frac{3 \times 1}{17} \times 100 = 17.65\%$$

2. (b,c,d)

	C	+	O <sub>2</sub>	→	CO <sub>2</sub>
Mass	27		88		
Moles	$\frac{27}{12}$		$\frac{88}{32}$		

C is limiting reagent

$$\text{Moles of CO}_2 \text{ produced} = \text{moles of C} = \frac{27}{12} = 2.25$$

$$\therefore \text{Volume of CO}_2 \text{ at STP} = 2.25 \times 2.4 = 50.4 \text{ L}$$

$$\text{Ratio of C and O in CO}_2 = 12 : 32 = 3 : 8$$

$$\text{Moles of unreacted O}_2 = 2.75 - 2.25 = 0.5$$

$$\therefore \text{Volume of unreacted O}_2 \text{ at STP} = 0.5 \times 22.4 = 11.2 \text{ L}$$

3. (a,c)

$$0.5 \times n = \frac{216}{108} = \text{mol of Ag}$$
$$n = 4$$

$$\text{M.wt} = 58 + [165]n \text{ g/mol} = 718 \text{ g/mol}$$

4. (a,c)

Convert all the wt. in mole and use limiting reagent concept ind out the mole produced of NH<sub>3</sub>.

In (a) & (c) it comes equal to 10 moles

5. (a,b,c)

$$(\text{M wt. of Na}_2\text{CO}_3 = 106 \text{ M wt. of HCl} = 36.5, \text{ M wt. of NaCl} = 58.5)$$

$$\text{Moles of Na}_2\text{CO}_3 = \frac{106}{106} = 1.0 \text{ mol}$$

$$\text{Moles of HCl} = \frac{109.5}{36.5} = 3.0 \text{ mol}$$

(a) Since for 1 mol of Na<sub>2</sub>CO<sub>3</sub>, 2 mol of HCl is required.

So, HCl is in excess (3 - 2) = 1.0 mol

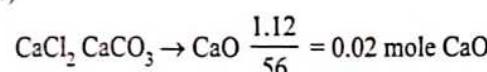
Therefore, Na<sub>2</sub>CO<sub>3</sub> is the limiting quantity.

(b) Weight of NaCl formed = (1.0 mol Na<sub>2</sub>CO<sub>3</sub>)

$$\left( \frac{2 \text{ mol NaCl}}{\text{mol Na}_2\text{CO}_3} \right) \left( \frac{58.5 \text{ g NaCl}}{\text{mol NaCl}} \right) = 1 \times 58.5 = 117.0 \text{ g NaCl}$$

(c) 1 mol of Na<sub>2</sub>CO<sub>3</sub> = 1 mol of CO<sub>2</sub> = 22.4 L at NTP

6. (a,c)

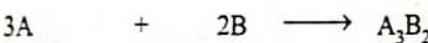


∴ Moles of CaCl<sub>2</sub> = 0.02 Mole

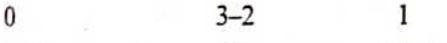
$$\text{Mass of CaCl}_2 = 0.02 \times 111 = 2.22 \text{ g}$$

$$\therefore \% \text{ of CaCl}_2 = \frac{2.22}{4.44} \times 100 = 50 \%$$

7. (b,d)



Initial mole	3	3	0
Final mole	0	3-2	1



Initial mole	1	1	0
Final mole	1 - $\frac{1}{2}$	0	$\frac{1}{2}$

8. (a,c)

$$\text{M wt. of CaCO}_3 = 100, \text{ M wt. of Na}_2\text{CO}_3 = 106$$

$$\text{M wt. of HNO}_3 = 63 \text{ g mol}^{-1}$$



$$(a) \text{ moles of CaCO}_3 = \frac{10}{100} = 0.1 \text{ mol}$$

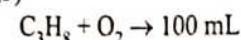
$$\text{moles of Na}_2\text{CO}_3 = \text{moles of CaCO}_3 \equiv 2 \times \text{moles of NaCl}$$

$$\text{Weight of Na}_2\text{CO}_3 = 0.1 \times 106 = 10.6 \text{ g}$$

$$(c) \% \text{ purity Na}_2\text{CO}_3 = \frac{10.6}{21.2} = 100 = 50\%$$

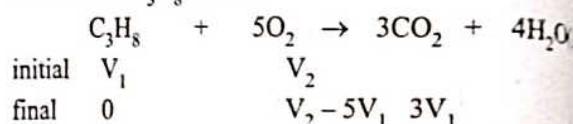
$$(d) \text{ moles of NaCl} = 2 \times 0.1 = 0.2 \text{ mol}$$

9. (a,b)



Case I:

Let assume C<sub>3</sub>H<sub>8</sub> is L.R.



$$\text{Vol. contraction} = V_i - V_f$$

$$= (V_1 + V_2) - (V_2 - 5V_1 + 3V_1)$$

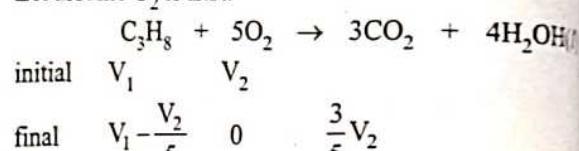
$$45 = 3V_1$$

$$V_1 = 15 \text{ mL (C}_3\text{H}_8)$$

$$V_2 = 85 \text{ mL (O}_2)$$

Case II:

Let assume O<sub>2</sub> is L.R.



$$\text{Vol contraction} = V_i + V_f$$

$$(V_1 + V_2) - \left( V_1 - \frac{V_2}{5} + \frac{3}{5}V_2 \right)$$

$$45 = \frac{3}{5}V_2$$

$$V_2 = 75 \text{ mL}$$

$$V_1 = 25 \text{ mL}$$

10. (b,d)

$$\text{Molality of Cl}^- = \frac{2 \times 1000 \times 2}{(1000 \times 1.09) - 190} = 4.44$$

11. (a,b)

Mol. wt. of HCOOH is 46.

$$\text{Mass of HCOOH in 46 g of 70\% } \left( \frac{w}{v} \right) \text{ HCOOH (d}_{\text{soln}} \text{)} = 1.40 \text{ g/mL} \text{ is } (46/1.4) \times 0.7 = 23 \text{ gm.}$$

$$\text{Mass of HCOOH in 50 g of 10 M HCOOH (d}_{\text{soln}} \text{)} = 1 \text{ g/mL} \text{ is } 50 \times 10 \times 46/1000 = 23 \text{ gm.}$$

12. (a,c,d)

Molecular weight of KI, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, CuSO<sub>4</sub>.5H<sub>2</sub>O and Al<sup>3+</sup> are 166, 132, 250 and 27 g/mol respectively.

$$(a) \text{ For KI, Molarity} = \frac{166 \times 100}{166 \times 100} = 1.0 \text{ M}$$

$$(b) \text{ For (NH}_4\text{)}_2\text{SO}_4, \text{Molarity} = \frac{33 \times 1000}{132 \times 200} = 1.25 \text{ M}$$

$$(c) \text{ For } \text{CuSO}_4 \cdot 5\text{H}_2\text{O, Molarity} = \frac{\frac{25 \times 1000}{250 \times 100}}{1000} = 1.0\text{M}$$

$$(d) \text{ For } \text{Al}^{3+}, \text{Molarity} = \frac{27 \times 10^{-3} \times 1000}{27 \times 1} = 1.0\text{M}$$

13. (a,b,d)

$$(a) \text{ Molarity of second solution is} = \frac{10 \times d \times x}{M} = 1\text{M}$$

$$(b) \text{ Volume} = 100 + 100 = 200 \text{ mL}$$

$$(d) \text{ Mass of H}_2\text{SO}_4 = \frac{200 \times 1}{1000} \times 98 = 19.6 \text{ g.}$$

$$14. (c) 11.2 \text{ g of N}_2 = \frac{11.2}{28} = 0.4 \text{ mole}$$

$$\therefore \text{ air} = 0.5 \text{ mole} \Rightarrow 0.5 \times 22.4 = 11.2 \text{ L}$$

18. (b)

Element	Symbol	Percentage of element	At. mass of element	Relative no. of atoms = Percentage at. mass	Simplest atomic ratio	Simplest whole no. atomic ratio
Carbon	C	40	12	$\frac{40}{12} = 3.33$	$\frac{3.33}{3.33} = 1$	1
Hydrogen	H	6.67	1	$\frac{6.67}{1} = 6.67$	$\frac{6.67}{3.33} = 2$	2
Oxygen	O	53.33	16	$\frac{53.33}{16} = 3.33$	$\frac{3.33}{3.33} = 1$	1

So empirical formula is  $\text{CH}_2\text{O}$

19. (b) For molecular formula

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{178}{30} = 6$$

So, molecular formula is  $\text{C}_6\text{H}_{12}\text{O}_6$

20. A → r; B → p; C → q

$$\% \text{ of Y} = \frac{89 \times 3}{(89 \times 3) + (5 \times 27) + (12 \times 16)} \times 100$$

$$= \frac{267 \times 100}{594} = 44.95\%$$

$$\% \text{ Al} = \frac{5 \times 27}{594} \times 100 = 22.73$$

$$\% \text{ O} = \frac{12 \times 16}{594} \times 100 = 32.32\%$$

21. A → p,s; B → s; C → p,q; D → r

$$(a) \text{ Molarity of cation} = \frac{\frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}}{500} = \frac{0.2 \times 100 + 0.1 \times 400}{500} = 0.12$$

$$\text{Molarity of Cl}^- = \frac{3(0.2)100 + 0.1 \times 400}{500} = \frac{0.6 + 0.4}{5} = 0.2$$

$$(b) \text{ Molarity of cation} = \frac{50 \times 0.4 + 0}{100} = 0.2$$

15. (b) 1 mole of air  $\Rightarrow 0.8$  mole of  $\text{N}_2 = 0.8 \times 28 \text{ g N}_2$   
 $\Rightarrow 0.2$  mole of  $\text{O}_2 = 0.2 \times 2 \text{ g O}_2$

$$\therefore \% \text{ w/w O}_2 = \frac{w_{\text{O}_2} \times 100}{w_{\text{O}_2} + w_{\text{N}_2}} = \frac{0.2 \times 32 \times 100}{0.2 \times 32 + 0.8 \times 28} = 22.2\%$$

16. (b) Density of air at NTP

$$1 \text{ mole of air} = 0.8 \text{ mole N}_2 + 0.2 \text{ mole O}_2 = 0.8 \times 28 + 0.2 \times 32 = 28.8 \text{ g} = 22.4 \text{ Ltr volume.}$$

$$D = \frac{m}{V} = 28.8 = 1.2857 \text{ g/L} = \frac{288}{22.4} = 1.2857 \text{ g/L}$$

$$17. (a) \% \text{ O} = 60 \times \frac{16}{18} = 53.33\%$$

$$\text{Molarity of Cl}^- = \frac{0.4 \times 50 + 0}{100} = 0.2$$

$$(c) \text{ Molarity of cation} = \frac{2(0.2)30 + 0}{100} = 0.12$$

$$\text{Molarity of SO}_4^{2-} = \frac{30 \times 0.2}{100} = 0.06$$

(d) 24.5 g  $\text{H}_2\text{SO}_4$  in 100 mL solution

$$\text{Molarity} = \frac{25.4}{0.1} = 2.5$$

$\therefore$  Concentration of cation =  $2 \times 2.5 \text{ M}$

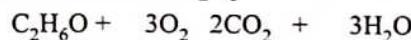
Concentration of  $\text{SO}_4^{2-} = 2.5 \text{ M}$ .

22. (d) A → q,s; B → p,s; C → p,q,r; D → q,r

$$(a) \text{ C : H : O} = \frac{51.17}{12} : \frac{13.04}{1} : \frac{34.78}{16} = 4 : 12 : 2 \text{ or } 2 : 6 : 1$$

$\therefore$  Empirical formula =  $\text{C}_2\text{H}_6\text{O}$  & molar mass = 46 g/mol

$\therefore$  Mol formula =  $\text{C}_2\text{H}_6\text{O}$



(b) Mass of C in organic compound = mass of C in  $\text{CO}_2$   
 $= \frac{0.44}{44} \times 12 = 0.12 \text{ g}$

Mass of H in organic compound = Mass of H in  $\text{H}_2\text{O}$   
 $= \frac{0.18}{18} \times 2 = 0.02 \text{ g}$

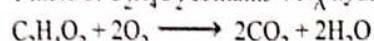
$\therefore$  Mass of O in organic compound =  $0.3 - (0.12 + 0.02)$   
 $= 0.16 \text{ g}$

$\therefore \text{C : H : O} = \frac{0.12}{12} : \frac{0.02}{1} : \frac{0.16}{16} = 0.01 : 0.02 : 0.01$   
 $= 1 : 2 : 1$

$\therefore$  Empirical formula =  $\text{CH}_2\text{O}$ , but it contains 2 O atom per molecule

$\therefore$  Molecular formula =  $\text{C}_2\text{H}_4\text{O}_2$

1 mole of  $\text{C}_2\text{H}_4\text{O}_2$  contains  $4 N_A$  hydrogen atoms.



1 mole  $44.8 \text{ L}$

0.25 mole  $11.2 \text{ L}$

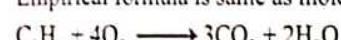
(c)  $\text{C : H} = 42.857 : 57.143$

$= 3 : x$  (given)

On solving,  $x = 4 \therefore$  molecular formula =  $\text{C}_3\text{H}_8$

1 mole of  $\text{C}_3\text{H}_8$  contains  $4 N_A$  hydrogen atoms.

Empirical formula is same as molecular formula



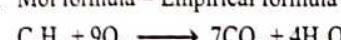
$n_{\text{CO}_2} > n_{\text{H}_2\text{O}}$

(d)  $\text{C : H} = \frac{10.5}{12} : \frac{1}{8} = \frac{7}{8} : 1 = 7 : 8$

Empirical formula =  $\text{C}_7\text{H}_8$

Mol wt. =  $2 \times \text{VD} = 2 \times 46 = 92$

$\therefore$  Mol formula = Empirical formula =  $\text{C}_7\text{H}_8$



$n_{\text{CO}_2} > n_{\text{H}_2\text{O}}$

23. [+] 8

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

$$x = +8$$

24. [-] 3

$$x + 4(+1) = +1$$

$$= -3$$

25. [500]

$$M = \frac{18 \text{ moles of solute}}{(1 \text{ lit. solution})}$$

$$\text{Mass of solution} = 1000 \times 1.8 = 1800 \text{ g.}$$

$$\text{Mass of solute} = 18 \times 98 = 1764.$$

$$\text{Mass of solvent} = 1800 - 1764 = 36 \text{ g.}$$

$$\text{Hence molality} = \frac{\text{moles of solute}}{\text{mass of solvent}} \times 1000 = \frac{18}{36} \times 1000 = 500.$$

26. [40]

$\therefore 40 \text{ gm NaOH contain } 16 \text{ gm of oxygen}$

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

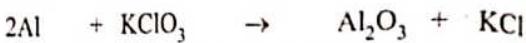
27. [6g]

$$N = \frac{W(\text{gm}) \times 1000}{V \times \text{Eq.wt.}}$$

1500 ml of 0.1N HCl = 150 ml (N)

$$1 = \frac{W(\text{gm}) \times 1000}{150 \times 40}, W(\text{gm}) = \frac{150 \times 40}{1000} = 6 \text{ gm.}$$

28. [1]



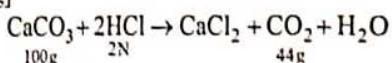
(excess) 1 mole ( $\text{KClO}_3$  is L.R.)

From mole-mole analysis

$$\frac{n_{\text{KClO}_3}}{1} = \frac{n_{\text{Al}_2\text{O}_3}}{1}$$

$$\Rightarrow n_{\text{Al}_2\text{O}_3} = 1 \text{ mole}$$

29. [22g]



100 g  $\text{CaCO}_3$  with 2 N HCl gives 44 g  $\text{CO}_2$

100 g  $\text{CaCO}_3$  with 1 N HCl gives 22 g  $\text{CO}_2$

30. [1]

$$\text{Conc. of cation} = \frac{400 + 300 + 200}{400}$$

$$\text{conc. of anion} = \frac{200 + 300 + 400}{400}$$

$\therefore$  ratio of the conc. = 1

31. [27g]

Let  $w$  g water added to 16 g  $\text{CH}_3\text{OH}$

$$\text{molality} = \frac{16 \times 1000}{W \times 32} = \frac{500}{W}$$

$$\frac{500}{W} = \frac{x_A \times 1000}{(1-x_A)m_B}$$

$$= \frac{0.25 \times 1000}{0.75 \times 18}$$

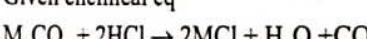
$$W = 27 \text{ gm}$$

## Exercise-4

### (Past Year Questions)

#### JEE MAIN

1. (b) Given chemical eq<sup>n</sup>



$$1 \text{ gm} \quad 0.01186 \text{ mol}$$

$\Rightarrow$  from the balanced chemical eq<sup>n</sup>

$$\frac{1}{M} = 0.01186 \Rightarrow M = 84.3 \text{ gm/mol}$$

2. (c) Mass in body of a healthy human adult has:

Oxygen = 61.4%, carbon = 22.9 %

Hydrogen = 10.0% and Nitrogen = 2.6%



Total weight of person = 75kg

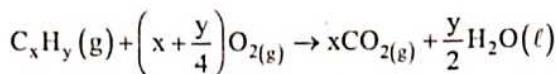
$$\text{Mass due to } {}^1\text{H} \text{ is } = 75 \times \frac{10}{100} = 7.5 \text{ kg}$$

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

So mass gain by person = 7.5 kg

$$3. (c) \frac{12x}{y} = \frac{6}{1}$$

$$[2x = y] \text{ for } \text{C}_x \text{H}_y \text{O}_z$$



no. of oxygen atom in  $\text{C}_x \text{H}_y \text{O}_z$  = z

no. of oxygen atom required for  $\text{C}_x \text{H}_y$

$$\text{combustion is } \left( x + \frac{y}{4} \right) \times 2 = \left( 2x + \frac{y}{2} \right)$$

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

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

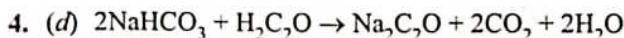
$$z = x + \frac{2x}{4} = \frac{3x}{2}$$

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

$$2x : 4x : 3x$$

$$2 : 4 : 3$$

Hence  $\text{C}_2 \text{H}_4 \text{O}_3$



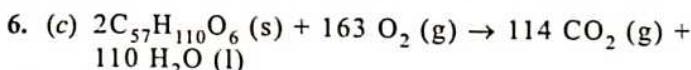
Let mass of  $\text{NaHCO}_3$  be x mg

$$n_{\text{CO}_2} = \frac{0.25}{25000} = 10^{-5}$$

$$w_{\text{NaHCO}_3} = 84 \times 10^{-5} \text{ g}$$

$$\% = \frac{84 \times 10^{-5}}{10^{-2}} \times 100 = 8.4\%$$

5. (a) More polluted water has high biological oxygen demand.



$$\frac{\text{Moles of C}_{57}\text{H}_{110}\text{O}_6}{2} = \frac{\text{Moles of H}_2\text{O}}{110}$$

$$\frac{445}{890} = \frac{\text{mass of H}_2\text{O}}{18}$$

$$\text{Mass of H}_2\text{O} = 495 \text{ g}$$

7. (a) Eq. of  $(\text{COOH})^2$  = Eq. of  $\text{NaOH}$

$$50 \times 0.5 \times 2 = 25 \times M \times 1$$

$$\text{Mass of NaOH in 50 mL} = \frac{50 \times 2}{1000} \times 40 = 4 \text{ g}$$

$$8. (c) \text{ Molality of } \text{Na}^+ = \left( \frac{w}{M} \times \frac{1000}{W} \right) \times 2 \quad (\text{Na}_2\text{SO}_4 \text{ contains two } \text{Na}^+ \text{ ions}) \\ = \left[ \left( \frac{92}{23} \times \frac{1000}{1000} \right) \right] \times 2 = 8$$

9. (d) As 1L solution have  $10^{-3}$  mol  $\text{CaSO}_4$   
Eq. of  $\text{CaSO}_4$  = eq. of  $\text{CaCO}_3$   
In 1L solution

$$n_{\text{CaSO}_4} \times \text{v.f.} = n_{\text{CaCO}_3} \times \text{v.f.}$$

$$10^{-3} \times 2 = n_{\text{CaCO}_3} \times 2$$

$$n_{\text{CaCO}_3} = 10^{-3} \text{ mol in 1L}$$

$$\therefore w_{\text{CaCO}_3} = 100 \times 10^{-3} \text{ g in 1L solution}$$

$\therefore$  hardness in terms of  $\text{CaCO}_3$

$$= \frac{w_{\text{CaCO}_3}}{w_{\text{Total}}} \times 10^6 = \frac{100 \times 10^{-3} \text{ g}}{1000 \text{ g}} \times 10^6 = 100 \text{ ppm}$$

$$10. (c) 0.1 = \frac{n_{\text{C}_{12}\text{H}_{22}\text{O}_{11}}}{2}$$

$$n_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} = 0.2$$

$$\text{Wt. of C}_{12}\text{H}_{22}\text{O}_{11} = 0.2 \times 342 = 68.4$$

$$11. (c) \text{ Moles of NaOH} = \frac{8}{40} = 0.2$$

$$\text{Moles of H}_2\text{O} = \frac{18}{18} = 1$$

$$\text{Moles fraction of NaOH} = \frac{0.2}{1.2} = 0.167$$

$$\text{Molality} = \frac{8}{40} \times \frac{1000}{18} = 11.11$$

12. (c) Volume strength =  $11.35 \times M = 11.35$  (STP)

$$13. (b) n_{\text{eq}} \cdot \text{CaCO}_3 = N_{\text{eq}} \text{Ca}(\text{HCO}_3)_2 + n_{\text{eq}} \text{Mg}(\text{HCO}_3)_2$$

$$\text{Or, } \frac{W}{100} \times 2 = \frac{0.81}{162} \times 2 + \frac{0.73}{146} \times 2$$

$$\therefore w = 1.0$$

$$\therefore \text{Hardness} = \frac{1.0}{100} \times 10^6 = 10000 \text{ ppm}$$

Correct option : (b)



1 mole  $\text{N}_2$  required 3 moles of  $\text{H}_2$ .

$$(a) \frac{14}{28} \quad \frac{4}{2}$$

$$0.5 \text{ mole} \quad 2 \text{ mole}$$

$\text{N}_2$  is L.R.

$$(b) \frac{28}{28} \quad \frac{6}{2}$$

$$1 \text{ mole} \quad 3 \text{ mole}$$

No L.R.

$$(c) \frac{56}{28} \quad \frac{10}{2}$$

$$2 \text{ mol.} \quad 5 \text{ mole}$$

$\therefore 2 \text{ mole } \text{N}_2 \text{ required 6 moles of}$

So,  $\text{H}_2$  is L.R.

15. (d) In  $\text{CH}_4$

$$\% \text{ by mole of carbon} = \frac{1 \text{ mol atom}}{5 \text{ mol atom}} \times 100 = 20\%$$

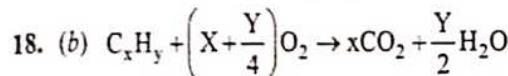
16. (d) The maximum prescribed concentration of Cu in drinking water is 3 ppm.

17. (b) Volume strength =  $11.2 \times \text{molarity} = 11.2$

$$\Rightarrow \text{molarity} = 1 \text{ M}$$

$$\Rightarrow \text{strength} = 34 \text{ g/L}$$

$$\Rightarrow \% \text{ w/w} = \frac{34}{1000} \times 100 = 3.4\%$$



$$\begin{aligned} \left(\frac{25}{M}\right)X \times \frac{25}{M} &= 2 \\ \frac{y}{2} \times \frac{25}{M} &= 0.5 \end{aligned}$$

$$\text{C} \quad x \times \frac{25}{M} = 2$$

$$\text{H} \quad y \times \frac{25}{M} = 1$$

$$\text{C}_{2y}\text{H}_y \equiv 24y \text{ gm C} + y \text{ gm H}$$

or

24:1 ratio by mass

19. (c)  $\frac{W}{W} \% = 20$

100 gm solution has 20 gm KI

80 gm solvent has 20 gm KI

$$M \frac{\frac{20}{166}}{\frac{80}{1000}} = \frac{20 \times 1000}{166 \times 80} = 1.506 \approx 1.51 \text{ mol/kg}$$

20. (c)  $5[M_A + 2M_B] = 125$

$$M_A + 2M_B = 25 \quad \dots(i)$$

$$2M_A + 2M_B = 30 \quad \dots(ii)$$

from eq. (i) & (ii)

$$M_A = 5$$

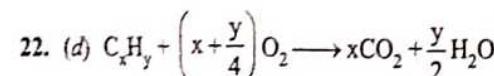
$$M_B = 10$$

21. (c)  $X_{\text{solvent}} = 0.8$

If  $n_T = 1$

$$n_{\text{Solvent}} = 0.8$$

$$\text{molality} = \frac{2}{\frac{0.8 \times 18}{1000}} = 13.88$$

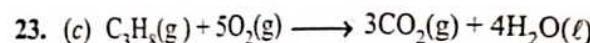


$$10 \quad 10 \left(X + \frac{Y}{4}\right) \quad 10x$$

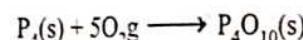
$$\text{By given data, } 10 \left(X + \frac{Y}{4}\right) = 55 \quad \dots(i)$$

$$10x = 40 \quad \dots(ii)$$

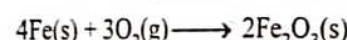
$$\therefore x = 4, y = 6 \Rightarrow \text{C}_4\text{H}_6$$



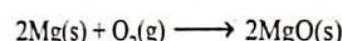
Each 1 g of  $\text{C}_3\text{H}_8$  requires 3.63 g of  $\text{O}_2$



Each 1 g of  $\text{P}_4$  requires 1.29 g of  $\text{O}_2$



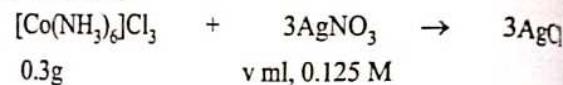
Each 1 g of Fe requires 0.428 g of  $\text{O}_2$



Each 1 g of Mg requires 0.66 g of  $\text{O}_2$  therefore less amount of  $\text{O}_2$  is required in option (iii).

24. (a) Refer Notes

25. [26.80 to 27.00]



$$0.3 \text{ g} \quad v \text{ ml, } 0.125 \text{ M}$$

$$\frac{0.3}{267.46} \times 3 = 0.125 \times v \times 10^{-3} \quad \text{or,}$$

$$v = \frac{0.3 \times 3 \times 1000}{267.46 \times 0.125} = 26.92 \text{ ml}$$

26. [2130 g]

mol of  $\text{NaClO}_3$  = mol of  $\text{O}_2$

$$\text{mol of O}_2 = \frac{PV}{RT} = \frac{1 \times 492}{0.082 \times 300} = 20 \text{ mol}$$

$$\text{mass of NaClO}_3 = 20 \times 106.5 = 2130 \text{ g}$$

27. [100.00]

$10^{-3}$  molar  $\text{MgSO}_4$  =  $10^{-3}$  moles of  $\text{MgSO}_4$  present in 1 L solutions.

$$n_{\text{CaCO}_3} = n_{\text{MgSO}_4}$$

$$\text{ppm (in term of CaCO}_3) = \frac{10^{-3} \times 100}{1000} \times 10^6$$

$$\text{ppm (in term of CaCO}_3) = 100 \text{ ppm}$$

28. [25.00]

Mass of  $6.023 \times 10^{22}$  molecules of a substance = 10 g  
Mass of  $6.023 \times 10^{23}$  molecules of the substance = 100 g

$$\text{Molar mass of the substance} = \frac{5}{100 \times 2} = 2.5 \times 10^{-2}$$

$$= 25 \times 10^{-3}$$

29. (a) Volume strength = 5.6

$$\text{V.S.} = 11.2 \times \text{Molarity}$$

$$\text{Molarity (M)} = \frac{\text{V.S.}}{11.2} = \frac{5.6}{11.2} = 0.5$$

0.5 M → 0.5 mole in 1L



$$\text{Mass percentage} = \frac{0.5 \times 34}{1000 \times d} \times 100 \\ = \frac{17 \times 100}{1000 \times 1} = 1.7$$

30. [47]  $X_{C_6H_{12}O_6} = 0.1$

Let total mole is 1 mole then mole of glucose will be 0.1 and mole of water will be 0.9

so, mass % of water =  $(0.9 \times 18) / (0.1 \times 180 + 0.9 \times 18) \times 100$

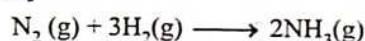
$$= 47.36 \\ = 47$$

31. [100]

Molarity of  $H_2O_2$  solution = 8.9 M

Volume strength of  $H_2O_2$  solution  
=  $8.9 \times 11.2 = 100 V$

32. [3400]



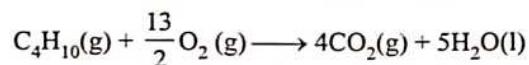
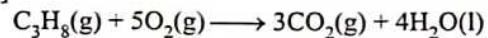
Number of moles of  $N_2 = \frac{2.8 \times 10^3}{28} = 100$

Number of moles of  $H_2 = \frac{1000}{2} = 500$

Number of moles of  $NH_3$  produced = 200

Mass of  $NH_3$  produced =  $200 \times 17 = 3400$  gm

33. [18]



No. of moles of  $O_2$  required to oxidise 1 mole of propane

and 2 moles of butane =  $5 + 2 \times \frac{13}{2} = 18$

34. (c) Average molar mass =  $\frac{35 \times 3 + 37 \times 1}{4} = 35.5$

$\Rightarrow {}^{35}Cl : {}^{37}Cl = 3 : 1$

35. (b) To express  $C_2$  in terms of mole fraction  $x_2$

1<sup>st</sup> component      2<sup>nd</sup> component

mole                   $n_1$                    $n_2$

m.w                   $M_1$                    $M_2$

mass                   $n_1M_1$                    $n_2M_2$

mass of solution =  $n_1M_1 + n_2M_2$

mole fraction  $x_2 = \frac{n_2}{n_1 + n_2}$

$n_1 = \frac{n_2(1-x_2)}{x_2}$

Mass of solution =  $n_1M_1 + n_2M_2$

=  $\frac{n_2M_1(1-x_2)}{x_2} + n_2M_2$

=  $\frac{n_2}{x_2}[M_2x_2 - x_2M_1 + M_1]$

Volume of solution

$$= \frac{n_2[M_2x_2 - x_2M_1 + M_1]}{1000dx_2} \text{ Litre}$$

$$C_2 = \frac{1000n_2dx_2}{n_2[M_2x_2 - x_2M_1 + M_1]}$$

$$C_2 = \frac{1000dx_2}{M_1 + x_2(M_2 - M_1)}$$

36. [64]

Given, mass of  $CuSO_4 \cdot 5H_2O = 80$  g

The concentration of copper sulphate solution is  $x \times 10^{-3}$  mol/L.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution(L)}} \quad \dots(i)$$

Molar mass of  $CuSO_4 \cdot 5H_2O = 63.54 + 32 + 16 \times 4$

=  $5 \times 18 = 249.54$  g/mol

Number of moles of solute

$$= \frac{\text{Weight of solute}}{\text{Molecular mass of solvent}}$$

$$= \frac{90\text{g}}{249.54\text{g/mol}} = 0.32 \text{ mol}$$

Volume of solution = 5L

From Eq. (i),

$$\text{Molarity} = \frac{0.3205}{5} = 64.11 \times 10^{-3} \text{ mol/L}$$

$\therefore x = 64.11$

or  $x \approx 64$

Hence, Ans. is 64.

37. [2] Given, mass of Na = 8 g

Molar mass of Na =  $23\text{gmol}^{-1}$

$$\frac{8\text{g}}{23\text{g}} = \frac{\text{Number of atoms}}{6.022 \times 10^{23}}$$

$$\text{Number of atoms} = \frac{8 \times 6.022}{23} \times 10^{23}$$

Number of atoms =  $2.09 \times 10^{23}$

$x \geq 2$

Hence, Ans. is 2

38. [13]



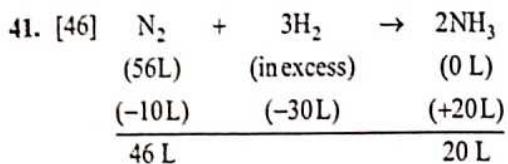
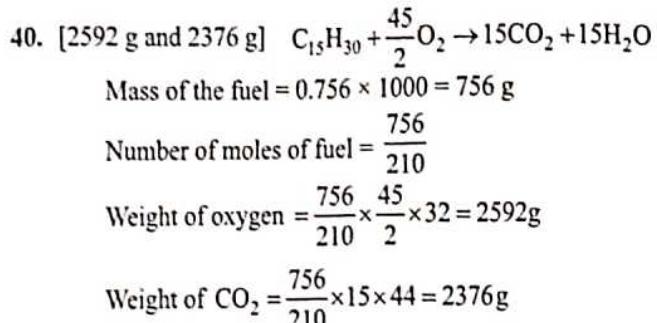
$$\frac{20}{62} \text{ moles}$$

$$\text{Moles of NaOH formed} = \frac{20}{62} \times 2$$

39. [20]  $[H_2C_2O_4 \cdot 2H_2O] = \frac{\text{weight/M.M}}{V(L)}$

$$\Leftrightarrow \approx \times 10^{-2} = \frac{6.3 \times 125}{250/1000}$$





42. [24]  $ppm = \frac{W_{Mg}}{V_{soln}} \times 10^6 = 48$

$$\Rightarrow W_{Mg} = \frac{48 \times 2 \times 1000}{10^6} = 96 \times 10^{-3} \text{ g}$$

$$\text{No. of Mg atoms} = \frac{96 \times 10^{-3}}{24} \times 6.02 \times 10^{23} = 24.08 \times 10^{20}$$

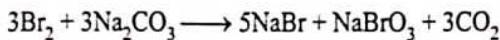
43. [54]  $n_{HNO_3} = 0.4 \text{ mol}$

$$\text{Remaining } n_{HNO_3} = 0.4 - \frac{11.5}{63} = 0.2175$$

$$\therefore \text{Molarity} = \frac{0.2175}{400} \times 1000 = 0.5437 \text{ mol/L} = 54 \times 10^{-2} \text{ mol/lit}$$

## JEE ADVANCED

44. [5] The balance chemical equation is



45. (c) Mole =  $\frac{120}{60} = 2$

mass of solution = 1120 g

$$V = \frac{1120}{1.15 \times 1000} = \frac{112}{115} \text{ L}$$

$$M = \frac{2 \times 115}{112} = 2.05 \text{ mol/litre}$$

46. [8 mL.]

29.2% (w/w) HCl has density = 1.25 g/ml

Now, mole of HCl required in 0.4 M HCl =  $0.4 \times 0.2$   
 mole = 0.08 mole

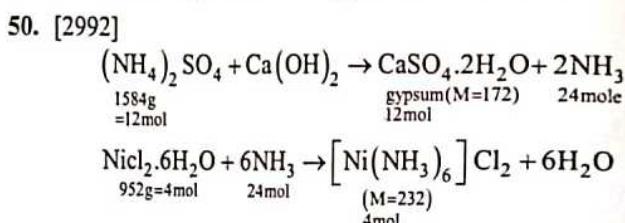
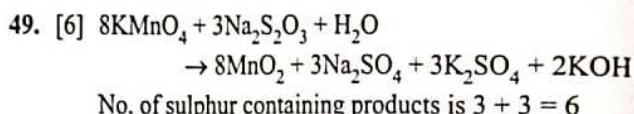
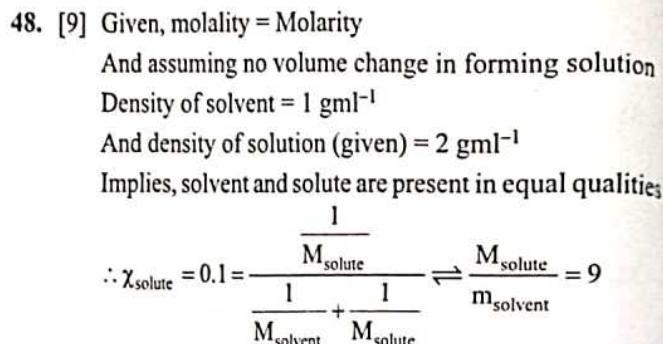
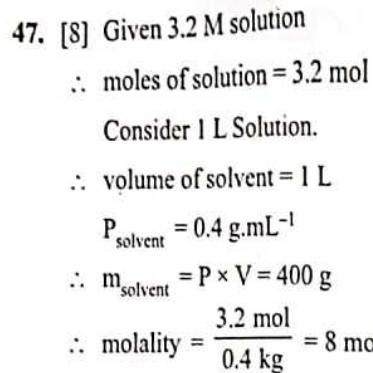
if v mol of orginal HCl solution is taken

then volume of solutio = 1.25 v

mass of HCl =  $(1.25 v \times 0.292)$

$$\text{mole of HCl} = \frac{1.25 v \times 0.292}{36.5} = 0.08$$

$$\text{so, } v = \frac{36.5 \times 0.08}{0.29 \times 1.25} \text{ mol} = 8 \text{ mL}$$



$$\text{Total mass} = 12 \times 172 + 4 \times 232 = 2992 \text{ g}$$

51. [2.98 or 2.99]

$$X_{\text{urea}} = 0.05 = \frac{n}{n+50}$$

$$19n = 50$$

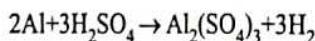
$$n = 2.6315$$

$$V_{\text{sol}} = \frac{(2.6315 \times 60 + 900)}{1.2} = 881.5789 \text{ ml}$$

$$\text{Molarity} = \frac{2.6315 \times 1000}{881.5789} = 2.9849$$

$$\text{Molarity} = 2.98 \text{ M}$$

52. [6.15]



$$\text{Moles of Al takes} = \frac{5.4}{27} = 0.2$$

$$\text{moles of } H_2SO_4 \text{ taken} = \frac{50 \times 5.0}{1000} = 0.25$$

As  $\frac{0.2}{2} > \frac{0.25}{3}$ ,  $H_2SO_4$  is limiting reagent

$$\text{Now, moles of } H_2 \text{ formed} = \frac{3}{3} \times 0.25 = 0.25$$



$$\therefore \text{Volume of } \text{H}_2 \text{ gas formed} = \frac{nRT}{P}$$

$$= \frac{0.25 \times 0.082 \times 300}{1} = 6.15 \text{ L}$$

53. (b,c)

(a) Compound 3 if compound is

$$\text{P}_3\text{O}_4 \Rightarrow \frac{3P}{4Q} = \frac{40}{60} = \frac{2}{3}$$

$$\frac{P}{Q} = \frac{8}{9}$$

Compound 2

$$\text{P}_3\text{O}_5 \Rightarrow \frac{3P}{5Q} = \frac{44.8}{55.6}$$

$$\frac{P}{Q} = \frac{5}{3} 0.8$$

$$\frac{4}{3} = \frac{8}{6}$$

Option 'a' is wrong

(b) Compound 3

$$P \frac{40}{20} = 2 \quad 1.5 \quad 3$$

$$\text{formula} = \text{P}_3\text{Q}_2$$

$$Q \frac{60}{45} = \frac{4}{3} \quad 1 \quad 2$$

$$(c) \text{ Compound 2} \Rightarrow P \frac{44.4}{Q} = \frac{55.6}{0.8}$$

$$\text{Compound 1} \Rightarrow \frac{5P}{4Q} = \frac{5}{4} \Rightarrow \frac{P}{Q} = 1$$

(d) Compound 1

$$P \frac{50}{70} 1$$

$$Q \frac{50}{35} 2$$

## CHAPTER

## 2

## Atomic Structure



## Exercise-1 (Topicwise)

1. (a) Volume fraction =  $\frac{\text{Volume of nucleus}}{\text{Total volume of atom}}$

$$= \frac{\left(\frac{4}{3}\right)\pi(10^{-13})^3}{\left(\frac{4}{3}\right)\pi(10^{-8})^3}$$

$$= 10^{-15}$$

2. (c)  $r = RoA^{1/3}$

$r$  = radius of nucleus

$Ro$  = Constant = 1.25

A = Atomic mass of element

$$\therefore r = 1.25 \times (64)^{1/3} = 5\text{ fm}$$

3. (b) Since the charge and mass of an electron is fixed, the ratio of e/m for a cathode ray is fixed.

4. (d) Cathode rays have both charge and mass.

5. (c) Proton is ionized hydrogen atom i.e. it contains only protons and no neutrons or electrons.

6. (d) Rutherford observed that the positively charged  $\alpha$ -particles were repelled and deflected by the positive charge in the atom. Rutherford named this positively charged portion of atom as nucleus.

7. (c) Most of the space in an atom is empty.

8. (d) e/m for neutron =  $\frac{0}{1} = 0$

e/m for alpha particles =  $\frac{2}{4} = 0.5$

e/m for proton =  $\frac{1}{1} = 1$

e/m for electron =  $\frac{1}{\left(\frac{1}{1850}\right)} = 1850$

9. (a) Nucleons are protons and neutrons.

10. (d) As neutrons are neutral particles, the scientists were unable to observe neutrons.

11. (d) Atomic number represents the number of protons in an atom.

12. (c) e/m for nitrogen =  $\frac{14}{28} = 0.5$

e/m for oxygen =  $\frac{16}{32} = 0.5$

e/m for hydrogen =  $\frac{2}{2} = 1$

e/m for helium =  $\frac{2}{4} = 0.5$

13. (a)  $v = \frac{c}{\lambda} = \frac{3 \times 10^8}{\lambda}$

$$\lambda = \frac{c}{v} = \frac{3 \times 10^8}{400 \times 10^6} = 0.75$$

14. (a) I.E. of one mole Na atom =  $\frac{hc \times Na}{\lambda}$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8 \times 6 \times 10^{23}}{242 \times 10^{-9}}$$

$$= 494.65 \text{ kJ/mol}$$

15. (d) Energy emitted by a bulb = Power  $\times$  Time  
 $= 40 \times 20 = 800 \text{ J}$

Energy of photons emitted by a bulb =  $\frac{80}{100} \times 8000 = 640 \text{ J}$

Energy of photon =  $\frac{hc}{\lambda} = \frac{12400 \times 1.6 \times 10^{-19} \times 10^{-10}}{620 \times 10^{-9}}$   
 $= 2 \times 10^{21} \text{ photons}$

16. (c)  $h\nu = h\nu_0 + \text{K.E.}$   
 K.E. varies from 0 to any positive number.

Hence,  $h\nu \geq h\nu_0$

$$\frac{hc}{\lambda} \geq \frac{hc}{\lambda_0}$$

$$\Rightarrow \lambda \leq \lambda_0$$

17. (c) Absorbed energy =  $h\nu = 6.626 \times 10^{-34} \times 6 \times 10^{14}$   
 $= 2.49 \text{ eV}$   
 $2.49 = 2 + \text{KE}$   
 $\Rightarrow \text{KE} = 0.49 \text{ eV}$

18. (c)  $E = \frac{nhc}{\lambda}$   
 $\Rightarrow n = \frac{E\lambda}{hc} = \frac{600 \times 331.3 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8}$   
 $n = 1 \times 10^{21}$

19. (d) Photoelectric effect can be explained by assuming that light consists of quanta.

20. (c)  $h\nu_1 = h\nu_0 + KE_1$  .....(i)  
 $2h\nu_1 = h\nu_0 + KE_2$  .....(ii)  
 Solving (i) and (ii), we get  
 $KE_2 = 2KE_1 + h\nu_0$

21. (a) Wavelength of 1st photon =  $\lambda_1$   
 Wavelength of 2nd photon =  $\lambda_2$   
 $E(\text{total}) = E_1 + E_2 = \text{Emitted Energy}$   
 $\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$   
 $\frac{1}{300} = \frac{1}{400} + \frac{1}{\lambda_2}$   
 $\lambda_2 = 759 \text{ nm}$

22. (b) For H-atom,  $E_1 = -13.6 \times \frac{1^2}{1^2} = -13.6 \text{ eV/atom}$   
 For  $\text{He}^+$  ion,  $E_2 = -13.6 \times \frac{(2)^2}{(2)^2} = -13.6 \text{ eV/atom}$   
 For  $\text{Li}^{2+}$  ion,  $E_3 = -13.6 \times \frac{(3)^2}{(3)^2} = -13.6 \text{ eV/atom}$   
 For  $\text{Be}^{3+}$  ion,  $E_4 = -13.6 \times \frac{(4)^2}{(4)^2} = -13.6 \text{ eV/atom}$

23. (a) Velocity =  $\frac{2\pi Ze^2}{nh}$   
 $v \times \frac{Z}{n}$   
 Velocity of  $\text{H}_2^{\oplus} \propto 1$   
 Velocity of  $\text{Li}^{2+} \propto \frac{3}{3} = 1$

24. (a) radius  $\propto \frac{n^2}{Z}$   
 $r_{n2} - r_{n1} = 24 \times r_0$

Since,

$$n_2^2 - n_1^2 = 24$$

$$n_2 = 7, n_1 = 5 \text{ or } n_2 = 5, n_1 = 1.$$

25. (b)  $S_1: PE \propto \frac{1}{r}$   
 $S_2: KE \propto \frac{1}{n^2}$   
 $S_3: PE = 2 \times T.E.$

$$PE = 2 \left( -13.6 \times \frac{2^2}{n^2} \right)$$

$$P.E. \propto \frac{-1}{n^2}$$

$$S_4: E = -13.6 \times \frac{(2)^2}{(2)^2}$$

$$= -13.6 \text{ eV}$$

26. (a)  $En = -R_H \times \frac{Z^2}{n^2}$

Energy of orbit becomes less negative as n increases.

27. (b)  $r = \frac{0.0529 \times n^2}{Z}$

$$\text{radius of 1st orbit of H-atom} = \frac{0.0529 \times 1^2}{3}$$

$$= 0.0529 \text{ \AA}$$

$$\text{radius of 1st orbit of Li}^{2+} \text{ ion} = \frac{0.0529 \times 1}{3}$$

$$= \frac{0.0529}{3} \text{ \AA}$$

28. (b)  $L = \frac{nh}{2\pi} = \frac{5h}{2\pi} = \frac{2.5h}{\pi}$

29. (a) Amount of energy  $\propto \frac{1}{n_1^2} - \frac{1}{n_2^2}$

The difference is maximum from  $n_1 = 1$  to  $n_2 = 2$

30. (b)  $E_n = \frac{-313.6}{n^2}$  .....(i)

$$E_n = -34.84$$
 .....(ii)

From (i) and (ii)

$$-34.84 = \frac{-313.6}{n^2}$$

$$n^2 = \frac{313.6}{34.84} = 9$$

$$n = 3$$

31. (b)  $V \propto \frac{Z}{n}; V_1 \propto \frac{1}{1}$

In 3rd orbit,  $n = 3, Z = 1$

$$V_3 \propto \frac{1}{3}$$

32. (a)  $r = \frac{n^2 h^2}{4\pi^2 m k z e^2}$

Since,  $n = 1$  and  $Z = 1$  for both hydrogen and deuterium nucleus, the ratio of the radius is  $1 : 1$ .

33. (d) Energy given to electron =  $1.5 \times 13.6 \text{ eV}$   
 $= 20.4 \text{ eV}$   
 Excess energy =  $20.4 - 13.6$   
 $= 6.8 \text{ eV}$

34. (c) Bohr's theory is not valid for multielectron atom.

35. (c) Radius of  $n^{\text{th}}$  orbit =  $\frac{n^2 r_1}{Z}$

$r_1$  = radius of first orbit of H-atom

$$r_2 = \frac{(2)^2 r_1}{1} = 4r_1$$

$$r_3 = \frac{(3)^2 r_1}{1} = 9r_1$$

$$r_4 = \frac{(4)^2 r_1}{1} = 16r_1$$

36. (c) Number of lines in the infrared region

= Total emitted lines - [Number of lines in visible region + Number of lines in U.V. region]

$$n_1 = 6 ; n_2 = 1$$

$$\text{Total emitted lines} = \frac{(n_1 - n_2)(n_1 - n_2 + 1)}{2}$$

All the lines falling onto  $n = 2$  are in the visible bond, the number of lines of the visible region = 4

All the lines falling onto  $n = 1$  are in the U.V. region, the number of lines in the ultraviolet region = 5

$$\therefore \text{Number of lines in infrared region} = 15 - 4 - 5 \\ = 6$$

37. (b) Total number of lines in Lyman series is given by  $n - 1$

38. (d) Number of spectral lines =  $\frac{n(n-1)}{2}$

$$= \frac{5(5-1)}{2}$$

$$= 10$$

39. (d) The transition  $3 \rightarrow 2$  will correspond to red line as it has lowest energy.

40. (d)  $\frac{1}{\lambda} = Rz^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

Balmer :  $n_1 = 2 ; n_2 = 3$

Paschen :  $n_1 = 3 ; n_2 = \infty$

$$V_B - V_P = R(3)^3 \left[ \frac{1}{4} - \frac{1}{9} \right] - R(3)^2 \left[ \frac{1}{9} - \frac{1}{\infty} \right]$$

$$= \frac{R}{4}$$

41. (c) Lyman series corresponds to transition to  $n = 1$  level.

42. (c) Paschen series corresponds to transition to  $n = 3$  level.

43. (c) Series limit of Lyman series,  $n = 1$

$$\frac{1}{\lambda} = R \left( \frac{1}{n^2} \right) = R$$

$$\lambda = \frac{4}{R} = 4 \times 912 \text{ Å}$$

44. (a)  $\frac{1}{\lambda} = R_H \left[ \frac{1}{l^2} - \frac{1}{(\infty)^2} \right]$

$$\frac{1}{\lambda} = 109678$$

$$\lambda = 911.7 \times 10^{-8} \text{ cm}$$

45. (b)  $\frac{1}{\lambda} = Z^2 R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

In both the cases, transition states are same,

$$\frac{1}{\lambda} \propto Z^2$$

$$\therefore v \propto Z^2$$

$$\Rightarrow \frac{v_1}{v_2} = \frac{Z_1^2}{Z_2^2}$$

Let  $v'$  be the frequency of line emitted by  $\text{He}^+$

$$\frac{v_0}{v'} = \left( \frac{1}{2} \right)^2$$

$$v' = 4v_0$$

46. (c) Paschen series of hydrogen atom lies in the visible region of electromagnetic radiation.

47. (d)  $\bar{v} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$

$$\bar{v} = R_H \left( \frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$\bar{v} = \frac{5R_H}{36} \text{ cm}^{-1}$$

48. (d)  $\frac{1}{\lambda} = R \times (l)^2 \left[ \frac{1}{(l)^2} - \frac{1}{(3)^2} \right]$

$$\frac{1}{\lambda} = \frac{8R}{9}$$

$$\lambda = \frac{9}{8R}$$

49. (b)  $\frac{r_1}{r_3} = \frac{(l)^2}{(3)^2}$

$$r_3 = 9r_1 = 9x$$

According to De Broglie;

$$mv r_3 = \frac{3h}{2\pi} ; \frac{h}{mv} = \frac{2\pi r_3}{3}$$

$$\lambda = \frac{2\pi(9x)}{3}$$

$$6\pi x$$

50. (b) For  $\text{Li}^{2+}$  ion,  $\frac{Z}{n} = \frac{3}{2}$

For  $\text{C}^{5+}$  ion,  $\frac{Z}{n} = \frac{6}{4} = \frac{3}{2}$

51. (c)  $\lambda = \frac{h}{p}$

52. (d)  $\lambda = \frac{h}{m \times v}$

$$m = \frac{h}{\lambda \times v}$$

$$m = \frac{6.62 \times 10^{-34}}{6.62 \times 10^{-35} \times 100}$$

$$m = 0.1 \text{ kg}$$

53. (a)  $\lambda = \frac{h}{\sqrt{2mE}}$

$$\frac{\lambda_1}{\lambda_2} = \sqrt{\frac{E_2}{E_1}}$$

$$\frac{3}{5} = \sqrt{\frac{E_2}{E_1}}$$

$$\frac{E_1}{E_2} = \frac{25}{9}$$

54. (d)  $\Delta n = \frac{h}{4\pi \times \frac{1}{5} \times 0.01}$

$$= 2.62 \times 10^{-32} \text{ m}$$

55. (b)  $\frac{r_1}{r_3} = \frac{(1)^2}{(3)^2}$

$$r_3 = 9r_1 = 9 \text{ times}$$

According to De Broglie;

$$mv r_3 = \frac{3h}{2\pi} ; \quad \frac{h}{mv} = \frac{2\pi r_3}{3}$$

$$\lambda = \frac{2\pi(9x)}{3}$$

$6\pi$  times

56. (b)  $\lambda = \frac{h}{mv}$

molecule with smallest mass will have maximum De broglie wavelength.

57. (a)  $\sqrt{n(n+2)} = 24$

$\Rightarrow n = 4$  (No. of unpaired electrons)

$$Z = 26$$

$$X^{n+} \rightarrow X = \text{Fe}, n = 2$$

58. (b)  $\text{Fe}^{2+} \rightarrow [\text{Ar}]3d^64s^0$

4 unpaired electrons

59. (b) The number of electrons with  $l = 1$  is 12.  
The number of electrons with  $l = 2$  is 5

60. (b)  $|L| = \sqrt{l(l+1)} \frac{h}{2\pi}$

$$= \sqrt{0(0+0)} \frac{h}{2\pi} = 0$$

61. (c)  $\text{Cl}^- \rightarrow [\text{Ne}]3s^23p^6$   
for 3p orbital,  $l = 1$  and  $m$  is any one of  $-1, 0, 1$ .

62. (c) No. of radial nodes  $= n - l - 1$

$$l = 3 - l - 1$$

$$l = 1$$

$$|L| = \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{l(l+1)} \frac{h}{2\pi}$$

$$= \sqrt{2} \frac{h}{2\pi}$$

63. (a) For 1st orbital, the distance at which maximum radial probability occurs is  $r_0$ .

64. (c) The maximum probability of finding an electron in the  $d_{xy}$  orbital is at an angle of  $45^\circ$  from the x and y-axis

65. (c)  $3p_y$  orbital has ZX modal plane.

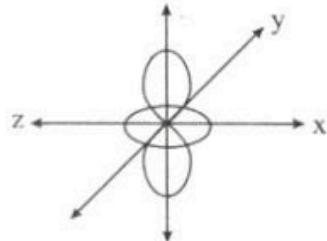
66. (c) Total no. of nodes  $= n - l$   
 $= 3 - 1 = 2$

Radial nodes  $= 3 - l - 1 = 1$   
Angular nodes  $= l = 1$

67. (b) According to Schrodinger model, the nature of an electron in an atom is only as a wave.

68. (d) (A)  $3d_{x^2-y^2}$  orbital has lobes in x and y axis.  
(B)  $3d_z^2$  is a mixed orbital.

69. (d)  $d_z^2$  has doughnut shape.



70. (b) Spin quantum number was discovered before Schrodinger even gave his equation.



## Exercise-2 (Learning Plus)

1. (a)  $E = K.E + w$

$$E = hv = \frac{hc}{\lambda}$$

$$\frac{hc}{\lambda} = 1 + w \quad \dots(i)$$

when light of wavelength  $\frac{\lambda}{3}$  is incident

$$\frac{hc}{\lambda/3} = 5 + w \quad \dots(ii)$$

$$\frac{3hc}{\lambda} = 5 + w$$

put the value of  $\frac{hc}{\lambda}$  in equation (ii) we get

$$3(1 + w) = 5 + w$$

$$2w = 2$$

$$w = 1 \text{ eV}$$

2. (c)  $r_1 = R$

$r_2 = 4R$

we know radius  $\propto n^2$

$$\therefore r_2 = 4r_1 \Rightarrow n_2 = 2r_1$$

$$v \propto \frac{1}{n}$$

$v_1 = 2v_2$

$$\text{Time} = \frac{\text{Distance}}{\text{Speed}} = \frac{2\pi r}{v}$$

$$\therefore \frac{T_1}{T_2} = \frac{2\pi r_1}{v_1} \times \frac{v_2}{2\pi r_2} = \frac{r_1 \times 0.5v_1}{v_1 \times 4r_1} \Rightarrow \frac{1}{8}$$

3. (d) P.E. =  $\frac{-ze^2}{4\pi\epsilon_0 r}$

for Be;  $z = 4$

$$\text{P.E.} = -\frac{4e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{\pi\epsilon_0 r}$$

4. (c) Some wavelength means energy equal.

$$\text{Energy} = \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) z^2 \quad z \text{ for Li} = 3, \text{He} = 2$$

$$\left( \frac{1}{2^2} - \frac{1}{4^2} \right) \times 2^2 = \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \times 3^2$$

$$\left( \frac{1}{4} - \frac{1}{16} \right) \times 4 = \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \times 9$$

$$\left( \frac{4-1}{16} \right) \times 4 = \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \times 9$$

$$\frac{3 \times 4}{16 \times 9} = \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{12} = \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$n_1 = 3, n_2 = 6 \text{ then } \frac{1}{12} = \left( \frac{1}{9} - \frac{1}{36} \right)$$

5. (a)

$$hv_1 = 13.6 \left( \frac{1}{1} - \frac{1}{\infty} \right)$$

$$v_1 = C_0 \left( \text{where } C_0 = \frac{13.6}{h} \right)$$

Then,

$$hv_2 = 13.6 \times \left( \frac{1}{1} - \frac{1}{2} \right)$$

$$v_2 = \frac{v_1}{2}$$

Also,  $hv_3 = 13.6$

$$v_3 = \frac{v_1}{2}$$

$$\Rightarrow [v_2 + v_3 = v_1]$$

$$[v_1 - v_2 = v_3]$$

6. (b) For shortest wave length of Lyman series

$$n_1 = 1, n_2 = \infty$$

$$\therefore \frac{1}{x} = R \left[ \frac{1}{1^2} - \frac{1}{\infty} \right]$$

$$\text{So, } x = 1/R \text{ or } R = 1/x$$

for first line of Balmer

$$n_1 = 2, n_2 = 3$$

$$\frac{1}{\lambda} = R(1^2) \left[ \frac{1}{2^2} - \frac{1}{3^2} \right]$$

$$\frac{1}{\lambda} = R \left[ \frac{5}{36} \right] \quad R = \frac{1}{x}$$

$$\lambda = \frac{36x}{5}$$

7. (a) Balmer series corresponds to transition upto second energy level.

So, total no. of lines = 2

$$4 \rightarrow 2 \text{ and } 3 \rightarrow 2$$

Hence,  $n = 4$

$$\text{Energy} = \frac{-13.6}{n^2} = \frac{13.6}{4^2} = 0.85$$

The kinetic energy of the ejected photoelectrons

$$= 13 - 0.85 = 12.15 \text{ eV}$$

8. (b) Acc. to question

$$M_y = M_x \times \frac{25}{1000} = 0.25 M_x$$

$$\text{and } V_y = V_x \times \frac{75}{1000} = 0.75 V_x$$

$$\text{De-Broglie } \lambda = \frac{h}{mv}$$

$$\lambda_x = 1 \text{ \AA} = \frac{h}{M_x \times V_x}$$

$$\lambda_y = \frac{h}{0.25M_x \times 0.75V_x} = 5.33 \frac{h}{M_x \times V_x}$$

$$\lambda_y = 5.33 \text{ \AA}$$

9. (b)  $\lambda = \frac{h}{mv}$

$$\frac{\lambda_1}{\lambda_2} = \frac{m_2 v_2}{m_1 v_1}$$

$$\frac{v_1}{v_2} = \frac{m_2 \lambda_2}{m_1 \lambda_1}$$

$$\frac{v_1}{v_2} = \frac{4m_a \lambda_a}{m_p \lambda_p}$$

$$\frac{\lambda_p}{\lambda_a} = \frac{1}{2} \Rightarrow \frac{\lambda_a}{\lambda_p} = \frac{2}{1}$$

$$\Rightarrow \frac{\lambda_p}{\lambda_a} = 4 \times 2 = 8 : 1$$

10. (d) by de-broglie hypothesis  $mvr = \frac{nh}{2\pi}$

$$2\pi r = n \left( \frac{h}{mv} \right) = n\lambda$$

11. (c) In case of  $dx^2 - y^2$  orbital electron density lies on x and y axis.

So, probability of finding electron is maximum along x and y-axis.

12. (b) Magnetic moment =  $2.83 = \sqrt{n(n+2)}$

So no. of unpaired electron =  $2 = n$   
no. of unpaired is in  $Ni^{2+} = 2$ .

13. (d) The expression for calculating the total number of electrons in any energy level is  $\sum_{l=0}^{l=n-1} 2(2l+1)$

14. (d) The spin quantum numbers  $+1/2$  and  $-1/2$  represents two quantum mechanical spin states which have no classical analogue.

15. (a)  $\lambda = \frac{h}{\sqrt{2mK.E.}}$

Mass of electron is significantly lower than the mass of a proton or alpha particle K.E. order 16 E = electron, 4 E = Proton, E = alpha particle.

$$\lambda_e > \lambda_p = \lambda_\alpha$$

(mass of alpha particle is 4 times mass of proton)

16. (c)  $r_1 = R$

$$r_2 = 4R$$

we know radius  $\propto n^2$

$$\therefore r_2 = 4r_1 \Rightarrow n_2 = 2r_1$$

$$v \propto \frac{1}{n}$$

$$v_1 = 2v_2$$

$$\text{Time} = \frac{\text{Distance}}{\text{Speed}} = \frac{2\pi r}{v}$$

$$\therefore \frac{T_1}{T_2} = \frac{2\pi r_1}{v_1} \times \frac{v_2}{2\pi r_2} = \frac{r_1 \times 0.5v_1}{v_1 \times 4r_1} \Rightarrow \frac{1}{8r_1}$$

17. (c) Total nodes =  $n - 1$

Angular node =  $l$

radial nodes =  $n - l - 1$

for 3p,  $n = 3; l = 1$

angular node = 1, radial node = 1

Total nodes = 2.

18. (b) angular momentum

$$L_n = \frac{nh}{2\pi}$$

$$\Rightarrow L_{n+1} - L_n = (n+1) \frac{h}{2\pi} - \frac{nh}{2\pi}$$

$$\Rightarrow \frac{nh}{2\pi} + \frac{h}{2\pi} - \frac{nh}{2\pi}$$

$$\frac{h}{2\pi}$$

19. (b) Potential difference = 6V

$$\frac{1}{2}mv^2 = e = P.D$$

$$\therefore V = \sqrt{\frac{2e6}{m}} = \sqrt{\frac{2 \times 1.6 \times 10^{-19} \times 6}{4 \times 1.67 \times 10^{-27}}} = 2.4 \times 10^4$$

As de broglie wave length  $\lambda$  is given by

$$\lambda = \frac{h}{mv}$$

$$\Rightarrow \frac{6.6 \times 10^{-34}}{4 \times 1.67 \times 10^{-27} \times 2.4 \times 10^4}$$

$$= 4.15 \text{ pm}$$

20. (c) Energy of photon  $\Delta E = 2.55 \text{ eV} = 2.55 \times 1.6 \times 10^{-19} \text{ J}$

$$\Delta E = \frac{hc}{\lambda} ; \quad \lambda = \frac{hc}{\Delta E}$$

$$\lambda = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{2.55 \times 1.6 \times 10^{-19}} = 4861 \text{ Å}$$

Corresponds to the second line of balmer series  $n_1 = 2$  to  $n_2 = 4$

$$\text{So, } \Delta\lambda = \frac{h}{mv'} - \frac{h}{mv} \Rightarrow \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31}} \left( \frac{2}{2.19 \times 10} \right)$$

$$\Delta\lambda = 6.64 \text{ Å}$$

21. (d) Principal quantum number (n)

$$n = 3$$

Now, magnetic quantum number (m) given the relative position of the electrons in orbitals.

$$m = -l \text{ to } +l$$

$$l = |m|$$

$$l = |m| = 2 = 1$$

22. (b) Ground state configuration of Boron =  $1s^2 2s^2 2p^1$   
Excited state configuration of Boron =  $1s^2 2s^1 2p^2$

23. (d) Most probable radius =  $\frac{a_o}{Z}$

$$a_o = 52.9 \quad z \text{ for helium} = 2$$

$$r_{mp} = \frac{52.9}{2} = 26.45 \text{ pm}$$

24. (b)  $E_{H-H}$  bond dissociation

$$= \frac{429 \times 10^3}{6.023 \times 10^{23}} = 7.12 \times 10^{-19} \text{ J / molecule}$$

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{270 \times 10^{-9}} = 7.36 \times 10^{-19} \text{ J}$$

Energy converted into kinetic Energy = Energy left after bond dissociation

$$\Rightarrow (7.36 - 7.12) \times 10^{-19} \text{ J}$$

$$\Rightarrow 0.24 \times 10^{-19} \text{ J}$$

% energy converted into K.E

$$\Rightarrow \frac{0.24 \times 10^{-19}}{7.36 \times 10^{-19}} \times 100 = 3.26\%$$

25. (d) Orbital angular momentum

$$= \sqrt{l(l+1)} \frac{h}{2\pi} \quad \dots(i)$$

$$\Rightarrow \sqrt{5} \frac{h}{2\pi} \quad \dots(ii)$$

Comparing both

$$\sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{5} \frac{h}{2\pi}$$

$$\sqrt{l(l+1)} = \sqrt{20}$$

$$l(l+1) = 20$$

$$l = 4$$

g subshell

$\Rightarrow$  9 orbitals possible.

26. (a)  $Ne = 10$  es

$$F^- = 10 \text{ e}^- \text{s}, Na^+ = 10 \text{ e}^- \text{s}, Mg^{2+} = 10 \text{ e}^- \text{s}, Cl^- = 18 \text{ e}^- \text{s}$$

27. (b) Pauli's exclusion principle :- two electrons can't have the same values for all four quantum numbers.

28. (c) Total number of electrons in shell =  $2n^2$

$$\Rightarrow 2 \times (3)^2 = 2 \times 9 = 18$$

29. (c)  $l = 0, 1, 2, 3, \dots = n - 1$  to 0

$$l = |m|$$

$$4f \text{ orbital} = n = 4 \quad l = 3$$

$$m = 3, 2, 1$$

30. (c) In any subshell, the maximum number of electrons having same value of spin quantum number is  $2l + 1$

31. (b) For  $l = 0$  (s) =  $m = 0$

$$\text{For } l = 1 \text{ (p)} = m = -1, 0, 1$$

$$\text{For } l = 2 \text{ (d)} = m = -2, -1, 0, 1, 2$$

$$\text{For } l = 3 \text{ (f)} = m = -3, -2, -1, 0, 1, 2, 3$$

$$\text{total } m \text{ value} = 1 + 3 + 5 + 7 = 16$$

32. (d) The electronic configuration of an atom / ion can be defined by Aufbau's principle, Hund's rule of maximum multiplicity and pauli's exclusion principle.

33. (c) Energy will be higher if value of  $n + l$  higher of valence of  $n + 1$  is same then lower  $n$  have lower energy.

$n + l$	
4s	$4 + 0 = 4$
4p	$4 + 1 = 5$
3d	$3 + 2 = 5$

34. (b) Aufbau's principle: electrons are filled in increasing order of energy level. If we compare ns or np energy level ns have less energy So, ns will be filled first.

35. (b) Cu  $\Rightarrow$  29 electrons

$$Cu^+ \Rightarrow 28 \text{ electrons}$$

$$\text{in K shell} = 2 \times 1^2 = 2$$

$$\text{in L shell} = 2 \times 2^2 = 8$$

$$\text{in M shell} = 2 \times 3^2 = 18$$

So in outer most shell 18 e<sup>-</sup>s.

36. (d) A strong argument for the particle nature of cathode rays is they are deflected by electric and magnetic fields. The deflection through electric and magnetic fields indicate that cathode rays are streams of minute particles carrying a negative charge.

37. (b) Let a,b,c be the relative abundances of three isotopes having mass numbers M(M+1) and (M+2) respectively.

$$\frac{aM + b(M+1) + c(M+2)}{a+b+c} = M + 0.5$$

$$aM + bM + b + cM + 2c = aM + bM + cM + 0.5a + 0.5b + 0.5c$$

$$b + 2c = 0.5a + 0.5b + 0.5c$$

$$0.5b + 1.5c = 0.59$$

$$b + 3c = a$$

This is true for the option (b)

$$\Rightarrow a : b : c$$

$$\Rightarrow 4 : 1 : 1$$

38. (c) The statement (c) is not correct. The energy of an electron in an atomic orbita of a multi-electron atom depends on the principal quantum number as well as azimuthal quantum number.

39. (b) At high pressure the mean free path of electron is low as the atoms of gas are closely packed at high pressure but when the gas pressure is low, the atoms are not closely spaced, the electrons get enough time to accelerate. As a result they collide with another atom, they gain sufficient energy from electric field to ionize other atoms. So gas conducts at low pressure.

40. (c) The uncertainty in the position of electron is

$$\Delta x = \frac{h}{4\pi\Delta p}$$

$$\Rightarrow \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 1.0 \times 10^{-5}}$$

$$\Delta x = 5.27 \times 10^{-30} \text{ m}$$



### Exercise-3 (JEE Advanced Level)

1. (a,c)  $r_n = \frac{n^2}{Z} (0.529 \text{ \AA})$ , radius of first Bohr's orbits = 0.529

$$\text{\AA} = r_1$$

For  $\text{He}^{2+}$ ,  $Z = 2$ ,  $n = 2$

$$r_{\text{He}^{2+}} = \frac{4}{2} r_1 \quad \text{or} \quad r_{\text{He}^{2+}} = 2r_1$$

For  $r_{\text{O}^{2-}}$ ,  $Z = 8$ ,  $n = 4$

$$r_{\text{O}^{2-}} = r_1 \times \frac{16}{8} \quad \text{or} \quad r_{\text{O}^{2-}} = 2r_1$$

2. (a,b,c)

Maximum no. of electron in the subshell is given by  $= 2(2l + 1)$

3. (a,b,c,d)

$\Psi$  is a mathematical function  $|\Psi|^2$  denotes the probability density  $R^2(r)_{\max}$  at nucleus.

4. (b,c)

Cathode rays when strikes to fluorescent material, produces fluorescence.

Cathode rays behaves as negatively charge in magnetic field or electric field.

5. (a,b,c,d)

Total no. of spherical nodes =  $n - l - 1$

Total angular nodes =  $l$

No. of maxima in an orbital =  $n - l$

6. (a,c,d)

$$E = \frac{-13.6}{n^2} \text{ eV} \quad (\text{For excited state})$$

$$n = 2, E_2 = \frac{-13.6}{4} \text{ eV} = -3.4 \text{ eV}$$

$$n = 3, E_3 = \frac{-13.6}{9} \text{ eV} = -1.51 \text{ eV}$$

$$n = 4, E_4 = \frac{-13.6}{16} \text{ eV} = -0.85 \text{ eV}$$

7. (b,c,d)

(b) We know,  $2 \times \text{K.E.} = -\text{P.E.}$

(T.E.) or  $E = \text{K.E.} + \text{P.E.}$  or  $E = \text{K.E.} - 2 \text{ K.E.}$

or  $E = -\text{K.E.}$

$\therefore E : \text{K.E.} : \text{P.E.} = -\text{K.E.} : \text{K.E.} : -2 \text{ K.E.}$

$= 1 : 1 : 2$

(c)  $v = 6 \times 10^{14} \text{ Hz}$

$$c = v\lambda \quad \text{or} \quad \lambda = \frac{c}{v} = \frac{3 \times 10^8 \text{ m/s}}{6 \times 10^{14} \text{ s}^{-1}}$$

or  $\lambda = 500 \text{ nm}$ .

(d)  $\lambda = \frac{h}{\sqrt{2m \text{K.E.}}}$ , K.E. are same for all species.

$\lambda \propto \frac{1}{\sqrt{m}}$ ,  $m$  = molecular mass

$$\lambda_H : \lambda_{He} : \lambda_{CH_4} = \frac{1}{\sqrt{1}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{16}} = 4 : 2 : 1$$

8. (a,b,c)

We know,  $\lambda \propto \frac{1}{p}$  and  $\text{K.E.} \propto p^2$

or,  $\text{K.E.} \propto \frac{1}{\lambda^2}$

$$\therefore \frac{T_A}{T_B} = \frac{\lambda_B^2}{\lambda_A^2}$$

Given,  $\lambda_B = 2\lambda_A$

$$\therefore \frac{T_A}{T_B} = \frac{2^2}{1^2} = 4 \quad \text{or} \quad T_A = 4 T_B$$

$$T_B = T_A - 1.50 \text{ eV} \quad \text{or} \quad T_B = 0.5 \text{ eV}$$

$$\text{or} \quad T_A = 2.00 \text{ eV}$$

Work function is given as for metal (A) is  $= 4.25 \text{ eV} - T_A$   
or  $(4.25 - 2) \text{ eV}$  or  $2.25 \text{ eV}$

Similarly work function is given as for metal B =  $4.20 \text{ eV} - T_B = (4.20 - 0.50) \text{ eV}$

$$= 3.70 \text{ eV}$$

9. (a,b,c) Na ( $Z = 11$ )  $1s^2 2s^2 2p^6 3s^1$

10. (a) For node  $= (12 - 8\sigma + \sigma^2) = 0$

$$\text{or } (\sigma - 6)(\sigma - 2) = 0$$

$$\text{or } \sigma = 6 \text{ and } \sigma = 2$$

$$\frac{2Zr}{na_0} = 6 \quad \text{and} \quad \frac{2Zr}{na_0} = 2$$

$$\frac{Zr}{na_0} = 3 \quad \text{Radial node}$$

$$\frac{Zr}{na_0} = 1 \quad \text{Angular node}$$

11. (b) Radial node  $= n - l - 1 = 3$  and

Angular node  $= l = 1$

$\therefore n = 5, l = 1$  i.e., P-subshell.

Hence, 5p orbital.

12. (c)  $p_z$ -orbital

13. (d) Radial node occurs where probability of finding  $e^-$  is zero

$$\therefore \Psi^2 = 0 \text{ or } \Psi = 0$$

$$(1 - \sigma)(12 - 8\sigma + \sigma^2) = 0$$

$$(1 - \sigma)(\sigma - 6)(\sigma - 2) = 0$$

$$\text{or } \sigma = 1, \sigma = 6, \sigma = 2,$$

For max. distance.

$$\sigma = \frac{2Zr}{na_0} = 6 \text{ or } \frac{2Zr}{5a_0} = 6$$

$$\text{or } r = \frac{15a_0}{Z}$$

$$14. (a) E_n = -13.6 \frac{Z^2}{n^2} \text{ eV i.e., } E_n \propto Z^2, E_n \propto \frac{1}{n^2}$$

$$\text{and } E_n = \frac{hc}{\lambda} \text{ or } E_n = hv \text{ or } E_n \propto v$$

$$T \propto \frac{1}{v}$$

15. (c) Values of m varies from  $+l$  to  $-l$  (including 0)

So, for  $l = 2$ , values of m have  $-2, -1, 0, 1, 2$ , i.e., 5

$$16. (a) E_n = -13.6 \frac{Z^2}{n^2} \text{ eV}$$

$$r_n = 0.529 \frac{n^2}{Z} \text{ A}^\circ$$

$$mv^2 = \frac{nh}{2\pi} \text{ or } v = \frac{nh}{2\pi mr}$$

$$\text{or } v = \frac{nh}{2\pi m \times 0.529 \frac{n^2}{Z} \text{ A}^\circ} \text{ or } v \propto \frac{Z}{n}$$

17. (b) For Lyman's series  $= n_h$  to  $n_l = 1$ , lies in UV region.

For Paschen series  $= n_h$  to  $n_l = 3$  lies in IR.

Last line of Balmer series lies in visible region.

$$18. (c) mv^2 = \frac{nh}{2\pi} = \sqrt{\ell(\ell+1)} h$$

$$\text{Magnetic moment} = \sqrt{n(n+2)}$$

$$\text{spin angular momentum} = \sqrt{s(s+1)} h$$

19. (d) For 3s orbital it has two nodes in (R vs. r graph)

Similarly for 4s it has 3

Similarly for 3p it has 1

20. (a,c) In a vacuum, the speed of all electromagnetic radiations is equal to the speed of light. Hence, option (a) is correct.  
He<sup>+</sup> and H both are monoelectronic species so it will have similar spectrum as of hydrogen atom.

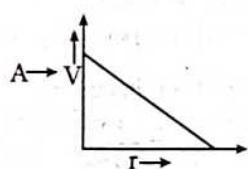
21. (b,c,d)

$$V \propto \frac{z}{n} \quad \therefore V \propto \frac{1}{n}$$

$$r \propto \frac{n^2}{z} \quad \therefore r \propto n^2$$

$$\text{P.E.} \propto -\frac{1}{r}$$

$$\text{K.E.} \propto \frac{1}{r}$$



$$22. (c,d) E \propto v \text{ and } E_n \propto \frac{1}{n^2}$$

$$\text{Also, } v \propto \frac{1}{\lambda}$$

23. (a,c)

Max. number of different photons emitted is

$4[(4 \rightarrow 3 \rightarrow 1 \text{ and } 4 \rightarrow 2 \rightarrow 1) \text{ or } (4 \rightarrow 3 \rightarrow 2 \rightarrow 1 \rightarrow 4 \rightarrow 1)]$ .

Minimum number of different photons emitted is  
 $1(4 \rightarrow 1 \text{ and } 4 \rightarrow 1)$ .

24. (a,b,c)

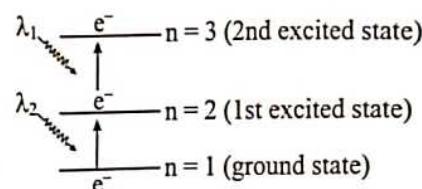
$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mKE}} = \frac{h}{\sqrt{2mqV}}$$

When v, KE and V are same, as m increasing, decreases.  $\lambda_e > \lambda_p > \lambda_a$  (if v, KE and V are same).

25. (b,c)

If intensity or no. of photons falling per unit area increased then photocurrent will increase in surface area also causes increases in no. of photons.

$$26. (b) \frac{1/\lambda_1}{1/\lambda_2} = \frac{R_H \times l^2 \left[ \frac{1}{2^2} - \frac{1}{3^2} \right]}{R_H \times l^2 \left[ \frac{1}{1^2} - \frac{1}{2^2} \right]}$$



$$\frac{\lambda_2}{\lambda_1} = \frac{1}{x} = \frac{5}{27}$$

$$x = \frac{27}{5}$$

$$\text{As, } \lambda = \frac{h}{mc}$$

for photons

$$\therefore \frac{(mc)_1}{(mc)_2} = \frac{h/\lambda_1}{h/\lambda_2}$$

$$\frac{\lambda_2}{\lambda_1} = \frac{5}{27} = y$$

$$\frac{E_1}{E_2} = \frac{hc/\lambda_1}{hc/\lambda_2} = \frac{\lambda_2}{\lambda_1} = z = \frac{5}{27}$$

27. (c,d)

For s orbital  $\theta$  &  $\phi$  are zero  $\therefore$  independent s-orbital spherical  $\therefore$  no angular component

2p,  $n = 2$

$l = 2 \rightarrow$  angular dependence

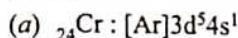
$m = 0$

28. (a,b,c)

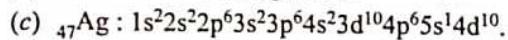
$$n = 4, m = 2$$

Value of  $\ell = 0$  to  $(n - 1)$  but  $m = 2$ .  $\therefore \ell = 2$  or 3 only  
Value of  $s$  may be  $+1/2$  or  $-1/2$ .

29. (a,b,c)



(b)  $m = -\ell$  to  $+\ell$  through zero.

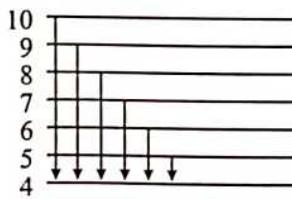


Since only one unpaired electron is present.

$\therefore$  23 electrons have spin of one type and 24 of the opposite type.

30. [14] Radius =  $0.529 \frac{n^2}{Z} \text{ Å} \Rightarrow 10 \times 10^{-9} \text{ m} = 0.529 n^2 \text{ Å}$   
So,  $n^2 = 189$  or,  $n \approx 14$

31. [6]



First Excited level = 2  
 $\therefore$  ninth level = 10

Total line = 6

32. [6] infrared lines = total lines - visible lines - UV lines

$$= \frac{6(6-1)}{2} - 4 - 5 = 15 - 9 = 6.$$

(visible lines = 4 6 → 2, 5 → 2, 4 → 2, 3 → 2)

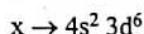
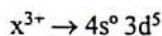
(UV lines = 5 6 → 1, 5 → 1, 4 → 1, 3 → 1, 2 → 1)

33. [5] For 3d → 

1	1	1	1	1
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34. [26]  $\sqrt{n(n+2)} = \sqrt{35}$

$$\therefore n = 5$$



i.e.,  ${}_{26}^{54}\text{Fe}$

35. (4)  $E = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9}} \text{ J}$

$$\text{or, } E = 4.125 \text{ eV}$$

Work function of the given metal must be less than energy of incident photon. i.e., Li, Na, K, Mg.

36. (5) Let excited state of  $\text{He}^+$  is  $n_2$ . Then according to question.

$$\frac{1}{\lambda_2} = R_H Z^2 \left[ \frac{1}{l^2} - \frac{1}{n_1^2} \right]$$

Putting all values, we get

$$n_1 = 2$$

Now, for  $\lambda_1$ ,  $n_1 = 2$  and  $n_2 = n$

$$\frac{1}{\lambda_1} = R_H Z^2 \left[ \frac{1}{l^2} - \frac{1}{n^2} \right] \Rightarrow n = 5$$

37. [20] For closest approach distance

$$\frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} = 3.6 \times 10^6 \times 1.6 \times 10^{-19}$$

$$\text{or, } \frac{9 \times 10^9 \times (Z \times 1.6 \times 10^{-19}) \times (2 \times 1.6 \times 10^{-19})}{1.6 \times 10^{-14}} = 3.6 \times 10^{-13}$$

$$\text{or, } Z = 20$$

38. [3] Let,  $\lambda_1$  is the wavelength of 1<sup>st</sup> line in Balmer series

$$\frac{1}{\lambda_1} = Z^2 R_H \left[ \frac{1}{l^2} - \frac{1}{3^2} \right] \text{ or } \lambda_1 = \frac{36}{5 R_H Z^2}$$

Let, wavelength of 1<sup>st</sup> line in lyman series  $\lambda_2$ .

$$\frac{1}{\lambda_2} = Z^2 R_H \left( \frac{1}{l^2} - \frac{1}{2^2} \right) \text{ or } \lambda_2 = \frac{4}{3 R_H Z^2}$$

According to question,

$$\lambda_1 - \lambda_2 = 59.3 \times 10^{-9} \text{ m} = \left[ \frac{36}{5} - \frac{4}{3} \right] \frac{1}{R_H Z^2}$$

$$\text{or } Z = 3$$

39. [4]  $K.E. = E_{\text{Photon}} - B.E._{n=1}$

$$K.E. = E_{\text{Photon}} - B.E._{n=n}$$

$$K.E. - K.E. = B.E._{n=1} - B.E._{n=n}$$

$$= 13.6 Z^2 \left[ \frac{1}{l^2} - \frac{1}{n^2} \right] = 12.75 \text{ (given)}$$

$$\therefore n^2 = 16 \text{ or } n = 4$$

40.  $\left[ \frac{5R}{9} \right] mvr = \frac{nh}{2\pi}$

$$3.1652 \times 10^{-34} = \frac{n \times 6.6 \times 10^{-34}}{2 \times 3.14} \text{ or } n = 3$$

$$v = R_H q^2 \left[ \frac{1}{l^2} - \frac{1}{3^2} \right] \Rightarrow \frac{5R}{9}$$

41. [1240]  $E = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{960 \times 10^{-10}} = 2.0625 \times 10^{-18} \text{ J}$

For one mol of photon

$$E = 6.023 \times 10^{23} \times 2.0625 \times 10^{-21} \text{ kJ}$$

$$= 1240 \text{ kJ/mol}$$

42. [31]  $w_0 = 40 \text{ eV}$  or  $w_0 = 40 \times 1.6 \times 10^{-14} \text{ J} = 6.4 \times 10^{-18} \text{ J}$

Given,  $v = 0$  or K.E. = 0 and  $\lambda = x$

$$hv = w_0 + \text{K.E.}$$

$$\text{or } \frac{hc}{\lambda} = w_0$$

$$\text{or } x = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{6.4 \times 10^{-18}} = 31.05 \text{ nm}$$

43. [12]

1<sup>st</sup> ionization potential or B.E. of that nucleus i.e., from  $n = 1$  to  $n = \infty$ .

$$E_\infty - E_1 = 16 \text{ V} \text{ or } E_1 = -16 \text{ eV}$$

For 1<sup>st</sup> excitation i.e.,  $n = 1$  to  $n = 2$ .

$$E_2 - E_1 = -\frac{16}{2^2} - (-16) = 12 \text{ eV}$$

44. [5] No. of spectral lines

$$\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2} = 3$$

$$\text{or } n_2^2 - 5n_2 + 6 = 6$$

$$\text{or } n_2(n_2 - 5) = 0 \text{ or } n_2 = 5.$$

$$45. [12] \text{ K.E. of emitted } e^- = \frac{150}{(12.016)^2} = 13.6 \times \frac{11}{144}$$

$$\text{B.E. of 2nd E.S. of H} = \frac{13.6}{n^2} = \frac{13.6}{9}$$

Total energy = B.E. + K.E.

$$13.6 Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{13.6}{9} + 13.6 \times \frac{11}{144}$$

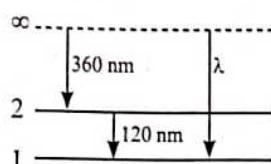
$$3^2 \left[ \frac{1}{6^2} - \frac{1}{n_2^2} \right] = \frac{1}{9} + \frac{11}{144} \text{ or } n_2 = 12$$

$$46. [-435.2 \text{ eV}] \text{ T.E.} = \frac{-kZe^2}{r} \text{ or } r = \frac{n^2 h^2}{4\pi^2 m k Z e^2}$$

$$\text{or T.E.} = -\frac{kZe^2}{\frac{n^2 h^2}{4\pi^2 m k Z e^2}} \text{ or } \frac{\text{T.E.}_2}{\text{T.E.}} = \frac{m_2 e_2^4}{m_1 e_1^4} = 2^5 = 32$$

$$\text{T.E.}_2 = -13.6 \times 32 \text{ eV} = -435.2 \text{ eV}$$

$$47. [90 \text{ nm}] \frac{1}{\lambda} = \frac{1}{120} + \frac{1}{360} \Rightarrow \lambda = 90 \text{ nm}$$



$$48. [91 \text{ nm}] E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E}$$

$$\lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2.17 \times 10^{-18}} = 91 \text{ nm}$$

$$49. [973.5 \text{ Å}] \Delta E = 13.6 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = \frac{hc}{\lambda}$$

$n_1 = 4, n_2 = 1$  putting these values in above equation

$$\lambda = 973.5 \text{ Å}$$

$$50. [5 \times 10^{-26}] \Delta x \cdot \Delta v \geq \frac{h}{4\pi m} \text{ or } \Delta x \geq \frac{h}{4\pi m \Delta v}$$

$$\Delta x \geq \frac{6.626 \times 10^{-34}}{4\pi \times 10^{-3} \times \frac{3.13}{\pi} \times 10^{-3}} \text{ or } \Delta x \geq 5 \times 10^{-26} \text{ m}$$

51.  $[3.63 \times 10^6 \text{ m}^{-1}]$  Energy of accelerated electron

$$= 1.6 \times 10^{-19} \times 4.5 \text{ or } 7.2 \times 10^{-19} \text{ J}$$

The above energy completely converted in light.

$$\frac{hc}{\lambda} = 7.2 \times 10^{-19}$$

$$\bar{v} = \frac{1}{\lambda} = \frac{7.2 \times 10^{-19}}{6.6 \times 10^{-34} \times 3 \times 10^8} = 3.63 \times 10^6 \text{ m}^{-1}$$

52. [300303] General equation of  $\Psi(r)$

$$= 4pk_i e^{-r/k_i} \times r^l (\text{Polynomial})^{n-l-1}$$

On comparing

$$n - l - 1 = 2, l = 0$$

$\therefore n = 3$  i.e., 3s-orbital

$$\therefore A = 3, B = 0, C = 0$$

For D  $\Rightarrow$  8s to 8p there are 3 orbitals which are 6d, 5f, 7g

For F = 3 (on solving)  $r^2 - 5r + 6 = 0$ .

## Exercise-4 (Past Year Questions)

### JEE MAIN

1. (d) De-Broglie equation

$$\lambda = \frac{h}{mv}$$

$$\therefore KE = \frac{1}{2} mv^2$$

$$\therefore mv = \sqrt{2mKE}$$

$$KE = eV$$

$$mv = \sqrt{2meV}$$

Put in equation (i)

$$\frac{h}{\lambda} = \sqrt{2meV}$$

2. (d) Radius of  $n^{\text{th}}$  Bohr orbit in H-atom =  $0.53 n^2 \text{ Å}$

$$\text{Radius of II<sup>nd</sup> Bohr orbit} = 0.53 \times (2)^2 = 2.12 \text{ Å}$$

3. (d) 2s feels maximum attraction from the nucleus due to more  $Z_{\text{eff}}$

$$4. (c) (A) mv = \frac{nh}{2\pi}$$

As n increases, angular momentum increases.

$$(C) \text{Angular momentum} = \frac{nh}{2\pi}$$

$$5. (d) \lambda = \frac{h}{mv}$$

According to Einstein's theory of photoelectric effect:

$$hv = hv_0 + KE$$

$$hv = hv_0 + \frac{1}{2} mv^2$$



$$2h(v - v_0) = mv^2$$

$$\frac{2h(v - v_0)}{m} = v^2$$

$$v \propto (v - v_0)^{1/2}$$

$$\lambda \propto \frac{h}{m(v - v_0)^{1/2}}$$

$$\lambda \propto \frac{1}{(v - v_0)^{1/2}}$$

6. (a) [i]  $900 \text{ nm} = 9000 \text{ Å}$

It is in far infra red region hence paschen.

7. (d) For emission line

$$n_f < n_i$$

$$\therefore \bar{v} = RZ^2 \left[ \frac{1}{n_i^2} - \frac{1}{n_f^2} \right] = R \left[ \frac{1}{8^2} - \frac{1}{n^2} \right]$$

$$\text{or, } \bar{v} = R_H \left( \frac{1}{64} - \frac{1}{n^2} \right)$$

$$= \frac{R_H}{64} - \frac{R_H}{n^2}$$

$$\bar{v} = -R_H \left( \frac{1}{n^2} \right) + \frac{R_H}{64}$$

$$\therefore y = mx + c$$

$$\text{Slope} = -R_H$$

8. (c) The isotopes are:

$${}^1\text{H}, {}^2\text{H} \text{ and } {}^3\text{H} \equiv \text{P, D, T}$$

9. (c)  $hv = \phi + hv^\circ$

$$\frac{1}{2}mv^2 = hc \left( \frac{1}{\lambda} - \frac{1}{\lambda_0} \right)$$

$$\phi = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}} - \frac{1}{2} \times 9 \times 10^{-31} \times (6 \times 10^5)^2$$

$$\phi = 3.35 \times 10^{-19} \text{ J} \Rightarrow \phi = 2.1 \text{ eV}$$

10. (c) The electron configuration is [Xe] 4f<sup>14</sup> 5d<sup>1</sup> 6s<sup>2</sup>

$$11. (c) E = -13.6 \frac{Z^2}{n^2} \text{ eV}$$

$$E_{He}^+ = -13.6 \frac{4}{9} = -6.04$$

12. (d)  $2\pi r = n\lambda$

$$\lambda = \frac{2\pi r}{n} = \frac{2\pi n^2 a_0}{n \times Z} = 2\pi \frac{n}{Z} a_0$$

$$\lambda = 1.5 \pi a_0$$

$$\therefore 2\pi \frac{n}{Z} a_0 = 1.5 \pi a_0$$

$$\therefore \frac{n}{Z} = \frac{1.5}{2} = 0.75$$

13. (a) 3 and 1

14. (c) K.E =  $hv - hv_0$ , so (c) is not correct.

15. (b) According to (n + ℓ) rule : 3p < 3d < 4p < 4d  
Correct option : (b)

16. (b) For isoelectronic species the size is compared by nuclear charge.  
Correct option: (b)

17. (b) K = 2, 8, 8, 1

After removal of one electron, second electron we have to remove from another shell, hence there is large difference between first and second ionization energies.

18. (d) For Lyman

$$\bar{v}_{\max} = R_H \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) = R_H$$

$$\bar{v}_{\min} = R_H \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} R_H$$

$$\Delta \bar{v}_{\text{Lyman}} = \frac{R_H}{4}$$

For Balmer

$$\bar{v}_{\max} = R_H \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) = \frac{R_H}{4}$$

$$\bar{v}_{\min} = R_H \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R_H$$

$$\Delta \bar{v}_{\text{Balmer}} = \frac{R_H}{4} - \frac{5R_H}{36} = \frac{4R_H}{36} = \frac{R_H}{9}$$

$$\frac{\Delta \bar{v}_{\text{Lyman}}}{\Delta \bar{v}_{\text{Balmer}}} = \frac{R_{H/4}}{R_{H/9}} = \frac{9}{4}$$

19. (d)  $hv - \phi = KE$

$$\Rightarrow \left( \frac{hc}{\lambda} \right)_{\text{incident}} = KE + \phi$$

$$\left( \frac{hc}{\lambda} \right)_{\text{incident}} \approx KE$$

$$KE = \frac{p^2}{2m} = \frac{hc}{\lambda_{\text{incident}}} = \frac{hc}{\lambda} \quad \dots(i)$$

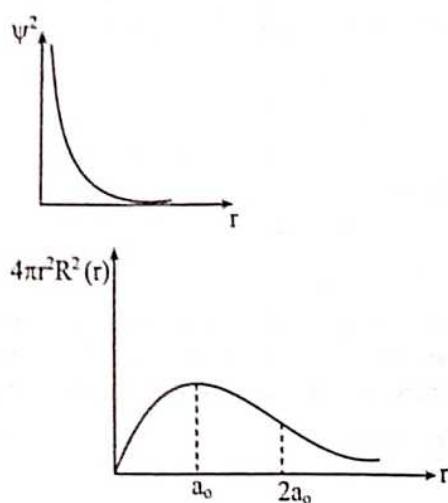
$$\Rightarrow \frac{p^2 \times (1.5)^2}{2m} = \frac{hc}{\lambda'} \quad \dots(ii)$$

divide (i) and (ii)

$$(1.5)^2 = \frac{\lambda}{\lambda'}$$

$$\Rightarrow \lambda' = \frac{4\lambda}{9}$$

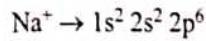
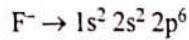
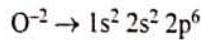
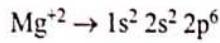
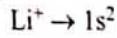
20. (d)



21. (b)  $P(x) = 4\pi x^2 \times [\psi_x]^2$

Probability will be maximum at A and C.

22. (d)  $N^{-3} \rightarrow 1s^2 2s^2 2p^6$

 $N^{-3}$ ,  $O^{-2}$ ,  $F^-$  and  $Na^+$  are isoelectronic23. (d) Graph of  $|\psi|^2$  v/s  $r$  touches  $r$  axis at 1 point so it has one radial node and since at  $r = 0$ , it has some value so it should be for 's' orbital.

$\therefore n - \ell - 1 = 1$  where  $\ell = 0 \Rightarrow n - 1 = 1$

$\therefore n = 2 \Rightarrow '2s'$  orbital

24. (b)

$$\frac{1}{\lambda_2} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) Z^2$$

$$\frac{1}{\lambda_2} = R_H \left( \frac{1}{m_1^2} - \frac{1}{m_2^2} \right) Z^2$$

as for shortest wavelengths both  $n_2$  and  $m_2$  are  $\infty$ 

$$\therefore \frac{\lambda_1}{\lambda_2} = \frac{9}{1} = \frac{m_1^2}{n_1^2}$$

Now if  $m_1 = 3$  &  $n_1 = 1$  it will justify the statement hence Lyman and Paschen (b) is correct.

25. (d) Balmer series lies in visible region.

26. (b) No. of orbitals =  $1 + 3 + 5 + 7 + 9 = 25$ 27. (b) I. As wavelength decreases, the spacing between the lines ( $\Delta\lambda$ ) becomes smaller and smaller.II. For balmer series,  $n_1 = 2$ III.  $n_2 = 3$  to  $n_1 = 1$  will produce the longest wavelength.28. (c) 
$$\begin{array}{ccccccc} {}^1H & & {}^2H(D) & & {}^3H(T) \\ \text{Number of neutrons} & 0 & + & 1 & + & 2 & = 3 \end{array}$$

29. (c)  $r = \frac{a_0 n^2}{Z}$

For  $Li^{2+}$   $r = \frac{a_0 (2)^2}{3} = \frac{4a_0}{3}$

30. (d)  $2\pi r = n\lambda$

$2\pi \times \frac{n^2}{Z} a_0 = n\lambda$

$2\pi \times \frac{4^2}{1} a_0 = 4\lambda$

$\lambda = 8\pi a_0$

31. (222)

w, work function of sodium metal =  $4.41 \times 10^{-19} J$  $\lambda$ , wavelength of incident light =  $300 nm = 3 \times 10^{-7} m$ 

According to Photoelectric effect,

$$\frac{hc}{\lambda} = w + KE$$

$$\frac{6.63 \times 10^{-34} \times 3 \times 10^8}{3 \times 10^{-7}} = 4.41 \times 10^{-19} + KE$$

$$6.63 \times 10^{-19} = 4.41 \times 10^{-19} + KE$$

$$KE = 2.22 \times 10^{-19} J = 222 \times 10^{-21} J$$

32. (d) Cs has least work function value because of its electronegativity that's why it is used in photoelectric cells.

33. (a) 2 subshells are associated with  $n = 4$  and  $m = -2$ .34. (b) Explanation of variation of internal energy of Ar with temperature (Straight line and  $U \propto T$ ) is not a direct manifestation of the quantum nature of atoms. While explanation of absorption spectrum, nature of emission of radiation from hot bodies (black body radiation) and photoelectric effect are direct manifestation of the quantum nature of atoms.35. (d) Under hypothetical situation, the value of  $l$  is greater than  $n$  which varies from 0 to  $n + 1$ for  $n = 1, l = 0, 1, 2$  $n = 2, l = 0, 1, 2, 3$ Atomic number ( $Z$ ) = 9 $1s^2 1p^6 1d^1$ 

Atomic number 6

 $1s^2 1p^4$ 

Atomic number 8

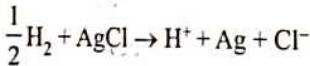
 $1s^2 1p^6$ 

Atomic number 13

 $1s^2 1p^6 1d^5$ 

Here atomic number of first noble gas will be 18.

36. [142]

Pt| $H_2$  (1 bar)|HCl( $pH = 1$ )|AgCl|Ag

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.06}{1} \log [H^+][Cl^-]$$

$$= 0.22 - 0.06 \log 10^{-2} = 0.34 \text{ V}$$

Work function of Na metal = 2.3 eV

KE of photoelectron = 0.34 eV

Energy of incident radiation =  $2.3 + 0.34 = 2.64 \text{ eV}$

Also energy of incident radiation for K metal = 2.64 eV

Work function of K metal = 2.25 eV

KE of photoelectrons =  $2.64 - 2.25 = 0.39 \text{ eV}$

$$\therefore E_{\text{cell}} = 0.39 \text{ V} = 0.22 - 0.06 \log [H^+]^2$$

$$= 0.22 + 0.12 \times pH$$

$$pH \approx 1.42 = 142 \cdot 10^{-2}$$

37. (d) Shortest wavelength  $\rightarrow$  Max energy ( $\infty \rightarrow 1$ )  
(Lyman series)

$$\frac{1}{\lambda_1} = R_H (1)^2 \left[ \frac{1}{1} - 0 \right]$$

$$\frac{1}{\lambda_1} = R_H \Rightarrow R_H = \frac{1}{\lambda_1}$$

For Balmer series,

$$\frac{1}{\lambda_1} = R_H (2)^2 \left[ \frac{1}{2^2} - \frac{1}{3^2} \right]$$

$$\Rightarrow \frac{1}{\lambda_1} = R_H (4) \left( \frac{9-4}{36} \right)$$

$$\frac{1}{\lambda_1} = \frac{5R_H}{9} \Rightarrow \lambda = \frac{9}{5R_H} = \frac{9\lambda_1}{5}$$

38. (b)  $\psi^2$  (probability density) can be zero for 3p orbital other than infinite distance. It has one radial node.

$$39. (c) r_n = a_0 \frac{n^2}{Z}$$

$$r_n \propto \frac{n^2}{Z}$$

$$\therefore \frac{\Delta R_1}{\Delta R_2} = \frac{Z_{He^+}}{Z_{Li^{2+}}} = \frac{2}{3}$$

40. (b) Gd<sup>3+</sup> ( $Z = 64$ ) = [Xe] 4f<sup>7</sup>

$$m = \sqrt{n(n+2)} = \sqrt{7(7+2)} = 7.9 \text{ B.M.}$$

41. (a) Filling of electrons in orbitals in any period takes place as: ns, (n-2)f (n-1)d np  
if possible if possible

- $\therefore$  for sixth period  $n = 6$ ,  
orbitals that are filled are 6s, 4f, 5d and 6p

42. [2]

$$\text{Energy of photon is given as } E = \frac{Nh}{\lambda} \quad \dots(i)$$

where, E = energy of photon (50W),

n = number of photon

h = Planck's constant ( $6.63 \times 10^{-34} \text{ Js}$ )

c = speed of light ( $3 \times 10^8 \text{ m/s}$ )

$\lambda$  = wavelength of light ( $795 \times 10^{-9} \text{ m}$ )

E = 50W = 50J = energy of photon

$$50J = \frac{n \times 6.63 \times 10^{-34} J_{j,j} \times 10^{-9} \text{ m/s}}{795 \times 10^{-9} \text{ m}}$$

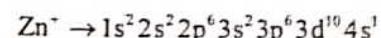
$$\Rightarrow n = \frac{50 \times 195 \times 10^{-9}}{6.63 \times 10^{-34} \times 3 \times 10^3}$$

$$= 1998.49 \times 10^{17} = 1.998 \times 10^{20}$$

$$\approx 2 \times 10^{20}$$

$$\therefore x = 2$$

43. [0]



Outermost electron is in 4s subshell  
 $m = 0$

44. [7]

1s <sup>2</sup>	2s <sup>2</sup>	2p <sup>6</sup>	3s	3p <sup>6</sup>	4s <sup>2</sup>	3d <sup>10</sup>	4p <sup>2</sup>
1 1	1 1	1 1 1 1	1 1	1 1 1 1 1 1	1 1	1 1 1 1 1 1 1	1 1 1
$m = 0$ (1)	0 (1)	-1 0 +1 (1)	0 (1)	-1 0 +1 0 (1) (1)	0 (1)	-2 -1 0 +1 +2 (1) (1)	

Completely filled orbital with  $m_l = 0$  are

$$= 1 + 1 + 1 + 1 + 1 + 1 = 7$$

45. [50] Energy emitted in 0.1 sec. =  $0.1 \text{ sec.} \times 10^{-3} \frac{\text{J}}{\text{s}} = 10^{-4} \text{ J}$

If 'n' photons of  $\lambda = 1000 \text{ nm}$  are emitted, then

$$10^{-4} = n \times \frac{hc}{\lambda}$$

$$\Rightarrow 10^{-4} = \frac{n \times 6.63 \times 10^{-34} \times 3 \times 10^8}{1000 \times 10^{-9}}$$

$$\Rightarrow n = 5.02 \times 10^{14} = 50.2 \times 10^{13} \Rightarrow 50$$

$$46. [2] \lambda = \frac{h}{\sqrt{2meV}}$$

$$\frac{\lambda_{Li}}{\lambda_p} = \sqrt{\frac{m_p(e)(V)}{m_{Li}(3e)(V)}} ; m_{Li} = 8.3m_p$$

$$\frac{\lambda_{Li}}{\lambda_p} = \sqrt{\frac{1}{8.3 \times 3}} = \frac{1}{5} = 0.2 = 2 \times 10^{-1}$$

$$X = 2$$

47. (b) (I) KE = -TE

$$KE = 13.6 \times \frac{Z^2}{n^2} \text{ eV}$$

$$KE \propto \frac{Z^2}{n^2}$$

$$(II) V = 2.188 \times 10^6 \times \frac{Z}{n} \text{ m/s}$$

$$V_n \propto Z$$

$$(III) F = \frac{V}{2\pi r}$$

$$F \propto \frac{Z^2}{n^2} \left[ \because r \propto \frac{Z^2}{n^2} \text{ and } V \propto \frac{Z}{n} \right]$$

$$(IV) F \propto \frac{Z^2}{r^2} \propto \frac{Z^3}{n^4}$$

48. [180]

$$\begin{aligned} \text{Total energy required} &= N_A \times \frac{hc}{\lambda} \\ &= \frac{6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3 \times 10^8}{663 \times 10^{-9}} \\ &= 180.4 \text{ kJ/mol} \end{aligned}$$

49. (d) Angular nodes =  $l = 2$

$$\begin{aligned} \text{Radial nodes} &= n - l - 1 \\ &= 5 - 2 - 1 = 2 \end{aligned}$$

50. (d) Tritium is radioactive and emits low energy  $\beta^-$  particles.

$$51. [1.17] \Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$\begin{aligned} \Delta x &= \frac{h}{4\pi m \Delta V} \\ &= \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 10 \times 10^{-3} \times 90 \times 0.05} \\ &= 1.17 \times 10^{-33} \text{ m} \end{aligned}$$

$$52. [9] h\nu = h\nu_0 + KE$$

$$= \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{248 \times 10^{-9} \times 1.6 \times 10^{-19}} = 3.0 + KE$$

$$KE = 2.0 \text{ eV}$$

$$\begin{aligned} \lambda &= \frac{h}{\sqrt{2mKE}} = \frac{6.6 \times 10^{-34}}{2 \times 9.1 \times 10^{-31} \times 2 \times 10^{-19} \times 1.6} \\ &= 8.68 \times 10^{-10} \text{ m} = 9 \text{ Å} \end{aligned}$$

53. [25] No. of orbitals =  $1 + 3 + 5 + 7 + 9 = 25$

54. [0]  $n = 4, m_e = -3 \Rightarrow l = 3$

$$\begin{aligned} \text{Radial nodes} &= n - l - 1 \\ &= 4 - 3 - 1 = 0 \end{aligned}$$

55. (c)  $l = 0$

$$\begin{aligned} \text{Radial nodes} &= n - 0 - l = 2 \\ \Rightarrow n &= 3 \\ \therefore 3s \end{aligned}$$

56. [0]  $\text{Ga}^+ \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

Valence electrons  $\rightarrow 4s^2$

So, azimuthal quantum number,  $l = 0$

$$57. [6] \lambda = \frac{h}{\sqrt{2meV}}$$

$$= \frac{6.634 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times 40 \times 10^3}}$$

$$= 6 \times 10^{-12}$$

$$X = 6$$

58. [12]  $V \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

Number of electrons in p-orbital = 12

$$59. [2] E = \frac{nhc}{\lambda}$$

$$1000 = \frac{n \times 6.626 \times 10^{-34} \times 3 \times 10^8}{400 \times 10^{-3}}$$

$$n = 20.122 \times 10^{20} \text{ photons incident on metal surface in 10 seconds}$$

$$n = 2.0122 \times 10^{20} \text{ photons incident on metal surface in 1 second}$$

Number of electrons ejected = Number of incident photons

$$X = 2$$

$$60. [58] \text{Uncertainty in speed of electron} = \frac{0.02 \times 5 \times 10^6}{100}$$

$$= 10^3 \text{ ms}^{-1}$$

$$m \times \Delta v \times \Delta x = \frac{h}{4\pi}$$

$$\Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 10^3}$$

$$= 58 \times 10^{-9} \text{ m}$$

$$x = 58$$

61. (a) Rutherford model doesn't say anything about the electronic structure of atom.

Bohr's model gave exact formula for simultaneous calculations of speed and distance of electron from the nucleus, which was stated impossible by Heisenberg.

62. (a) As in Thomson model, protons are diffused, X-particles deviate by small angles and due to repulsion from protons, their speed decreases.

$$63. (b) V = 2.188 \times 10^6 \times \frac{Z}{n} \text{ m/s}$$

$$V \propto \frac{Z}{n}$$

$$64. [5] \frac{hc}{\lambda} = h\nu_0 + \frac{1}{2} m_e V^2$$

$$\frac{6.63 \times 10^{-34} \times 3 \times 10^8}{500 \times 10^{-9}}$$

$$= 6.63 \times 10^{-34} \times 4.3 \times 10^{14} + \frac{1}{2} \times 9 \times 10^{-31} \times V^2$$

$$V = 5 \times 10^5 \text{ ms}^{-1}$$

65. [3155]  $KE = \frac{1}{2} mv^2$

$$mv^2 = \frac{nh}{2\pi}$$

from both,

$$(mv)^2 = \frac{n^2 h^2}{4\pi^2 r^2}$$

$$mv^2 = \frac{1}{m} \times \frac{n^2 h^2}{4\pi^2 r^2}$$

put eqn (ii) in (i),

$$KE = \frac{1}{2} \times \frac{1}{m} \times \frac{n^2 h^2}{4\pi^2 r^2}$$

Now,  $n = 2$ ;  $r_1 = a_o$ ;  $r_2 = a_o(2)^2$ ;  $r_2 = 4a_o$

$$KE = \frac{1}{2} \times \frac{(2)^2 h^2}{4\pi^2 (4a_o)^2 \times m}$$

$$= \frac{h^2}{32\pi^2 \times ma_o^2} = \frac{h^2}{315.5 \times ma_o^2}$$

66. [4]  $Np \rightarrow [Rn] 5f^4 6d^1 7s^2$

$\therefore$  It has 4 electrons in the f-subshell of the anti penultimate shell.

67. [50] Power = 1mW

$$= 10^{-3} J \text{ in 1 second}$$

$$= 10^{-4} J \text{ in 0.1 second}$$

$$\therefore \text{Energy} = \frac{nhc}{\lambda}$$

$$10^{-4} = \frac{n \times 6.63 \times 10^{-34} \times 3 \times 10^8}{1000 \times 10^{-9}}$$

$$n = 50.2 \times 10^{13}$$

$$X = 50$$

68. (b)  $Eu \rightarrow [Xe] 4f^7 6s^2$

$$Eu^{2+} \rightarrow [Xe] 4f^7$$

69. (d)  $Fe \rightarrow [Ar] 3d^6 4s^2$

$$Fe^{3+} \rightarrow [Ar] 3d^5$$

70. (b) According to  $(n + l)$  rule.

71. (b)  $r = 0.529 \times \frac{n^2}{Z} A^\circ$

$$r_3 = 0.529 \times \frac{(3)^2}{1}$$

$$r_4 = 0.529 \times \frac{(4)^2}{1}$$

$$\frac{r_4}{r_3} = \frac{(4)^2}{(3)^2} = \frac{16}{9}$$

$$r_4 = \frac{16r_3}{9}$$

... (i)

... (ii)

### JEE ADVANCED

72. (c) Values of  $l$  lies between 0 to  $n - 1$

73. [1758]  $\lambda = \frac{h}{mv}$

$$\lambda_e = \lambda_N$$

$$\frac{h}{m_e V_e} = \frac{h}{m_N V_N}$$

$$V_e = \frac{m_N}{m_e} V_N$$

$$V_e = \frac{1.6 \times 10^{-27}}{9.1 \times 10^{-31}} V_N$$

$$\therefore X = 1758.24$$

74. [4] No. of neutrons = 26

No. of electrons = 25

$$\% \text{ of extra neutrons than electrons} = \left( \frac{26-25}{25} \right) \times 100 = 4$$

75. [22] According to Heisenberg uncertainty principle,

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

$$\Rightarrow 10^{-7} \times m \cdot \Delta V = \frac{6.62 \times 10^{-34}}{4 \times 3.14}$$

$$\Rightarrow 10^{-7} \times m \times 2.4 \times 10^{-24} = \frac{6.62 \times 10^{-34}}{4 \times 3.14}$$

$$m = 0.2196 \times 10^{-3} \text{ Kg}$$

$$m = 21.96 \times 10^{-5} \text{ Kg}$$

76. (a) The orbitals with same  $n$  and  $l$  value but with different  $m$  value are degenerate.

77. (c)  $mv(4a_0) = \frac{h}{\pi}$

$$so, v = \frac{h}{4m\pi a_0}$$

$$so, KE = \frac{1}{2} mv^2 = \frac{1}{2} m \cdot \frac{h^2}{16m^2\pi^2 a_0^2} = \frac{h^2}{32m\pi^2 a_0^2}$$

78. [8]  $^{63}_{29} Cu + {}^1_1 H \rightarrow {}^6_0 n + {}^4_2 \alpha + {}^2_1 H + X$

$$64 = 6 + 4 + 2 + A \Rightarrow A = 52$$

$$29 + 1 = 30 = 0 + 2 + 2 + z \Rightarrow z = 26$$

Element X should be iron in group 8.

79. (a,b)



If X is  ${}^0 \gamma^0$  then Y is  ${}^0 n^1$

If X is  ${}^1 P^1$  then Y is  ${}^1 D^2$

80. [6]  $n = 4$ ,  $m_\ell = 1, -1$

Hence  $\ell$  can be = 3, 2, 1

i.e.  $H_f$  ; 2 orbitals

$H_d$  ; 2 orbitals

$H_p$  ; 2 orbitals

Hence total of 6 orbitals, and we want  $m_s = -\frac{1}{2}$ , that is only one kind of spin. So, 6 electrons.

81. [3] Energy order of orbitals of H is decided by only principle quantum number (n) while energy order of  $H^-$  is decided by  $(n + \ell)$  rule:

Electronic configuration of ' $H^-$ ' is  $-1s^2$  its Energy order is decided by  $n + \ell$  rule.

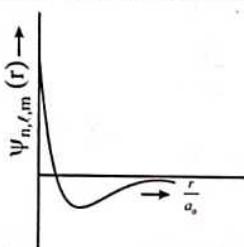
$$H^- = 1s^2 2s^0 2p^0$$

Its 2<sup>nd</sup> excited state is 2p and degeneracy of 2p is '3'

82. (d) The qualitative sketch of the dependence of P on r is the radial probability curve.

83. (c) s-orbital is non directional so wave function will be independent of  $\cos \theta$ .

84. (a) For 2s orbital, no. of radial nodes =  $n - \ell - 1 = 1$



85. (d) For 1s orbital,  $\Psi$  should be independent of  $\theta$ , also it does not contain any radial node.

86. (a,c)

$$-3.6 = \frac{-13.6 \times 4}{n^2}$$

$$n = 4$$

$$\ell = 2$$

$$m = 0$$

$$\text{Angular nodes} = \ell = 2$$

$$\text{Radial nodes} = (n - \ell - 1) = 1$$

$$n \ell = 4d \text{ state}$$

87. (c)  $r = 0.529 \times \frac{n^2}{z} \Rightarrow r \propto n^2 \Rightarrow (\text{I}) (\text{T})$

$$mv r = \frac{nh}{2\pi} \Rightarrow (mv)r \propto n \Rightarrow (\text{II}) (\text{S})$$

$$KE = +13.6 \times \frac{z^2}{n^2} \Rightarrow KE \propto n^{-2} \Rightarrow (\text{III}) (\text{P})$$

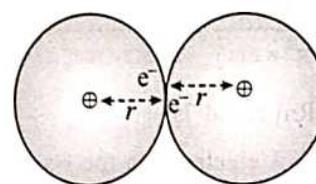
$$PE = -2 \times 13.6 \times \frac{z^2}{n^2} \Rightarrow PE \propto n^{-2} \Rightarrow (\text{IV}) (\text{P})$$

88. (d) Refer to Q 87.

89. [-5246.49]

At  $d = d_0$ , nucleus-nucleus & electron-electron repulsion is absent.

Hence potential energy will be calculated for 2 H atoms (P.E. due to attraction of proton & electron)



$$P.E. = \frac{-Kq_1 q_2}{r} = \frac{(9 \times 10^9)(1.6 \times 10^{-19})^2}{0.529 \times 10^{-10}} = -4.355 \times 10^{-21} \text{ kJ}$$

$$\text{For 1 mol} = -4.355 \times 10^{-21} \times 6.023 \times 10^{23}$$

$$= -2623.249 \text{ kJ/mol}$$

$$\text{For 2 H atoms} = -5246.49 \text{ kJ/mol}$$

90. [30]  $\lambda = \frac{h}{m(\Delta v)}$

$$330 \times 10^{-9} = \frac{6.6 \times 10^{-34}}{\left( \frac{4 \times 10^{-3}}{6 \times 10^{23}} \right) \times \Delta v}$$

$$\Delta v = \frac{6.6 \times 6 \times 10^{23} \times 10^{-34}}{4 \times 10^{-3} \times 330 \times 10^{-9}} = 30 \text{ cm/s}$$

# CHAPTER

# 3

# States of Matter

## Exercise-1 (Topicwise)

1. (c) Boyle's law is  $V \propto \frac{1}{P}$  at constant  $T$ .

2. (d)  $PV = nRT = K$  (Constant) (Boyle's law)

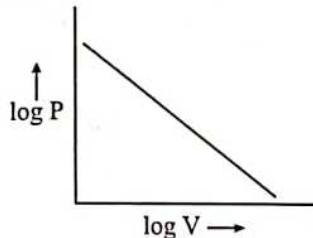
Taking log both side

$$\log P + \log V = \log k$$

$$\log P = -\log V + \text{constant}$$

$$y = mx + c$$

so



3. (a) At constant  $T$ ,  $P_1 V_1 = P_2 V_2$   
 $1 \times 20 = P_2 \times 50 \Rightarrow P_2 = 20/50$

4. (a)  $P_1 = 5 \text{ atm}$   $V_1 = 10 \text{ L}$   
 $P_2 = 1 \text{ atm}$   $V_2 = ?$

$$P_1 V_1 = P_2 V_2 \quad \text{or} \quad \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$\frac{5}{1} = \frac{V_2}{10}$$

$$V_2 = 50 \text{ L}$$

5. (d) According to Boyle's Law,  $PV = \text{constant}$ , at constant temperature either  $P$  increases or  $V$  increases both (b) & (c) are correct.

6. (c)  $V \propto T$

$$7. (a) P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 546}{44.8l} \text{ atm} = 2 \text{ atm}$$

$$8. (b) \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow \frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$$

9. (b) Molecular weight =  $V.d. \times 2 = 11.2 \times 2 = 22.4$

Volume of 22.4 gm Substance of NTP = 22.4 litre

$$1 \text{ gm substance at NTP} = \frac{22.4}{22.4} \text{ litre}$$

$$11.2 \text{ gm substance of NTP} = 11.2 \text{ litre}$$

$$10. (b) \frac{\text{M.wt. of O}_2}{\text{M.wt. of SO}_2} \Rightarrow \frac{M_1}{M_2} \Rightarrow \frac{32}{64} = \frac{1}{2}$$

The weight of oxygen will be  $\frac{1}{2}$  that of  $\text{SO}_2$

11. (d) The value of universal gas constant would depend only on the units of measurement rather than temperature and pressure

$$12. (b) \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{P \times 5}{300} = \frac{2P \times V_2}{600}$$

$$V_2 = 5L$$

$$13. (a) \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{1 \times 1}{273} = \frac{2 \times V_2}{300}$$

$$V_2 = \frac{300}{2 \times 273} L$$

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

$$\frac{760 \times 273}{273} = \frac{600 \times V_2}{300}$$

$$V_2 = 380mL$$

$$15. (d) \text{ Moles} = \frac{5.6}{22.4} = \frac{1}{4}$$

$$\frac{\text{Given mass}}{\text{molar mass}} = \frac{1}{4} \Rightarrow \text{molar mass} = 40 \text{ g}$$

$$\eta = \frac{\text{molecular mass}}{\text{empirical mass}} = \frac{40}{20} = 2$$

$$\text{molecular formula} = (\text{HF})_2 = \text{H}_2\text{F}_2$$

16. (b) moles of  $CO_2 = \frac{4400}{44} = 100$

$$100 = \frac{\text{volume}}{24.5 \text{ L}}$$

$$\text{volume} = 100 \times 24.5 \text{ L}$$

17. (c)  $P = \frac{dRT}{M}$

$$d_1 T_1 = d_2 T_2$$

$$d \times 300 = 0.75d \times T$$

$$T = 400 \text{ K}$$

18. (c) moles of  $CO_2 (n_1) = \frac{44}{44} = 1 \text{ mol}$

$$\text{moles of } H_2 (n_2) = \frac{44}{2} = 22 \text{ mol}$$

$$\frac{P_1}{n_1} = \frac{P_2}{n_2} \Rightarrow \frac{1}{1} = \frac{P_2}{22}$$

$$P_2 = 22 \text{ atm}$$

19. (d)  $P_{\text{total}} = P_1 + P_2 + P_3 + \dots$

There should be non reacting gases, behave ideally and temperature of the component gases remain constant

20. (c) From Dalton's partial pressure law

$$P_1 = \frac{1000}{1500} \times 600 + \frac{500}{1500} \times 800$$

$$= 400 + \frac{800}{3}$$

$$= \frac{2000}{3} \text{ torr.}$$

$$V_1 = 1500 \text{ mL}$$

$$P_2 = ?$$

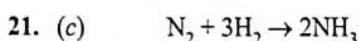
$$V_2 = 2L = 2000 \text{ mL}$$

$$\text{From } P \propto \frac{1}{V}$$

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

$$\Rightarrow \frac{2000/3}{P_2} = \frac{2000}{1500}$$

$$\Rightarrow P_2 = \frac{1500}{3} = 500 \text{ torr}$$



$$\begin{array}{ccccc} \text{Initial} & 1 & & 3 & \\ \text{final} & - & - & 2 & \end{array}$$

$$\text{ratio} = \frac{4}{2} = \frac{2}{1}$$

22. (a) Rate of effusion  $\propto$  Area of cross section

$$\therefore \frac{r_A}{r_B} = \frac{A_A}{A_B} = \frac{\pi r^2}{r^2} = \frac{\pi}{1}$$

23. (a)  $P = P_A + P_B + P_C$

24. (d)  $r \propto \frac{1}{\sqrt{M}}$

25. (b)  $\frac{d_1}{d_2} = \frac{1}{16}, \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{16} = \frac{4}{1}$

26. (b)  $NH_4Cl$  ring will first form near the  $HCl$  bottle because rate of diffusion of  $NH_3$  is more than that of  $HCl$  because  $M_{NH_3} : M_{HCl} = 17 : 36.5$ . So  $NH_3$  will reach first to  $HCl$  bottle & will react there with  $HCl$  to form  $NH_4^+$  ring.

27. (d)  $\frac{t_{(\text{gas})}}{t_{(O_2)}} = \sqrt{\frac{M_{(\text{gas})}}{M_{(O_2)}}}$

$$\Rightarrow \frac{40}{16} = \sqrt{\frac{M_{(\text{gas})}}{32}}$$

$$\Rightarrow \frac{5}{2} = \sqrt{\frac{M_{(\text{gas})}}{32}} \Rightarrow \frac{25}{4} = \frac{M_{(\text{gas})}}{32}$$

$$\Rightarrow M_{(\text{gas})} = 200 \text{ g/mol.}$$

28. (a)  $\frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{(\text{molar mass})_2}{(\text{molar mass})_1}}$

$$\frac{50}{40} = \sqrt{\frac{(\text{molar mass})_2}{8}}$$

$$m_2 = 100$$

29. (a)  $KE = \frac{3}{2} RT = \frac{3}{2} PV$

$$\therefore P = \frac{2E}{3V} \text{ for unit volume } (V=1) \Rightarrow P = \frac{2}{3} E$$

30. (d) The most accurate form in which velocity can be used in these calculations.

31. (c)  $d \propto M \Rightarrow \frac{d_1}{d_2} = \frac{M_1}{M_2}; \frac{3d}{d} = \frac{M}{M_2} \Rightarrow M_2 = \frac{M}{3}$

32. (a)  $V_{\text{rms}} = \sqrt{\frac{3RT}{M}}, V_{\text{av}} = \sqrt{\frac{8RT}{\pi M}}, \frac{V_{\text{rms}}}{V_{\text{av}}} = \sqrt{\frac{3\pi}{8}}$

$$= \sqrt{\frac{66}{56}} = \frac{1.086}{1}$$

33. (d) most probable velocity : mean velocity :  $V_{\text{rms}}$

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

34. (a) When average speed of molecule is increased due to increase in temperature then the change in momentum during collision between wall of container and molecules of gas also increases.



35. (d)  $\frac{U_1}{U_2} = \sqrt{\frac{m_2}{m_1} \cdot \frac{T_1}{T_2}}$   $\therefore T_1 = T_2$

$$\frac{U_1^2}{U_2^2} = \frac{m_2}{m_1} \quad \therefore m_1 U_1^2 = m_2 U_2^2$$

36. (d) Kinetic energy of the gas molecule remains the same.

$$K.E. = \frac{3}{2} kT \quad [K.E. \propto T]$$

37. (a) At constant volume, on increasing temperature  $\rightarrow$  Average speed of molecule increased due to which the pressure of gas also increase.

38. (c) The number of mole of the gas increases is the incorrect statement as mass doesn't change with temperature.

39. (a) Speed =  $\sqrt{\frac{3RT}{M}}$

Gas which has maximum value of  $\frac{T}{M}$  has highest speed.

40. (a)  $Z < 1$  shows that the gas has greater compressibility at intermediate pressure and all reactive forces are dominant, higher value of 'a' and lower value of 'b' above Boyle's temperature it is not possible because  $Z > 1$ .

41. (b) Because molecules of real gases have intermolecular forces of attraction so the effective impact on the wall of container is diminished. Pressure of real gas is reduced by  $\frac{a}{v^2}$  factor hence behaviour of real gas deviate from ideal behaviour.

42. (c)  $Z = \frac{PV}{RT}$   $\therefore$  for ideal gas  $PV = RT$  so  $Z = 1$

43. (d)  $\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$

44. (b) At low temperature and high pressure.

45. (c) Value of constant  $a$  is greater than other for  $\text{NH}_3$  that's why  $\text{NH}_3$  can be most easily liquefied.

46. (b) If  $Z < 1$  then molar volume is less than 22.4 L.

47. (b) Critical temperature is defined as the temperature above which a gas cannot be liquefied.

48. (a)  $\left( P + \frac{a}{v^2} \right)$  term represent the intermolecular force in non-ideal gas equation.

## Exercise-2 (Learning Plus)

1. (c)  $\frac{V_1}{V_2} = \frac{T_1}{T_2}; \frac{3}{2.7} = \frac{320}{T_2} \Rightarrow T_2 = 288\text{K} = 15^\circ\text{C}$

2. (d)  $n, T \rightarrow \text{constant}$

$$PV = \text{constant}$$

3. (d)  $n \rightarrow \text{constant}$

$v \rightarrow \text{fixed}$

$\therefore P \& T \rightarrow \text{constant}$

4. (b)  $V = 2 \text{ litre}$

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

$$\Rightarrow \frac{2}{4} = \frac{273}{T(\text{in K})} \Rightarrow T = 546 \text{ K} \Rightarrow T = 273^\circ\text{C}$$

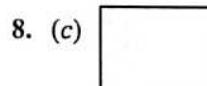
5. (b)  $n = \text{constant}$

no of molecules = constant

same number of molecules

6. (c)  $\frac{10}{V_2} = \frac{273}{373} \Rightarrow V_2 = 13.66 \text{ L.}$

7. (c)  $P = CRT; T = \frac{P}{RC} = \frac{1 \times 12}{1 \times 1} = 12 \text{ K.}$



A  $0.5 \text{ dm}^3$

B  $1 \text{ dm}^3$

$PV = nRT$

$$PV = \frac{W}{M} \cdot RT$$

$\Rightarrow P \times M = \rho RT$

$\frac{P_A \times M_A}{P_B \times M_B} = \frac{\rho_A RT}{\rho_B RT}$

$$\frac{P_A}{P_B} \times \frac{1/2 M_B}{M_B} = \frac{3}{1.5}$$

$$\frac{P_A}{P_B} = 4$$

9. (b)  $\rho \propto \frac{P}{T}$

10. (d)  $\frac{P_{H_2}}{P_{C_2H_6}} = \frac{n_{H_2}}{n_{C_2H_6}} = \frac{30}{2} = \frac{15}{1}$

$$X_{H_2} = 15/16, P_{H_2} = X_{H_2} \cdot P_T \Rightarrow \frac{P_{H_2}}{P_T} = \frac{15}{16}$$

11. (d) Weight of  $H_2 = 20 \text{ g}$  in  $100 \text{ g}$  mixture;  
Weight of  $O_2 = 80 \text{ g}$

$$\therefore \text{Moles of } H_2 = \frac{20}{2} = 10; \therefore \text{Moles of } O_2 = \frac{80}{32} = \frac{5}{2}$$

$$\therefore \text{Total moles} = 10 + \frac{5}{2} = \frac{25}{2}$$

$$\therefore P_{H_2} = (P_T) \times (\text{mole fraction of } H_2) = 1 \times \frac{10}{25/2} = 0.8 \text{ bar}$$

$$12. (d) r \propto \frac{1}{\sqrt{M}}$$

$$13. (b) \frac{20}{60} \times \frac{30}{V} = \sqrt{\frac{32}{64}}$$

$$\Rightarrow V = 14.14 \text{ l}$$

$$14. (c) r \propto \frac{1}{\sqrt{M}}$$

So NH<sub>3</sub> diffuses with faster rate.

$$15. (b) \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{x/5}{x/t_2} = \sqrt{\frac{M_2}{2}} \Rightarrow \frac{t_2}{5} = \sqrt{\frac{M_2}{2}}$$

when t<sub>2</sub> = 20

$$\frac{20}{5} = \sqrt{\frac{M_2}{2}}$$

$$M_2 = 32.$$

$$16. (d) \text{ Given } \frac{r_A}{r_B} = \frac{16}{3}; \frac{w_A}{w_B} = \frac{2}{3}$$

$$\text{We have } \frac{r_A}{r_B} = \frac{n_A}{n_B} \sqrt{\frac{M_B}{M_A}}$$

$$\frac{16}{3} = \frac{w_A}{M_A} \frac{M_B}{w_B} \sqrt{\frac{M_B}{M_A}}$$

$$\frac{16}{3} = \frac{2}{3} \left( \frac{M_B}{M_A} \right)^{3/2} \Rightarrow \left( \frac{M_B}{M_A} \right)^{3/2} = 8$$

$$\Rightarrow \frac{M_B}{M_A} = 4 \quad \therefore \text{mole ratio} = \frac{8}{3}$$

$$17. (a) \frac{r_{N_2}}{r_{H_2}} = \sqrt{\frac{(MM)_{H_2}}{(MM)_{N_2}}}$$

$$= \sqrt{\frac{2}{28}} = \sqrt{\frac{1}{14}}$$

$$1:\sqrt{14}:\sqrt{7}$$

$$18. (d) C_3H_6O + O_2 \rightarrow 3CO_2$$

$$40 \text{ (excess)}$$

$$— \qquad 40 \times 3 = 120 \text{ ml.}$$

$$19. (b) U_{rms} = \sqrt{\frac{3RT}{M}}$$

$$\frac{T_1}{M_1} = \frac{T_2}{M_2}$$

$$\frac{T_1}{32} = \frac{300}{20}$$

$$T_1 = 480 \text{ K}$$

$$20. (b) v \propto \sqrt{T}$$

$$21. (c) \frac{(V_{rms})_1}{(V_{rms})_2} = \sqrt{\frac{T_1 M_2}{M_1 T_2}} = \sqrt{\frac{50 \times 32}{2 \times 800}} = 1$$

$$22. (a) K.E. = \frac{3}{2} nRT$$

$$n_1 T_1 = n_2 T_2$$

$$T_1 = \frac{0.4 \times 400}{0.3} \Rightarrow T_1 = 533 \text{ K}$$

$$23. (c) U_{rms} = \sqrt{\frac{3RT}{M}} = \frac{5 \times 10^4}{10 \times 10^3}$$

$$= \frac{\sqrt{\frac{3RT_1}{M}}}{\sqrt{\frac{3RT_2}{M}}} = \frac{1}{4} = \frac{T_1}{T_2}$$

$$T_2 = 4T_1$$

$$T_2 = 4 \text{ times } T_1$$

$$24. (a) T_C = \frac{8a}{27Rb}$$

$$T_B = \frac{a}{Rb}$$

$$T_i = 2T_B$$

$$T_C < T_B < T_i$$

25. (c) In van der waals equation, the term  $\frac{n^2a}{v^2}$  represent the intermolecular forces.

26. (b) Boiling point  $\propto a$

$$27. (a) \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT.$$

28. (a) Van der waal's equation is

$$\left( P + \frac{n^2a}{V^2} \right) (V - nb) = nRT$$

For non-zero values of force of attraction

$$\left( P + \frac{n^2a}{V^2} \right) V = nRT$$

$$PV = nRT - \frac{n^2a}{V}$$

29. (c)  $PV = Pb + RT$

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$30. (a) \left( P + \frac{a}{V^2} \right) (V) = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} = 1 - \frac{a}{VRT}$$

31. (a)  $b = \left(\frac{4}{3}\pi r^3\right)(4N)$

$$24 \times 10^{-3} L \text{ mol}^{-1} = \left(\frac{4}{3} \times 3.14 \times 8^3\right) \left(4 \times 6.022 \times 10^{23}\right)$$

$$r^3 = 0.37 \times 10^{-27} \text{ dm}^3$$

$$r = 1.355 \text{ Å}$$

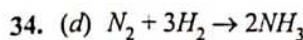
32. (c) The gas which has the largest size has the highest value of the van der waals constant 'b'.  $O_3$  has largest size among also option.

33. (b) Rate of effusion  $\propto \frac{1}{\sqrt{\text{molar mass}}}$

$$0.525 = \sqrt{\frac{16}{m}}$$

$$m = 58 \text{ g}$$

$C_4H_{10}$  is the answer



$N_2$  is the limiting reagent

After the completion of the reaction, 2 mol  $NH_3$  formed 5L water added which makes volume increases to 20L

$$PV = nRT$$

$$P \times 20 = 2 \times 0.0821 \times 300$$

$$\boxed{P = \frac{1 \times 0.0821 \times 300}{10}}$$



$$t=0 \quad 20ml \quad 0$$

$$t=t \quad 20 - 3x \quad 2x$$

$$20 - 3x + 2x = 17ml$$

$$x = 3ml$$

$$\text{volume of ozone} = 2x = 2(3) = 6 \text{ ml}$$

common oil absorb 6 ml ozone which result in contraction.

36. (b) More the value of 'a' constant means more the ability of a gas to get qualified and 'b' for  $N_2$  is greater than that of  $NH_3$

37. (b)  $U_{rms} \propto \sqrt{T}$

$$\frac{U_{rms1}}{U_{rms2}} = \sqrt{\frac{1200}{300}}$$

$$U_{rms2} = \frac{1}{2} U_{rms1}$$

38. (b)  $PV = nRT$

$$\text{If } P, V, R = \text{constant then } \frac{n_1}{n_2} = \frac{T_1}{T_2}$$

$$\text{Let } n_1 = 1 \text{ and } n_2 = x$$

$$\frac{1}{x} = \frac{400}{300} \rightarrow x = \frac{3}{4}$$

$$\text{So has escaped out will } = 1 - \frac{3}{4} = \frac{1}{4}$$

39. (c)  $PV = nRT$

Initially,

$$PV = \frac{4}{m} \times R \times T \quad \dots(i)$$

At higher temperature,

$$PV = \frac{8.2}{m} \times R \times (T + 50) \quad \dots(ii)$$

equate both equation (i) and (ii)

$$4T = 3.2 T + 160$$

$$T = 200 \text{ K}$$

40. (a)  $PV = nRT$

$$\frac{7.6 \times 10^{-6}}{760} \times \frac{1}{1000} = n \times 0.0821 \times 250$$

$$n = 4.87 \times 10^{-13} \text{ moles}$$

No of molecules

$$= 6.022 \times 10^{23} \times 4.87 \times 10^{-13} = 2.93 \times 10^{11} \text{ molecules}$$

41. (c)  $P = \frac{d}{m} RT$

$$m = \frac{2.64 \times 0.0821 \times 583}{(775/760)}$$

$$m = 124 \text{ g/mol}$$

$$\text{No. of } P \text{ atom} = \frac{124}{31} = 4$$

Molecular formula is  $P_4$

42. (c)  $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$T_2 = \frac{14.9 \times 300}{12} = 372.5 \text{ K} = 99.5^\circ C$$

43. (b)  $d_1 T_1 = d_2 T_2$

$$d_1 T_1 = d_2 (1.1 T_1)$$

$$d_1 = 1.1 d_2$$

$$\frac{d_1}{d_2} = \frac{1.1}{1}$$

$$\% \text{ decrease in density} = \frac{0.1}{1.1} \times 100 = 9.1\%$$

44. (a) At constant pressure and temperature

$$\frac{V}{n} = \text{constant}$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\frac{4/3\pi r_1^3}{n_1} = \frac{4/3\pi r_2^3}{n_2}$$

$$r_2 = r_1 \left[ \frac{n_2}{n_1} \right]^{1/3}$$

$$r_2 = \frac{10}{2} \left[ \frac{1}{8} \right]^{1/3}$$

$$r_2 = 5 \text{ cm}$$

45. (b) For  $H_2O$  vapour

$$PV = \frac{V}{m} RT$$

$$P \times 50 = \frac{1.2}{18} \times 0.0821 \times 300$$

$$P = 0.03284 \text{ atm} = 24.96 \text{ mm}$$

46. (a)  $PV$  curve for hydrogen gas lie above then  $PV$  curve for ideal gas.

47. (a)  $P(V_m - n) = RT$

$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

$$Z = \frac{Pb}{RT} + 1$$

$$Z = \frac{1}{9} + 1$$

$$Z = 10/9$$

$$PV_m - Pb = RT$$

$$P(10b) - Pb = RT$$

$$9Pb = RT$$

$$\frac{Pb}{RT} = \frac{1}{9}$$

48. (a)  $\frac{n}{v} = \frac{\rho}{m}$

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$\left( P + \frac{a\rho^2}{m^2} \right) \left( 1 - \frac{\rho}{m} b \right) = \frac{\rho}{m} RT$$

$$\left[ P + \frac{3.6(2.2)^2}{(44)^2} \right] \left( 1 - \frac{2.2 \times 0.05}{44} \right) = \frac{2.2}{44} \times 0.0821 \times 300$$

$$P = 1.23 \text{ atm}$$

49. (b) At moderate temperature,  $Z = 1$

$$Z = 1 + 0.35P - \frac{168}{T}P$$

$$0.35 = \frac{168}{T}$$

$$T = 480 \text{ K}$$

### Exercise-3 (JEE Advanced Level)

1. (a,b)

Suppose the cylinder will burst at  $T_2$ K, when  $V_1 = V_2$

$$T_2 = \frac{P_2 T_1}{P_1} = \frac{14.9 \times 300}{12} = 372.5 \text{ K}$$

2. (a,c)

(a)  $PV = nRT$

$$P \times 8.21 = 2 \times 0.0821 \times 300$$

$$P = 6 \text{ atm.}$$

(b) Open container

$$P_T = P_{\text{gas}} + P_{\text{atm}}$$

$$P_{\text{gas}} = \frac{2 \times 0.0821 \times 400}{8.21} = 8 \text{ atm}$$

So,  $P_T > 8 \text{ atm.}$

(c) Closed non-rigid

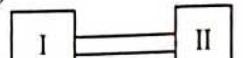
$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{8.21}{300} = \frac{V_2}{600}$$

$$V_2 = 16.42$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{6}{300} = \frac{P_2}{150}$$

$$P_2 = 3 \text{ atm}, P_1 = 6 \text{ atm.}$$

3. (a,d)



$$300 \text{ K} \quad 400 \text{ K}$$

$$16.42 \quad 8.211$$

$$(a) \text{ I. P.} = 3 \text{ atm by } P = \frac{nRT}{V}$$

(b) Pressure just after opening doesn't change.

(d) Pressure becomes same after some time.

4. (b,d)

$$r \propto \frac{1}{\sqrt{M}}$$

5. (b,d)

$$\text{Given } \frac{r_A}{r_B} = \frac{16}{3}; \frac{w_A}{w_B} = \frac{2}{3}$$

$$\text{We have } \frac{r_A}{r_B} = \frac{n_A}{n_B} \sqrt{\frac{M_B}{M_A}}$$

$$\frac{16}{3} = \frac{w_A M_B}{M_A w_B} \sqrt{\frac{M_B}{M_A}}$$

$$\frac{16}{3} = \frac{2}{3} \left( \frac{M_B}{M_A} \right)^{3/2} \Rightarrow \left( \frac{M_B}{M_A} \right)^{3/2} = 8$$

$$\Rightarrow \frac{M_B}{M_A} = 4$$

$$\therefore \text{Mole ratio} = \frac{8}{3}$$

6. (a,b,c,d)

With increase in temperature, most probable velocity increases & fraction of molecules with velocity equal to M.P. velocity decreases. Total no. of molecules remain same.

7. (d) According to Gay Lussac's law

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

$$\frac{1}{200} = \frac{P_2}{821k}$$

$$P_2 = 4.1 \text{ atm}$$

**8. (a,b,c,d)**

Vanderwaals constant 'a' represent the magnitude of intermolecular attractive forces and vanderwaal constant 'b' also represent the co-volume.

Unit of 'b' is L mol<sup>-1</sup>

9. (a,d) Average speed,  $\mu_{av} = \sqrt{\frac{8RT}{\pi M}}$   
 $\mu_{av} \propto T$

$$\mu_{av} \propto \frac{1}{M}$$

**10. (c,d)** According to kinetic theory of gas

K.E.  $\propto T$

Pressure of gas is due to collisions of molecules against the side of container and we assumed that there is no force of attraction exist between molecules.

**11. (a,b)** At temperature  $T$ ,

Mean velocity of  $A = V_{rms}$  of  $B$

$$\sqrt{\frac{8RT}{\pi M_A}} = \sqrt{\frac{3RT}{M_B}}$$

$$\frac{M_B}{M_A} = \frac{3\pi}{8}$$

$$M_B > M_A$$

If mean velocity of both  $A$  and  $B$  can be equal

$$\sqrt{\frac{8RT_A}{\pi M_A}} = \sqrt{\frac{8RT_B}{\pi M_B}}$$

$$\frac{M_B}{M_A} = \frac{T_B}{T_A}$$

$$T_B > T_A [M_B > M_A]$$

option B is correct

**12. (a,d)**

(a)  $PV = \frac{wRT}{m}$

If mass of gas is same

$PV$  depends only on ratio of  $(T/m)$  which is equal for both gases

(b) Pressure also depend upon density rather than temp and mass.

(c) K.E. is different for diff gases at diff. temperature.

(d)  $V_{rms} = \sqrt{\frac{3RT}{m}}$

This property has same magnitude as  $(T/m)$  is same for both gasses.

**13. (a,b,d)**

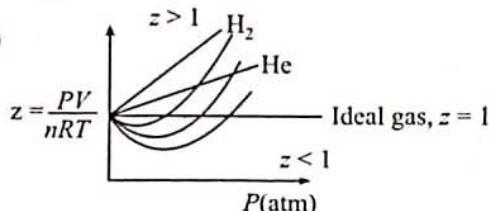
At critical point, the gases experience force of attraction and they can be liquified.

At high pressure and low temperature, there is force of attraction between molecules which can't be neglected.

**14. (a,b,c)**

Vapour may be condensed to liquid by pressure. if  $T < T_C$ , A gas can be liquified by applying pressure. At  $T_C$ , equilibrium exist between liquid and vapour state.

**15. (a,c)**



At high pressure, all real gas are less compressible than ideal gas

for  $H_2$  and  $He$ ,  $Z > 1$  and for other gas  $Z < 1$  at low pressure.

**16. (b,c)** Molar mass of Neon > Molar mass of He

$$U_{av} = \sqrt{\frac{8RT}{\pi M}}$$

$$U_{av} \propto \sqrt{\frac{1}{M}}$$

He has high  $U_{avg}$  and strike the wall more frequently.

17. (a,d) Speed  $\propto \sqrt{\frac{T}{m}}$

Option (a) and (d) are correct

Higher the temperature means Higher the value of  $c$

Lower the molar mass means Higher the value of  $c$ .

**18. (a,d)** Gas can be liquified if  $T < T_C$

or if  $T = T_C$  then high pressure ( $P > P_c$ ) is needed to liquify the gas.

**19. (a,b,c,d)**

(a) At critical condition, the substance exist as three phase equilibrium due to which physical state cannot be defined.

(b) At critical condition, due to equilibrium, their physical properties become identical.

(c) At critical condition, there is no separation between liquid and vapour state due to equilibrium.

(d) Gases which can be easily liquified  $\propto$  Boyle's temp.

20. (c)  $P = \frac{RT}{V_m}$

Gases behave ideally at or above  $T_B$  (Boyle's Temperature)

$$T = \frac{a}{Rb}$$

$$\text{so, } P = \frac{R \left( \frac{a}{Rb} \right)}{V_m} = \frac{a}{V_m b}$$

**21. (a,b,d)**

As we know  $P_c = \frac{a}{27b^2}$  ,  $T_c = \frac{8a}{27Rb}$  ,  $V_c = 3b$

22. (d)  $Z = z \frac{V}{N} N^*$

$$N^* \propto \frac{1}{V}$$

$$x \propto \frac{1}{V} = A$$

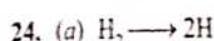
$$y \propto \frac{1}{2V} = \frac{A}{2}$$

Ratio = 2 : 1

None of these

23. (c) Total no. of collisions per unit volume  $\propto \frac{(N^*)^2}{V}$

Ratio = 1 :  $\sqrt{2}$



$$\frac{n_x}{n_y} = \frac{n_{He}}{n_H} = \frac{x/4}{x/1} = \frac{1}{4}$$

$$\frac{V_x}{V_y} = \frac{1}{2} \Rightarrow \frac{N_x}{N_y} = \frac{1}{4} \times 2 = \frac{1}{4}$$

$\frac{\sigma_x}{\sigma_y} = 2$  (because  $H_2$  become H)

$$\frac{U_{avg}(x)}{U_{avg}(y)} = \sqrt{\frac{(T/M)_x}{(T/M)_y}} = \sqrt{\frac{T/4}{2T/1}} = \frac{1}{2\sqrt{2}}$$

$$\frac{Z_{11x}}{Z_{11y}} = \left(\frac{N_x}{N_y}\right)^2 \times \left(\frac{U_{avg}(x)}{U_{avg}(y)}\right) \times \left(\frac{\sigma_x}{\sigma_y}\right)^2$$

$$= \frac{1}{4} \times \frac{1}{2\sqrt{2}} \times 4 \frac{1}{2\sqrt{2}}$$

$$Z_{11y} = 2\sqrt{2}; Z_{11x} = 2\sqrt{2} A$$

25. (c)  $w = -pv$

$$w = 0 \times (4)$$

$$w = 0$$

26. (d)  $n_{N_2} = \frac{0.82 \times 10}{0.082 \times 300} = 0.33$

$$n_{He} = \frac{4.1 \times 6}{0.052 \times 300} = 1$$

$$n_{Total} = 1.33$$

$$K.E = n_T \times \frac{3}{2} \times R \times T$$

$$= 1.33 \times \frac{3}{2} \times 8.314 \times 300$$

$$= 4982.4 J$$

27. (d)  $X_{N_2} = \frac{0.33}{1.33} = 0.248$

$$P_{N_2} = x_{N_2} \cdot P_T = 0.248 \times 1 = 0.248 atm$$

$$P_{N_2} \approx 0.25 atm$$

28. (b)  $n_f = 1 + 0.33 = 1.33$

$$P = \frac{1.33 \times 0.082 \times 300}{16} = 2.05$$

$$P = 2.05 atm$$

29. (a)  $A \rightarrow s; B \rightarrow q.s; C \rightarrow r; D \rightarrow p,r$

(A)  $PV = nRT$

At constant temperature

$$PV = K (T = \text{constant})$$

Higher the value of PV, higher the temperature.

$$So, T_3 > T_2 > T_1$$

$$\text{Since, } P_1 = P_2 = P_3$$

$$So, V \propto T \Rightarrow V_3 > V_2 > V_1$$

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

$$\text{Since, } P_1 = P_2 = P_3$$

$$d \propto \frac{1}{T} \Rightarrow d_1 > d_2 > d_3$$

(B) From Graph,

$$V_3 > V_2 > V_1 \text{ and } T_1 = T_2 = T_3$$

Higher the volume, lesser the pressure because temperature is same for all.

$$P_1 > P_2 > P_3$$

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

$$\text{Since, } T_1 = T_2 = T_3$$

$$So, d \propto P \Rightarrow d_1 > d_2 > d_3$$

(C) From the graph,

$$P_3 > P_2 > P_1 \text{ and } T_1 = T_2 = T_3$$

Higher the pressure, lesser the volume because temperature is same for all.

$$V_1 > V_2 > V_3$$

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

$$\text{Since, } T_1 = T_2 = T_3$$

$$So, d \propto P \Rightarrow d_3 > d_2 > d_1$$

(D) From the graph,

$$d_3 > d_2 > d_1 \text{ and } P_1 = P_2 = P_3$$

$$d = \frac{PM}{RT} \Rightarrow d \propto \frac{1}{T}$$

$$So, T_1 > T_2 > T_3$$

$$PV = nRT$$

$$\text{Since, } P_1 = P_2 = P_3$$

$$V \propto T$$

$$So, V_1 > V_2 > V_3$$



30. (b,d)

$$P_C = \frac{a}{27b^2}; T_C^2 = \frac{64a^2}{27 \times 27 R^2 b^2}$$

$$V_C = 3b; \frac{T_C^2}{P_C} = \frac{64a^2}{27 \times 27 R^2 b^2} \times \frac{27b^2}{a}$$

$$T_C = \frac{8a}{27Rb}, a = \frac{27R^2 T_C^2}{64 P_C}$$

31. (a,c,d)

For gaseous state, Thermal energy is always greater than the molecular attraction.

32. (a,b)

- (a) At Boyle's temperature a real gas behave as ideal irresp. of pressure.
- (b) At critical condition a real gas behave as ideal.

33. (a) A → p,q; B → r,s; C → p,q; D → r,s

- (A) At critical temperature, gas on liquify and deviate from ideal gas equation.
- (B) At or above Boyle's Temperature, gas behaves like ideally.
- (C)  $Z < 1 \rightarrow$  Means deviates from ideal gas equation ( $Z = 1$ ) and gas can be liquified.
- (D) At high temperature and low pressure, gas starts follow ideal gas equation and we assume vanderwalls constant 'a' is negligible.

34. (b) A → p,r; B → q,r,s; C → p,r; D → q,s

- (A) Diffusion  $\propto \frac{1}{\sqrt{m}}$  K.E. increase with increase in temperature due to which diffusion of gas increases.
- (B)  $Z < 1, V_{ideal} < V_{real}$  and  $Z$  increase with increase in temperature.

$$(C) V_{rms} = \sqrt{\frac{3RT}{M}}$$

- (D) Liquification of gas takes place easily when attractive force dominates and  $V_{ideal} > V_{real}$ .

35. (c) A → r; B → s; C → q; D → p

- (A) As we know,  $Z$  for ideal gas is always unity

$$(B) \text{ for real gas, at low } P, \left( P + \frac{a}{V_m^2} \right) V_m = RT$$

$$\frac{PV_m}{RT} = 1 - \frac{a}{RTV}$$

- (C) For real gas, at high  $P$

$$P(v - nb) = nRT$$

$$\frac{PV_M}{RT} = 1 + \frac{Pb}{RT}$$

- (D)  $Z$  for critical state

$$V_C = 3b \quad T_c = \frac{8a}{27Rb} \quad P_c = \frac{a}{27b^2}$$

$$Z = \frac{PV}{RT} = 3/8$$

36. (d) A → q,r; B → s; C → p; D → q

Translational K.E. per gram

$$= \frac{3}{2} \frac{RT}{m} \Rightarrow \text{Depends upon ratio of (T/m)}$$

Translational K.E. per mole

$$= \frac{3}{2} RT \Rightarrow \text{Depends upon only temperature.}$$

37. (c) A → s; B → r; C → q; D → p

$$(A) PV = nRT, \frac{P}{V} = y \text{ axis, } P = x \text{-axis}$$

$$v = \frac{x}{y}$$

$n, R, T = \text{constant}$

$PV = \text{constant}$

$$x \cdot \frac{y}{x} = \text{constant}$$

$$\frac{P}{V} \text{ vs } P \rightarrow y = x^2$$

$$(B) \frac{P}{V} \text{ vs } V \Rightarrow \frac{P}{V} = \frac{nRT}{V} \Rightarrow \frac{P}{V} \propto \frac{1}{V}$$

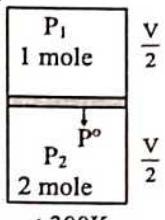
$$(C) \frac{V}{P} = y \text{ axis, } \frac{1}{P^2} = \text{axis} \rightarrow y/x = PV = \text{constant}$$

$$\text{so, } [y = kx]$$

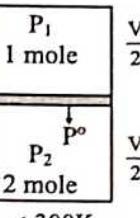
$$(D) \frac{P}{V} = y \text{ axis, } \log P = x \text{ axis} \rightarrow P = 10^x$$

$$v = \frac{10^x}{y} \rightarrow k10^{2x} = y$$

38. [90]



$P^\circ$  is the pressure due to weight of piston



at 300K

$$P_1 + P^\circ = P_2$$

$$P^\circ = \frac{2 \times R \times 300}{V} - \frac{1 \times R \times 300}{V}$$

at temperature T

$$P_1' + P^o = P_2' \quad P^o = \frac{2 \times R \times T}{V} - \frac{1 \times R \times T}{3V}$$

$$\frac{2 \times R \times 300}{V} - \frac{1 \times R \times 300}{2} = \frac{2RT}{V} - \frac{1 \times R \times T}{4}$$

Solving  $T = 90 \text{ K}$

39. [1]

$$V_1 = 500 \text{ ml}$$

$$V_2 = 1800 \text{ ml}$$

$$P_{\text{total}} = 3.2 \text{ atm}$$

$$T_2 = 360 \text{ K}$$

$$T_1 = 320 \text{ K}$$

$$\text{V.P.} = 0.6 \text{ atm}$$

$$\text{V.P.} = 0.2 \text{ atm}$$

$$P_{\text{gas}} = 3.2 - 0.2 = 3 \text{ atm}$$

For  $\text{H}_2\text{O}(\text{vap.})$

For gas :

$$\frac{0.2 \times 500}{320} = \frac{P_2 \times 1800}{360}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \frac{3 \times 500}{320} = \frac{P_2 \times 1800}{360}$$

$$P_2 = \frac{20}{320} = \frac{2}{32} \text{ atm } (< \text{V.P.})$$

$$P_2 = \frac{6 \times 500}{320 \times 10} = \frac{30}{320} \text{ atm}$$

$$P_{\text{total}} = \frac{30}{32} + \frac{2}{32} = 1 \text{ atm}$$

40. [4]  $\left( \sqrt{\frac{3RT}{M}} \right)_X = \left( \sqrt{\frac{2RT}{M}} \right)_Y$

$$\sqrt{\frac{3R400}{40}} = \sqrt{\frac{2R60}{M}}$$

$$\sqrt{30} = \sqrt{\frac{4 \times 30}{M}}$$

$$M = 4$$

41. [72]

$$\frac{1}{6} = \sqrt{\frac{2}{X}} \quad (\text{Where X is molecular weight of gas})$$

$$\frac{1}{36} = \frac{2}{x}$$

$$x = 72$$

42. [4] Rate of effusion  $\propto \frac{1}{\sqrt{M}}$

For Hydrogen ( $\text{H}_2$ ) and Oxygen ( $\text{O}_2$ )

$$\frac{\text{Rate}_{\text{H}_2}^4}{\text{Rate}_{\text{O}_2}^4} \propto \left( \frac{\sqrt{32}}{\sqrt{2}} \right)^4$$

Rate<sup>4</sup>  $\propto 256 \Rightarrow x = 256$ .

For Helium ( $\text{He}$ ) and Oxygen ( $\text{O}_2$ )

$$\frac{\text{Rate}_{\text{He}}^4}{\text{Rate}_{\text{O}_2}^4} \propto \left( \frac{\sqrt{32}}{\sqrt{4}} \right)^4$$

Rate<sup>4</sup>  $\propto 64 \Rightarrow y = 64$ .

$$\text{so, } \frac{x}{y} = \frac{4}{1}$$

43. [10]  $P_{\text{Final}} = 1 + \frac{40}{76} = \frac{116}{76} \text{ atm}$

Final Height = 19 cm

Final Volume =  $(19 \times A) \text{ cm}^3$

$$P_i V_i = P_f V_f$$

$$1 \times H_i(A) = \frac{116}{76} \times 19(A)$$

$$H_i = 29 \text{ cm}$$

Hence, length by which the mercury column shorts down is  $(29 - 19) \text{ cm} = 10 \text{ cm}$

44. [5] At STP, the amount of  ${}^{36}\text{Ar}$  found  $1.911 \text{ mm}^3$  per kg of meteorite.

$$1 \text{ mm}^3 = 10^{-6} \text{ litre}$$

$$1.911 \text{ mm}^3 = 1.911 \times 10^{-6} \text{ L}$$

As we know

$$22.4 \text{ L} = 1 \text{ mole}$$

$$1.911 \times 10^{-6} \text{ L} = \left( \frac{1}{22.4} \times 1.911 \times 10^{-6} \right) \text{ mol } {}^{36}\text{Ar}$$

$$\text{No. of } {}^{36}\text{Ar atoms} = \left( \frac{6 \times 10^{23} \times 1.911 \times 10^{-6}}{22.4} \right) \text{ atoms}$$

$$\frac{\text{No. of atoms } {}^{36}\text{Ar}}{10^{16}} = \left( \frac{6 \times 10^{23} \times 1.911 \times 10^{-6}}{22.4 \times 10^{16}} \right) = 5$$

45. [3] Density (at  $0^\circ\text{C}$  and 1 atm) =  $1.25 \text{ g/L}$

Volume =  $3L$

Amount of gas (in g) =  $1.25 \times 3 = 3.75 \text{ g}$

Let us say,  $x \text{ g}$  of gas goes out  $P$  decrease by 0.8 atm

$$\text{So, } \frac{P_1}{P_2} = \frac{n_1}{n_2}$$

$$\frac{P_1}{P_2} = \frac{w_1}{w_2}$$

$$\frac{1}{0.2} = \frac{3.75}{375 - x} \Rightarrow x = 3 \text{ g}$$

Hence, 3g gas comes out

46. [3]  $P'_2 = \frac{P_1 T_2}{T_1} - P_2 - 2$

$$P'_2 = \frac{P_1 T_2}{2 T_1} - 1$$

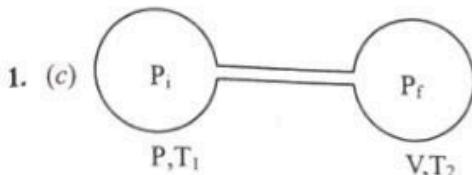
$$P'_2 = \frac{4 \times 600}{2 \times 300} - 1$$

$$= 4 - 1$$

$$P'_2 = 3 \text{ atm}$$

## Exercise-4 (Past Year Questions)

### JEE MAIN



$$\frac{P_i(V)}{RT_1} + \frac{P_i(V)}{RT_1} = \frac{P_f(V)}{RT_1} + \frac{P_f(V)}{RT_2}$$

$$\frac{2P_i}{T_1} = P_f \left( \frac{1}{T_1} + \frac{1}{T_2} \right)$$

$$P_f = \frac{2P_i T_2}{T_1 + T_2}$$

$$P_f = \frac{2P_i T_2}{T_1 + T_2}$$

2. (b)  $Z = PV/nRT$

$$P = \frac{ZnRT}{V}$$

at constant T and mol  $P \propto \frac{Z}{V}$

$$\frac{P_A}{P_B} = \frac{Z_A}{A_B} = \frac{V_B}{V_A} = \left(\frac{3}{2}\right) \times \left(\frac{1}{2}\right) = \frac{3}{2}$$

$$\therefore 2P_A = 3P_B$$

3. (d)  $PV = nRT$

$$200 \times 10 = (0.5 + x)R \times 1000$$

$$\text{On solving } x = \frac{4-R}{2R}$$

4. (a)  $T_c = \frac{8a}{27Rb}$

Greater value of  $\frac{a}{b} \Rightarrow$  higher is  $T_c$ ,

Gas  $\frac{a}{b}$

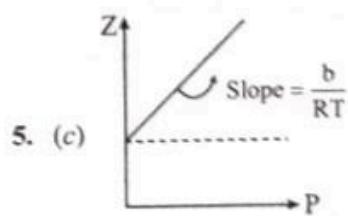
$$\text{Ar } \frac{1.3}{3.2} = 0.406$$

$$\text{Ne } \frac{0.2}{1.7} = 0.118$$

$$\text{Kr } \frac{5.1}{1} = 5.1$$

$$\text{Xe } \frac{4.1}{5} = 0.82$$

$\therefore T_c$  has order : Kr > Xe > Ar > Ne



5. (c)

As  $b \uparrow \Rightarrow$  slope  $\uparrow$

Hence, Xe, will have highest slope

6. (c) Gas A and C have same value of 'b' but different value of 'a' so gas having higher value of 'a' have more force of attraction so molecules will be more closer hence occupy less volume.

Gas B and D have same value of 'a' but different value of 'b' so gas having lesser value of 'b' will be more compressible.

$$7. (d) V_{mp} = \sqrt{\frac{2RT}{M}} \Rightarrow V_{mp} \propto \sqrt{\frac{2RT}{M}}$$

For N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>

$$\sqrt{\frac{300}{28}} < \sqrt{\frac{400}{32}} < \sqrt{\frac{300}{2}}$$

$V_{mp}$  of N<sub>2</sub>(300K) <  $V_{mp}$  of O<sub>2</sub>(400K) <  $V_{mp}$  of H<sub>2</sub>(300K)

8. (b) Radon is a radioactive substance. This is not present in atmosphere.

9. (d)  $C_{RMS} > C_{Avg} > C_{MPS}$

10. (b)  $PM = dRT$

$$\Rightarrow d \propto \frac{1}{T}$$

$$\Rightarrow d \propto P$$

11. (d) Pressure due to 1 mole of H<sub>2</sub> gas = 2 atm

$\therefore$  Pressure due to 1 mol of H<sub>2</sub> + 1 mol of He + 1 mol of O<sub>2</sub> = 6 atm.

12. [750]

At constant temperature and number of moles,

$$P_1 V_1 = P_2 V_2$$

$$P_1 = 48 \times 10^{-3} \text{ bar}; V_1 = \frac{4}{3} \pi (3)^3$$

$$V_2 = \frac{4}{3} \pi (12)^3$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{48 \times 10^{-3} \times (3)^3}{(12)^3}$$

$$= \frac{48 \times 10^{-3}}{64} = 7.5 \times 10^{-4} = 750 \times 10^{-6} \text{ bar}$$

13. [2]

Weight of empty LPG cylinder = 14.8 kg

Weight of full LPG cylinder = 29 kg

$\therefore$  Weight of gas = 29 - 14.8 = 14.2 kg

If weight of full LPG cylinder = 23 kg

Then weight of gas used =  $29 - 23 = 6 \text{ kg}$  at ambient temperature.

From ideal gas equation,  $pV = nRT$

$$\text{or } pV = \frac{\text{Weight of solute}}{\text{Molecular mass of solvent}} \times RT$$

$$\text{or } pV = \frac{W}{M} \times RT$$

Applying ideal gas to LPG cylinder when gas is full,  
 $pV = nRT$

$$3.47 \text{ atm} \times \bar{V} = \frac{14.2 \text{ kg}}{M} \times RT \quad \dots(i)$$

Applying ideal gas to LPG cylinder when gas is reduced to 23kg at ambient temperature,

$$pV = nRT$$

$$p \times V = \frac{8.2 \text{ kg}}{M_2} \times RT \quad \dots(ii)$$

Divide Eq. (i) by (ii)

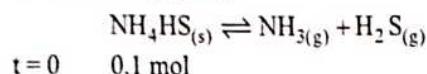
$$\frac{3.47}{p} = \frac{14.2}{8.2}$$

$$\Rightarrow p = \frac{3.47 \times 41}{71} = 2.003 \text{ atm}$$

14. [6]

$$\text{Moles of } \text{NH}_4\text{HS} \text{ initially taken} = \frac{5.1 \text{ g}}{51 \text{ g/mol}} = 0.1 \text{ mol}$$

Volume of vessel = 2l



$$t=0 \quad 0.1 \text{ mol}$$

$$t=\infty \quad 1(1-0.2) \quad 0.1 \times 0.2 \quad 0.1 \times 0.2$$

$\Rightarrow$  Partial pressure of each component

$$P = \frac{nRT}{V} = \frac{0.1 \times 0.2 \times 0.002 \times 300}{2} = 0.246 \text{ atm}$$

$$\Rightarrow k_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = (0.246)^2 = 0.060516 = 6.05 \times 10^{-2}$$

$$\Rightarrow 6$$

15. [927]

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{300 \times 10^3}{300} = \frac{1.2 \times 10^6}{T_2}$$

$$\Rightarrow T_2 = 1200 \text{ K}$$

$$\Rightarrow T_2 = 927^\circ\text{C}$$

16. [26]

$$n(\text{CH}_4) = \frac{PV}{RT}$$

$$= \frac{1 \times 4 \times 10^3 \times 1000}{0.083 \times 300}$$

Weight of  $\text{CH}_4$

$$= \frac{40 \times 16 \times 10^5}{0.033 \times 300} \text{ gm}$$

$$= 25.7 \times 10^5 \text{ gm}$$

17. [45] Using  $PV = nRT$

$$n_1 T_1 = n_2 T_2$$

$$\frac{3}{\text{Molar mass of A}} \times 300 = \frac{0.2}{2} \times 200$$

$\therefore$  Molar mass of A =  $45 \text{ g mol}^{-1}$

18. [32] Using  $\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{30}{300} = \frac{P_2}{318}$

$$\Rightarrow P_2 = 32 \text{ atm}$$

19. [1655]

Using  $PV = nRT$

$$2 \times 10^6 \times 2 \times 10^{-3} = \frac{11}{44} \times 8.3 \times T$$

$\therefore T = 1927.710 \text{ K} = 1654.56^\circ\text{C}$

20. [2]  $n_{\text{H}_2} = \frac{40}{2} = 20$  and  $n_{\text{O}_2} = \frac{60}{32} = \frac{15}{8}$

$$P_{\text{H}_2} = \left( \frac{20}{20 + \frac{15}{8}} \right) \times 2.2$$

$$= 2.0114 \text{ bar} = 2 \text{ bar}$$

21. [25]  $Z = 1 + \frac{Pb}{RT}$  (For real gas under high pressure)

$$2 = 1 + \frac{Pb}{RT} \Rightarrow b = \frac{RT}{P}$$

$$\Rightarrow b = \frac{0.083 \times 298}{99} = 0.25 = 25 \times 10^{-2} \text{ L mol}^{-1}$$

## JEE ADVANCED

$$22. [5] \lambda = \frac{h}{\sqrt{2m(KE)}} \quad KE \propto T$$

$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \sqrt{\frac{m_{\text{Ne}} KE_{\text{Ne}}}{m_{\text{He}} KE_{\text{He}}}} = \sqrt{\frac{20 \times 1000}{4 \times 200}} = 5.$$

23. (c) According to Grham's law, if all conditions are identical,

$$r \propto \frac{1}{\sqrt{M}}$$

As in this question, all conditions are identical for X and Y, it will be followed

$$\text{Hence } \frac{r_x}{r_y} = \sqrt{\frac{M_y}{M_x}}$$

$$\frac{d}{24-d} = \sqrt{\frac{40}{10}} \Rightarrow \frac{d}{24-d} = 2$$

$$d = 48 - 2d$$

$$3d = 48$$

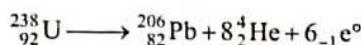
$$d = 16 \text{ cm.}$$

24. (d) The general formula of mean free path ( $\lambda$ ) is

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P} \quad (d = \text{diameter of molecule}, p = \text{pressure inside the vessel}).$$

$\therefore d$  &  $p$  are same for both gases, ideally their  $\lambda$  are same. Hence it must be the higher drift speed of X due to which it is seeing more collisions per second, with the inert gas in comparison to gas Y. So X sees comparably more resistance from noble gas than Y and hence covers lesser distance than that predicted by Graham's Law.

25. [9] Initial moles of gases = 1



Initial moles 1 moles

Moles after 8 mole decomposition

Total gaseous moles after decomposition =  $8 + 1 = 9$  moles

$$\text{Ratio of pressures } \frac{P_f}{P_i} = \frac{n_f}{n_i} = 9$$

26. (c)  $P(V-b) = RT$

$$\Rightarrow PV - Pb = RT$$

$$\Rightarrow \frac{PV}{RT} = \frac{Pb}{RT} + 1$$

$$\Rightarrow Z = 1 + \frac{Pb}{RT}$$

Hence  $Z > 1$  at all pressures.

This means, repulsive tendencies will be dominant when interatomic distance are small.

This means, interatomic potential is never negative but becomes positive at small interatomic distances.

27. [4 times]

Given diffusion coefficient is proportional to mean free path ( $\lambda$ ) and mean speed ( $V_{\text{mean}}$ )

And absolute T is increased by 4 times

$$\text{And average } K_E \propto T \Rightarrow \frac{1}{2}mv^2 \propto T$$

When T increased by 4 times  $\Rightarrow V_{\text{mean}}$  increases by 2 times (i)

Also mean free path,  $\lambda$

$$= \frac{KT}{\sqrt{2}\pi d^2 P} \Rightarrow \lambda \propto \frac{T}{P}$$

Increasing T 4 times and P 2 times,

$\lambda$  increases 2 times (ii)

from (i) and (ii) implies, diffusion coefficient increases 4 times

28. [2.22]

$$P_1 = 5 \quad P_2 = 1$$

$$v_1 = 1 \quad v_2 = 3$$

$$T_1 = 400T_2 = 300$$

$$n_1 = \frac{5}{400R} \quad n_2 = \frac{3}{300R}$$

Let volume be  $(v+x)$   $v = (3-x)$   $15 - 5x = 4 + 4x$

$$\frac{P_A}{T_A} = \frac{P_B}{T_B}$$

$$\frac{n_{b_1} \times R}{v_{b_1}} = \frac{n_{b_2} \times R}{v_{b_2}}$$

$$\Rightarrow \frac{5}{400(4+x)} = \frac{3}{300(3-x)}$$

$$\Rightarrow 5(3-x) = 4+4x \Rightarrow x = \frac{11}{9}$$

$$v = 1+x = 1+\frac{11}{9} = \left(\frac{20}{9}\right) = 2.22$$

29. (a,b,c)

$$U_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$E_{\text{avg}} = \frac{3}{2}kT$$

30. (b) Graph represents symmetrical distribution of speed and hence, the most probable and the average speed should be same. But the root mean square speed must be greater than the average speed.

# Chemical Thermodynamics and Energetics

## Exercise-1 (Topicwise)

1. (c) In isolated system neither exchange of matter nor exchange of energy is possible with surroundings.
2. (c) Work is not a state function as during a process its value depends on the path followed. The value of enthalpy, internal energy and entropy depends on the state and not on the path followed to get that state, hence these are state functions.
3. (b) Sliding of legs on roof surface results in mechanical energy loss.
4. (c) Critical density, viscosity, specific heat capacity, molar heat capacity, kinetic energy, specific gravity, dielectric constant, pH.
5. (c)  $PV = \text{constant}$  (Boyle's Law)  
 $PV = nRT$  (Ideal gas equation)  
 $PV/T = \text{Constant}$   
 $W = -q$   
 $\Delta V = 0$   
 $\Delta U = q + W = 0$
6. (a) In an ideal gas intermolecular forces are absent.
7. (b) The process starts and ends at the same point.
8. (c) In a well stoppered thermoflask, no exchange of energy or matter can take place.
9. (a) A  $\rightarrow$  B, Volume is constant  
B  $\rightarrow$  C, Slope ( $V/T$ ) of line is constant.  
C  $\rightarrow$  A, Temperature is constant.
10. (c) A  $\rightarrow$  B: Isochoric  
B  $\rightarrow$  C: Isothermal  
C  $\rightarrow$  D: Isochoric  
D  $\rightarrow$  A: Isothermal
11. (c)  $\Delta H = nC_p \Delta T = +\text{ve}$  [ $\because \Delta T = -\text{ve}$ ]  
 $W = -P(V_2 - V_1) = -\text{ve}$  [ $\because (V_2 - V_1)$  is +ve]
12. (d)  $q = 0$ ; because system is thermally insulated.  
 $W > 0$ ; because work is done on the system by stirring.
13. (b) (i) Volume = constant  
 $W = -PdV = 0$   
(ii) Pressure = constant  
 $W = -P(2V_1 - V_1) = -PV_1$

14. (b)  $W = -2.303 nRT \log \frac{V_2}{V_1}$   
 $= -2.303 \times 1 \times 8.314 \times 10^7 \times 298 \log \frac{20}{10}$   
 $= -298 \times 10^7 \times 8.314 \times 2.303 \log 2.$
15. (c)  $W_{ABCA} = \text{Area enclosed in figure ABCA}$   
 $= 1/2 \times (3V_1 - V_1)(6P_1 - P_1) = 5P_1V_1$
16. (c) Heat is released during freezing.
17. (a)  $C_p - C_v = nR$   
 $\therefore C_p - C_v = 2R$
18. (a)  $\Delta U = q + W$   
 $= 600 - 300 = 300 \text{ J}$
19. (a)  $\Delta V = 0$  for isochoric process  
 $\therefore q_v = \Delta E$
20. (d)  $dU = nC_v dT$   
 $dT = 0$   
 $\therefore dU = 0$   
 $W = -q$
21. (b)  $W = -PdV = -1 \times dV = -101.33 \times \Delta V \text{ J}$   
 $\because \Delta U = q + W$   
 $300 = 500 + (-101.3 \times \Delta V)$   
 $\Rightarrow \Delta V = 2 \text{ L}$
22. (b) Heat is evolved; so  $q_{sys} = -\text{ve}$   
 $W = -\Delta nRT$   
 $W = -(-1) RT$   
 $W = RT$   
 $\Delta U = q + W = -\text{ve}$
23. (d) The temperature of the system decreases in adiabatic expansion.
24. (a)  $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$   
 $(300)(V_1)^{1/3} = T_2 (8V_1)^{1/3}$   
 $T_2 = 150 \text{ K}$   
 $W = \frac{nR}{\gamma-1} [T_2 - T_1]$   
 $W = \frac{1 \times 2}{1.33 - 1} (150 - 300)$   
 $W = -900 \text{ Cal}$

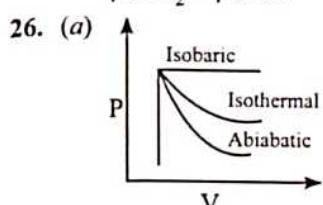
25. (b)  $\gamma = \frac{C_p}{C_v}$  increases with atomicity

Atomicity of B > Atomicity of A

	Ar	He	H <sub>2</sub>	O <sub>2</sub>
Atomicity	1	1	2	2

Atomicity of H<sub>2</sub> > Atomicity of He

$\gamma$  of H<sub>2</sub> >  $\gamma$  of He



Work done is area under the curve.

27. (b)  $\Delta H = \Delta U + \Delta n_g RT$   
 $= \Delta U + \Delta PV$   
 $= 40 + [(4)(5) - (1)(3)] = 57 \text{ L-atm}$

28. (d) H and U are functions of temperature.

$$\Delta U = nC_v dT$$

$$\Delta H = nC_p dT$$

29. (d)  $W = -P_{\text{ext}}(V_2 - V_1)$   
 $= -1(2) = -2 \times 101.3 \text{ J} = -202.6$   
 $q = \Delta H = 202.6 \text{ J}$   
 $\Delta U = q + W$   
 $= 202.6 - 202.6 = 0$

30. (b)  $W = -P(V_{\text{final}} - V_{\text{initial}})$   
 $= +ve [ \because V_{\text{final}} > V_{\text{initial}} ]$

31. (b) When water freezes, it gives up heat to the surrounding.  
This heat transfer is  $n\Delta H_{\text{fusion}}$ .

32. (c) Randomness of gaseous phase is maximum.

33. (c)  $\Delta S_{\text{reaction}} = \sum \Delta S_{\text{products}} - \sum \Delta S_{\text{reactants}}$   
Entropy of gases is higher than entropy of solids or liquid.

34. (b) Number of particles increases, number of ways of energy distribution increases, thus entropy increases.

35. (d) More the negative value of  $\Delta n_g$ , more will be the negative change in entropy.

(a)  $\Delta n_g = -1$  (b)  $\Delta n_g = -1$  (c)  $\Delta n_g = 0$  (d)  $\Delta n_g = -2$

36. (b)  $\Delta n_g = +1 \Rightarrow$  Entropy change is positive.  
Decomposition reactions are endothermic.

37. (c) In this reaction NaNO<sub>3</sub> changes from solid to its aqueous ions Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup>. Thus, entropy is greater than zero.

38. (b)  $\Delta n_g > 0$ , hence entropy change will be maximum.

39. (a) Entropy of universe is continuously increasing.

40. (b) For an isolated system,

$$\Delta S = 0$$

$$S_p - S_r = 0$$

$$S_p = S_r$$

41. (c)  $\Delta S = nC_{p,m} \ln \left( \frac{T_2}{T_1} \right)$

$$\Delta S = 2 \times \frac{5}{2} R \times \ln \left( \frac{600}{300} \right)$$

$$\Delta S = 5R \ln 2$$

42. (c)  $\Delta S = nC_{v,m} \ln \left( \frac{T_2}{T_1} \right)$

$$C_{p,m} - C_{v,m} = R$$

$$\frac{5}{2} R - C_{v,m} = R$$

$$C_{v,m} = \frac{3}{2} R$$

$$\Delta S = 2 \times \frac{3}{2} R \times \ln \left( \frac{600}{300} \right)$$

$$= 3R \ln 2$$

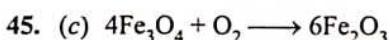
43. (c)  $\Delta S = nC_{v,m} \ln \left( \frac{T_2}{T_1} \right)$

$$= 2 \times \frac{3}{2} R \times \ln \left( \frac{573}{273} \right)$$

$$= 3R \ln \left( \frac{573}{273} \right)$$

44. (c) Total entropy change =  $\frac{\Delta H}{T_2} - \frac{\Delta H}{T_1}$

$$= \frac{-401.7}{273} - \left[ \frac{-401.7}{368} \right] = -0.38 \text{ J/K}$$



$$\Delta S^{\circ}_{\text{reaction}} = 6\Delta S^{\circ}(\text{Fe}_2\text{O}_3) - \Delta S^{\circ}(\text{O}_2) - 4\Delta S^{\circ}(\text{Fe}_3\text{O}_4)$$

$$-266 = 6 \times 87 - 205 - 4 \times \Delta S^{\circ}(\text{Fe}_3\text{O}_4)$$

$$\Delta S^{\circ}(\text{Fe}_3\text{O}_4) = 145.75 \text{ J K}^{-1}$$

46. (d) Gibbs free energy is an extensive property.

47. (b) When  $\Delta H = -ve$  and  $\Delta S = +ve$  then reaction is spontaneous.

48. (d) At equilibrium,  $\Delta G = 0$

$$-2.303 RT \log k = 0$$

$$\Rightarrow k = 1$$

49. (a) Curd forms from milk because of the chemical reaction between the lactic acid, bacteria and casein protein.

50. (d)  $\Delta G = nRT \ln \left( \frac{P_2}{P_1} \right)$

$$= nRT \ln (1) = 0$$

51. (b)  $\Delta G = \Delta H - T\Delta S$  must be less than zero

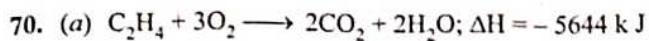
$$\Delta H - T\Delta S < 0$$

$$\Delta H = -ve$$

For  $\Delta G < 0$ ,  $\Delta S$  can be negative but the numerical value must be less than  $\frac{X}{298}$  Cal K<sup>-1</sup> mol<sup>-1</sup>.

52. (a)  $\Delta G = \Delta H - T\Delta S < 0$  [for spontaneity]  
 $-33 - T(-58) < 0$   
 $T < \frac{33}{58}$
53. (a)  $\Delta G = -RT \times \ln k$   
 $k = \frac{P_B}{P_A} = \frac{P}{4P} = \frac{1}{4}$   
 $\Delta G^\circ = -RT \ln \left( \frac{1}{4} \right)$   
 $= RT \ln (4)$
54. (b)  $2\text{Fe(s)} + \frac{3}{2}\text{O}_2\text{(g)} \longrightarrow \text{Fe}_2\text{O}_3\text{(s)}$ ;  $\Delta G = -177 \text{ k Cal}$   
 $4\text{Fe}_2\text{O}_3\text{(s)} + \text{Fe(s)} \longrightarrow 3\text{Fe}_3\text{O}_4\text{(s)}$ ;  $\Delta G = -19 \text{ k Cal}$   
 $\Delta G$  for  $3\text{Fe(s)} + 2\text{O}_2\text{(g)} \longrightarrow \text{Fe}_3\text{O}_4\text{(s)}$  can be obtained  
by taking  $[2 + 4(1)] \times \frac{1}{3}$
- Hence, we get  $\Delta G_f = [19 + 4 \times (-177)] \times \frac{1}{3}$   
 $= -242.3 \text{ k Cal for 1 mol. Fe}_3\text{O}_4$
55. (c) For spontaneity,  $\Delta G < 0$   
 $\Delta H - T\Delta S < 0$   
 $-76.6 - T(226 \times 10^{-3}) < 0$   
 $T < 338.93 \text{ K}$   
 $T < 66^\circ\text{C}$
56. (c) Free energy change for a reversible reaction at equilibrium is zero.
57. (a)  $\Delta n_g = 1 - 1 - 1 = -1$   
 $\Delta U = \Delta H^\circ - \Delta n_g RT$   
 $= -4600 - (-1 \times 2 \times 500)$   
 $= -3600 \text{ Cal} = -3.6 \text{ k Cal}$
58. (d)  $W = -\Delta n_g RT = -PdV$   
For I and II,  $\Delta n_g = -ve$   
 $\Rightarrow W = +ve$  (work done on the system)  
For III,  $\Delta n_g = +ve$   
 $\Rightarrow W = -ve$  (work done by the system)  
For IV,  $dV = -ve$   
 $\Rightarrow W = +ve$  (work done on the system)
59. (d)  $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \longrightarrow 2\text{HCl(g)}$ ;  $\Delta H = -185 \text{ k J}$   
2mole 2mole  
 $\Rightarrow 2\text{H}_2\text{(g)} + 2\text{Cl}_2\text{(g)} \longrightarrow 4\text{HCl(g)}$ ;  $\Delta H = -370 \text{ k J}$   
 $\Delta H = \Delta U + \Delta n_g RT$   
 $\Delta n_g = 0$   
 $\Rightarrow \Delta H = \Delta U = -370 \text{ k J}$
60. (b)  $\text{NH}_4\text{Cl(s)} \xrightarrow{\text{Sublime}} \text{NH}_3\text{(g)} + \text{HCl(g)}$   
Internal energy becomes more negative if the system expands.

61. (d)  $\Delta H = \Delta E + \Delta n_g RT$   
(a)  $\Delta n_g = 2 - 1 - 1 = 0$   
(b)  $\Delta n_g = 0 - 0 = 0$   
(c)  $\Delta n_g = 1 - 1 = 0$   
(d)  $\Delta n_g = 2 - 3 - 1 = -2 \neq 0$   
In (d),  $\Delta H \neq \Delta E$
62. (c)  $3\text{C(s)} + 3\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \longrightarrow \text{CH}_3\text{COOCH}_3(l)$   
 $\Delta n_g = 0 - (4) = -4$   
 $\Delta H = \Delta U + \Delta n_g RT$   
 $-442.9 = \Delta U + 4 \times 8.314 \times 10^{-3} \times 298$   
 $\Rightarrow \Delta U = -452.82 \text{ k J/mol}$
63. (b) The negative sign of  $\Delta H$  indicates that this reaction is exothermic.
64. (d) (i)  $\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$ ;  $\Delta H_1 = -94.3 \text{ k Cal mol}^{-1}$   
(ii)  $\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$ ;  $\Delta H_2 = -67.4 \text{ k Cal mol}^{-1}$   
(iii)  $\text{O}_2\text{(g)} \longrightarrow 2\text{O(g)}$ ;  $\Delta H_3 = 117.4 \text{ k Cal mol}^{-1}$   
(iv)  $\text{CO(g)} \longrightarrow \text{C(g)} + \text{O(g)}$ ;  $\Delta H_4 = 230.6 \text{ k Cal mol}^{-1}$   
 $\text{C(s)} \longrightarrow \text{C(g)}$ ; can be obtained by  
Target equation = Eq. (i) - Eq. (ii) -  $\frac{1}{2}$  Eq. (iii) + Eq. (iv)  
So, enthalpy change will be  
 $\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2}\Delta H_3 + \Delta H_4$   
 $= -94.3 + 67.4 - 58.7 + 230.6 = 145 \text{ k Cal mol}^{-1}$
65. (a)  $\Delta H$  represents heat of reaction.
66. (d) Eq. (i)  $\text{H}_2\text{(g)} + \text{Br}_2\text{(g)} \longrightarrow 2\text{HBr(g)}$ ;  $\Delta H = \Delta H_1^\circ$   
Eq. (ii)  $\text{Br}_2\text{(g)} \longrightarrow \text{Br}_2(l)$ ;  $\Delta H = \Delta H_2^\circ$   
eq. (i) - eq. (ii)  
 $\text{H}_2\text{(g)} + \text{Br}_2(l) \longrightarrow 2\text{HBr(g)}$   
 $\Delta H = \Delta H_1^\circ - \Delta H_2^\circ$   
For 1 mol of HBr,  $\Delta H = \frac{\Delta H_1^\circ - \Delta H_2^\circ}{2}$
67. C(diamond) +  $\text{O}_2 \longrightarrow \text{CO}_2\text{(g)}$ ;  $\Delta H = -94.3 \text{ k cal/mol}$   
C(graphite) +  $\text{O}_2 \longrightarrow \text{CO}_2\text{(g)}$ ;  $\Delta H = -97.6 \text{ k cal/mol}$   
eq. (i) - eq. (ii)  
 $\Delta H = -94.3 - (-97.6) = 3.3 \text{ k cal mol}^{-1}$
68. (a) Heat of combustion of 1 mole of sucrose = 1350 kCal  
Heat of combustion of 342g of sucrose = 1350 kCal  
Heat of combustion of 17.1g of sucrose  
 $= \frac{1350}{342} \times 17.1 = 67.5 \text{ kCal}$
69. (a) Given,  
 $\Delta H_1 = -298.2 \text{ k J mol}^{-1}$ ;  $\Delta H_2 = -98.7 \text{ k J mol}^{-1}$   
 $\Delta H_3 = -130.2 \text{ k J mol}^{-1}$ ;  $\Delta H_4 = -287.3 \text{ k J mol}^{-1}$   
By adding all the equations, we get  
 $\Delta H$  of formation of  $\text{H}_2\text{SO}_4$  at 298 K =  $-814.4 \text{ k J mol}^{-1}$



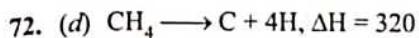
$$n_{\text{O}_2} = \frac{5644 \times 3}{1411} = 12$$

$$V_{\text{O}_2} = 12 \times 22.4 = 268.8 \text{ L}$$

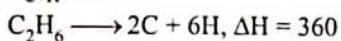
71. (a) Calorific value for ethane

$$= \frac{-341.1}{30} = -11.37 \text{ k Cal g}^{-1}$$

$$\text{Calorific value for ethyne} = \frac{-310}{26} = 11.92 \text{ k Cal g}^{-1}$$

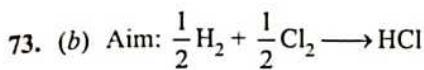


$$E_{\text{C-H}} = 80 \text{ cal}$$



$$\therefore 360 = E_{\text{C-C}} + 6E_{\text{C-H}}$$

$$\therefore E_{\text{C-C}} = 360 - 6 \times 80 = 120 \text{ cal}$$

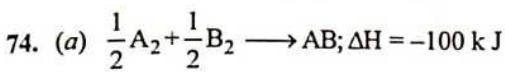


$$\Delta H = \Sigma \text{B.E.}_{(\text{products})} - \Sigma \text{B.E.}_{(\text{Reactants})}$$

$$= \text{B.E.}(\text{HCl}) - \left[ \frac{1}{2}\text{B.E.}(\text{H}_2) + \frac{1}{2}\text{B.E.}(\text{Cl}_2) \right]$$

$$= -103 - \left[ \frac{1}{2}(-104) + \frac{1}{2}(-58) \right]$$

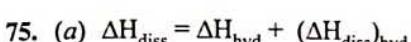
$$= -103 - (-52 - 29) = -22 \text{ k cal}$$



Let bond enthalpy of  $\text{A}_2$  and  $\text{AB}$  be  $X$  and that of  $\text{B}_2$  will be  $\frac{X}{2}$ .

$$\left( \frac{X}{2} + \frac{X}{4} \right) - X = -100$$

$$X = 400 \text{ kJ}$$



$$-25 = -30 + (\Delta H_{\text{diss}})_{\text{hyd}}$$

$$\Rightarrow (\Delta H_{\text{diss}})_{\text{hyd}} = 5 \text{ Cal mol}^{-1}$$

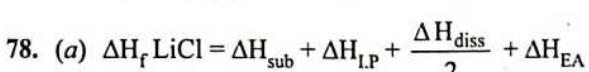
76. (a) Since process is exothermic, there heat is evolved due to which temperature of water increases.



$$\Delta H = \Delta U + P\Delta V$$

$$-0.5 = \Delta U + (-1.5)(0.05)$$

$$\Delta U = 0.25 \text{ kJ}$$



$$-400 = 160 + 520 + \frac{244}{2} - 365 + \text{I.E}$$

$$\text{I.E} = -837 \text{ k J mol}^{-1}$$

79. (c) Heat of neutralization of a strong acid and strong base is nearly  $-13.7 \text{ k Cal}$ .

80. (d) Methanoic acid is a weak acid and therefore, energy will be required for its dissociation.

81. (a)  $\Delta H = -13.7 + 0.7$

$$\Delta H = -13 \text{ k cal}$$

## Exercise-2 (Learning Plus)

1. (d) Boiling point, pH, pressure, temperature and density are intensive properties.

Mass, volume and entropy are extensive properties.

2. (b) For IV volume is constant  $\rightarrow$  Isochoric  
For I pressure is constant  $\rightarrow$  Isobaric

3. (b) Isothermal process  $\rightarrow$  Temperature constant  $\rightarrow \Delta T = 0$   
Isobaric process  $\rightarrow$  Pressure constant  $\rightarrow \Delta P = 0$   
Adiabatic process  $\rightarrow$  Heat constant  $\rightarrow q = 0$   
Isochoric process  $\rightarrow$  Volume constant  $\rightarrow \Delta V = 0$

4. (d) We know in P-V graph process will be either isothermal or Adiabatic but pressure will be different. But here given process is starting from some point and ending at same point so it is not possible.

5. (d) A  $\rightarrow$  B Isobaric process  
B  $\rightarrow$  C Isothermal process

C  $\rightarrow$  D Isobaric process

$$W_{\text{Isobaric}} = -P_{\text{ext}}(\Delta V) = -P_{\text{ext}}(V_f - V_i)$$

$$W_{\text{Isobaric}} = -pv \ln\left(\frac{V_2}{V_1}\right)$$

$$W_{\text{Total}} = W_{\text{A} \rightarrow \text{B}} + W_{\text{B} \rightarrow \text{C}} + W_{\text{C} \rightarrow \text{D}}$$

$$\Rightarrow -P_o(2V_o - V_o) + (-P_o V_o) \ln \frac{4V_o}{2V_o} + \left( \frac{-P_o}{2} \right) (2V_o - 4V_o)$$

$$\Rightarrow -P_o V_o - P_o V_o \ln 2 + P_o V_o$$

$$W_{\text{total}} \Rightarrow -P_o V_o \ln 2$$

6. (a)  $W = P\Delta V$

Volume increases by  $1\text{L} = V_2 = 51\text{L}$

$$V_1 = 50\text{L}$$

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

$$W = P\Delta V = 1\text{atm} \times [51\text{L} - 50\text{L}]$$

$$W \Rightarrow 1 \text{ atm L}$$

7. (c) For cyclic process :  $\Delta U = 0 \Rightarrow q = -W$

Isothermal process:  $\Delta U = 0 \Rightarrow q = -W$

Adiabatic process:  $q = 0 \Rightarrow \Delta U = -W$

Isochoric process:  $q = 0 \Rightarrow \Delta U = q$

In Adiabatic process  $q = 0 \neq \Delta E$



8. (c) Given

$$P_{\text{ext}} = 2 \text{ atm} \quad P_1 = 5 \text{ atm} \quad P_2 = 2 \text{ atm}$$

$$T_1 = 300 \text{ K} \quad T_2 = T, n = 1, C_V = \frac{5}{2} R$$

For an adiabatic process

$$w = nC_V dT = -P \Delta V$$

$$\therefore nC_V(T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1)$$

$$\Rightarrow 1 \times \frac{5}{2} R(T - 300) = -2 \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$\Rightarrow 1 \times \frac{5}{2} R(T - 300) = -2 \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$\Rightarrow \frac{5}{2} R(T - 300) = -2R \left( \frac{T}{2} - \frac{300}{5} \right)$$

$$\Rightarrow 5T - 1500 = -2T + 240$$

$$\Rightarrow 7T = 1740 \Rightarrow T = 248.57 \text{ K}$$

$$\therefore T_2 = T = 248.57 \text{ K.}$$

9. (b) As we know that,

$$\Delta H = \Delta U + P \Delta V$$

for adiabatic process,

$$\Delta H = \frac{f}{2} nR \Delta T + nR \Delta T = nC_p \Delta T$$

$$\therefore \Delta H \propto \Delta T \quad \dots \text{(i)}$$

Now the work done by the gas is maximum in reversible adiabatic process than irreversible adiabatic process.

$$\text{Now, } P \Delta V = W$$

$$\Rightarrow \Delta T \propto W \quad \dots \text{(ii)}$$

from equation (i) and (ii), we have

$$\Delta H_1 < \Delta H_2$$

10. (b) For the state 1

$$PV = nRT$$

$$1 \times 10 = n \times (0.082)(300)$$

$$n = 0.4$$

For the state 2

$$PV = nRT$$

$$4 \times 5 = 0.4 \times (0.082)(T_2)$$

$$T_2 = 600 \text{ K}$$

$$\Delta U = q + W$$

$$= 50 \times (\Delta T) + (-P_{\text{ext}}) \Delta V$$

$$= 50(600 - 300) - (1)(4 - 1)$$

$$\Delta U = 15000 - 300 \Rightarrow 14700 \text{ J}$$

$$\Delta H = \Delta U + \Delta PV$$

$$\Rightarrow 14700 + (5 \times 4 - 10) \text{ atm L}$$

$$\Rightarrow 14700 + 10 \times 100 \text{ J}$$

$$\Rightarrow 15700 \text{ J}$$

$$\Delta H \Rightarrow 15.7 \text{ kJ}$$

11. (c)  $\text{HgO(s)} \rightarrow \text{HgS(s)}$

Entropy also depends upon total molar mass.

Molar mass of  $\text{HgS} > \text{HgO}$ .

$\text{HgO}$  has lower entropy than  $\text{HgS}$ .

12. (c)  $\text{S}_2 \rightarrow \text{AlCl}_3 \rightarrow \text{Al}^{3+} + 3\text{Cl}^-$

$\text{Al}^{3+} \rightarrow$  high charge density

So water molecule Attracts  $\text{Al}^{3+}$  So Arrangement is highly order. So entropy decreases.

$\text{S}_2 \rightarrow$  Adsorption leads to exothermic process  $\Delta H = -V_e$

$\text{S}_3 \rightarrow$  Higher the molar mass Higher entropy  $\text{D}_2$  has higher entropy than  $\text{H}_2$ .

Statement 2 and 3 are correct.

13. (c) Isoentropic process is Adiabatic and reversible process.

14. (b) At absolute zero (At 0K) the entropy of a perfectly crystalline substance is taken as zero.

15. (c) for a chemical reaction:-

at equilibrium Gibbs free energy change is zero.

But for every chemical reaction at equilibrium standard Gibbs energy of reaction is not zero.

for a Spontaneous reaction  $\Delta G$  is negative.

Spontaneity is related to change in entropy of universe.

Statement 2 and 3 are correct.

16. (d)  $\Delta G = \Delta H - T\Delta S$

$$\Rightarrow -6000 - 300 \times 0.18 \Rightarrow -6054 \text{ kJ/mol}$$

So, for 34.2 gm (0.1 mol) of sucrose maximum available energy  $\Delta G = 605.4 \text{ kJ}$

17. (c)  $\Delta_f H = \Delta H_{\text{Reactants}} - \Delta H_{\text{Products}}$

$$\Delta_f H = -110.5 - (-266.3) = 155.8 \text{ kJ/mol}$$

Similarly,  $\Delta_f S = S_{\text{Reactants}} - S_{\text{Products}}$

$$\Delta_f S = (27.28 + 197.6) - (57.49 + 5.74)$$

$$\Rightarrow 161.65 \text{ J/mol k}$$

Therefore at  $\Delta_f G = 0$ ,  $\Delta_f H = T\Delta_f S$

$$T = \Delta_f H / \Delta_f S = \frac{155.8 \times 1000 \text{ J/mol}}{161.65} = 963.94 \text{ k}$$

$$T = 964 \text{ K}$$

18. (a)  $\Delta_f H = \Delta H_{\text{Product}} - \Delta H_{\text{Reactant}} = H_B - H_A$

$$\Rightarrow 15 - 40 = -25 \text{ kJ}$$

19. (c) Given  $\Delta H^\circ = -92.2 \text{ KJ}$

$$\Delta C_p = 2C_p(\text{NH}_3, g) - C_p(\text{N}_2, g) - 3C_p(\text{H}_2)$$

$$\Rightarrow 2 \times 35.1 - 29.1 - 3 \times 28.8$$

$$\Rightarrow 70.2 - 29.1 - 86.4 = -45.3 \text{ J/K}$$

$$\Delta H^\circ_{100^\circ\text{C}} = \Delta H^\circ_{25^\circ\text{C}} + C_p \Delta T = -92.2 - \frac{45.3 \times 75}{1000}$$

$$\Delta H^\circ_{100^\circ\text{C}} = -92.2 - 1.3975 = -95.6 \text{ kJ/mole}$$

Then, reaction at  $\rightarrow 100^\circ\text{C}$  as compared to that at  $25^\circ\text{C}$  will be more exothermic.



20. (c) The enthalpy of formation of pure elements is zero. Therefore,

$$\Delta H_f^\circ(X_2) = 0$$

Let the enthalpy of formation of  $AX_2$  (g) and  $BX_2$  (g) be  $4X$  and  $3X$  respectively.

$$\Delta H = \Delta H_{\text{Products}} - \Delta H_{\text{Reactants}}$$

$$\Delta H = [\Delta H_f^\circ(AX_2) - 2\Delta H_f^\circ(BX_2)] - [\Delta H_f^\circ(AB_2)]$$

$$\Delta H = [4x - (2 \times 3x)] - (+30) \text{ kJ mol}^{-1} = -270 \text{ kJ mol}^{-1}$$

$$\Rightarrow 4x - 6x - 30 = -270 \text{ kJ mol}^{-1}$$

$$2x = 240 \text{ kJ mol}^{-1}$$

$$x = 120 \text{ kJ mol}^{-1}$$

$$\text{Therefore, } \Delta H_f^\circ(AX_2) = 4x = 4 \times 120 = 480 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(BX_2) = -6x = -6 \times 120 = -720 \text{ kJ mol}^{-1}$$

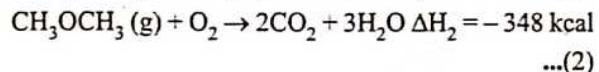
$$K_p = K_c (RT)^{\Delta n}$$

$$\Delta n = n_{AX_2} + n_{BX_2} - n_{X_2}$$

$$(2+1) - 3 = 0$$

$$\text{Therefore, } K_p = K_c (Rt)^\circ$$

$$K_p = K_c$$



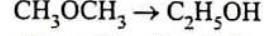
$$\Delta H(\text{H}_2\text{O}) = -68 \text{ kcal}$$

$$\Delta H(\text{O}_2) = -94 \text{ kcal}$$

$\Delta H$  of reaction 2

$$\Rightarrow -348 - (3(-68) + 2(-94)) \Rightarrow 44 \text{ kcal}$$

by adding equation (1) and (2)



$$\Delta H = +66 - 44 = 22 \text{ kcal}$$

$$\Delta E = 21.408 \text{ kcal/mol.}$$

22. (d)  $\Delta H_f = \Delta H_s + I.E + \frac{\Delta H_d}{2} + E.A + L$

$$L = -388.6 - 81.2 - \frac{243}{2} - 375.7 + 348.3$$

$$L = -618.7 \text{ kJ/mol.}$$

23. (a) Enthalpy of neutralization is the energy released when one equivalent of acid reacts with one equivalent of base to produce salt and water as products

∴ from question:

$$-12250x - 13000(1-x) = -12500 \text{ cal/mol}$$

Let  $x$  be the HCl acid dissolved in weak base AOH

$$\therefore 750x - 13000 = -12500$$

$$x = \frac{500}{750} = \frac{2}{3}$$

$$(1-x) = \frac{1}{3}$$

Ratio of acid in AOH & BOH = 2:1

24. (b)  $40 \text{ g of NaOH} = \frac{40}{40} = 1 \text{ mol NaOH}$

$$60 \text{ g CH}_3\text{COOH} = \frac{60}{60} = 1 \text{ mol CH}_3\text{COOH}$$

Since acetic acid is a weak acid, some of the heat is utilised to ionize it. So, enthalpy of neutralisation of 1 mol of NaOH by 1 mol  $\text{CH}_3\text{COOH}$  is less than 57.1 kJ

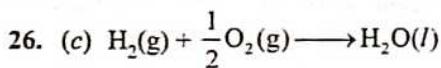
Enthalpy of neutralisation of a strong acid by a strong acid by a strong base is always 57.1 kJ

25. (b) HCN is a weaker acid than  $\text{CH}_3\text{COOH}$  from  $\Delta H$  ionization value

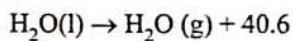
$$\text{pka} \propto \frac{1}{\text{Strength of acid}}$$

Since HCN is weaker acid

$$\therefore \text{pka}(\text{HCN}) > \text{pka}(\text{CH}_3\text{COOH})$$



$$\Delta_f H = -285.8 = -\frac{571.6}{2}$$



$$\therefore \text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) - 245.2 \text{ kJ/mol}$$

Let the average OH bond energy in  $\text{H}_2\text{O}$  be  $x$

$$\therefore -245.2 = (435 + 244.8) - (2x)$$

$$\Rightarrow 2x = 435 + 244.8 + 245.2$$

$$\Rightarrow x = \frac{925}{2} = 462.5 \text{ kJ/mol}$$

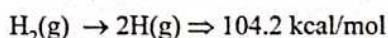
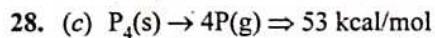
27. (b) When double bond of one molecule of  $\text{CH}_2 = \text{CH}_2$  breaks then addition of two  $-\text{CH}_2-$  groups takes place, that is two new single bonds are formed.

So, for each  $\text{C} = \text{C}$  two new  $\text{C}-\text{C}$  bonds are formed. Therefore, in the complete polymer of ethylene there are 2 single bonds per mole of ethylene.

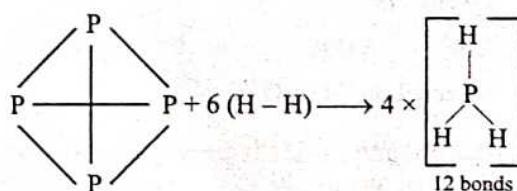
$$\Delta H \text{ polymerisation} = \Delta H_{(\text{CH}_2 = \text{CH}_2)} - 2\Delta H_{(-\text{CH}_2 - \text{CH}_2)}$$

$$2\Delta H_{(-\text{CH}_2 - \text{CH}_2)} = 600 - (-100) = 700 \text{ kJ mol}^{-1}$$

$$\Delta H_{(-\text{CH}_2 - \text{CH}_2)} = \frac{700}{2} = 350 \text{ kJ mol}^{-1}$$



In  $\text{P}_4(\text{s})$  6 bonds are present.



We know

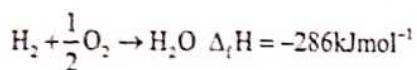
$$\Delta H_f(\text{reaction}) = \text{OH}(\text{reactant}) - \text{OH}(\text{product})$$

$$\Rightarrow 5.5 = (53.2 \times 6) + (104.2 \times 6) - 12x$$

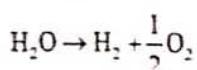
$$5.5 = 319.2 + 625.2 - 12x$$

$$x \approx 77$$

29. (c) Since formation reaction is the reaction involving formation of 1 mole of that species from its constituent elements while decomposition reaction is breaking down of 1 mole of any species into its constituent species. i.e. for water formation reaction :-



Decomposition reaction:-



Hence the formation reaction and decomposition reaction are reverse reaction of each other.

Hence, enthalpy of decomposition reaction will be negative of enthalpy of formation reaction:-

$$\Delta H_d(\text{H}_2\text{O}) = -\Delta H_f(\text{H}_2\text{O}) = -(286) = 286 \text{ kJ/mol}$$

30. (d)  $\text{P}_{(\text{yellow})} \rightarrow \text{P}_{(\text{Red})}$

$\Delta H = \text{heat of combustion of } \text{P}_{(\text{yellow})} - \text{heat of combustion of } \text{P}_{(\text{Red})}$

$$\Rightarrow -9.91 \text{ kJ} - (-8.78 \text{ kJ})$$

$$\Rightarrow -1.13 \text{ kJ}$$

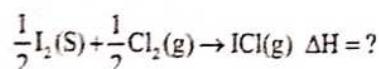
31. (c)  $\text{Cl}_2(g) \rightarrow 2\text{Cl}(g) \quad \Delta H_1 = 243.3 \text{ kJ/mol}$

$$\text{I}_2(g) \rightarrow 2\text{I}(g) \quad \Delta H_2 = 151 \text{ kJ/mol}$$

$$\text{ICl}(g) \rightarrow \text{I}(g) + \text{Cl}(g) \quad \Delta H_3 = 211.3 \text{ kJ/mol}$$

$$\text{I}_2(g) \rightarrow \text{I}_2(g) \quad \Delta H_4 = 62.8 \text{ kJ/mol}$$

Required equation :



$$\Delta H = \frac{62.8 + 151 + 242.3}{2} - 211.3$$

$$\Delta H = 16.75 \text{ kJ/mol.}$$

32. (a)  $\frac{1}{2}\text{x}_2 + \frac{3}{2}\text{y}_2 \rightleftharpoons \text{xy}_3 \quad \Delta H = 30 \text{ kJ}$

$$S_{x_2} = 60 \quad S_{y_2} = 40 \quad S_{xy_3} = 50$$

$$\therefore \Delta S_{rxn} = 50 - \frac{2}{2} \times 40 - \frac{1}{2} \times 60$$

$$\Rightarrow 50 - 60 - 30$$

$$\Delta S_{rxn} = -40 \text{ J/K}$$

at equation,  $\Delta G = 0$

$$\Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{40} = 750 \text{ K}$$

33. (d)  $\Delta H = 30.558 \text{ kJ/mol} \quad \Delta S = 0.066 \text{ kJ/K mol}^{-1}$

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

$$\Delta G = \Delta H - T\Delta S$$

$$0 = 30.558 - 0.066 \times T$$

$$T = \frac{30.558}{0.066}$$

$$\therefore T = 463 \text{ K} \Rightarrow$$

as temperature decreases  $\Delta G$  becomes positive which means that reaction becomes Non-spontaneous.

34. (b) As we know that melting of ice below 273K is a non-spontaneous process and the value of  $\Delta G$  for a non-spontaneous process is greater than 0.

Hence  $\Delta G > 0$ .

35. (c) A better gas welder is one which possesses high calorific value i.e., heat produced by 1g of Fuel.

Calorific value for ethane:-

$$\left( \frac{341.1}{30} \right) = 11.37 \text{ kcal/g (mol wt. = 30)}$$

Calorific value for ethyne:-

$$\left( \frac{310}{26} \right) = 11.92 \text{ kcal/g (mol wt = 26)}$$

Thus ethyne is better gas welder.

36. (c) 1 L of each rise in temperature  $3^\circ\text{C}$ .

37. (d)  $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)} \quad \Delta H = -110 \text{ kJ}$  Exothermic Reaction

- $\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO} + \text{H}_2(\text{g}) \quad \Delta H = 132 \text{ kJ}$  Endothermic Reaction

Total heat Evolved I = Total heat Evolved in II

$$n_1 \times 110 = n_2 \times 132$$

$$\therefore \frac{n_1}{n_2} = \frac{132}{110} = 1.2$$

$$\frac{n_1}{n_2} \approx 1 = \frac{1}{1}$$

38. (d) Rise in temperature will be highest if the extent of neutralization reaction is higher due to which the heat evolved will be greater in quantity

$g \text{ eq} = \text{eq} = \text{volume} \times \text{normality}$

normality = molarity  $\times$  n-factor

$g \text{ eq of acid} = g \text{ eq of base}$

$$V \times 0.5 \times 2 = (100 - V) \times 1 \times 1$$

$$V = 100 - V$$

$$2V = 100$$

$$V = 50$$

$$\therefore \text{Volume of H}_2\text{SO}_4 = V = 50 \text{ ml.}$$

$$\text{Volume of KOH} = 100 - V = 100 - 50 = 50 \text{ ml.}$$

$$50:50$$



39. (c)  $\Delta_r G^\circ = \sum \Delta_f G^\circ (\text{product}) - \sum \Delta_f G^\circ (\text{reactants})$   
 $\Rightarrow 2(\Delta_f G^\circ)_{\text{eff}} - 0$   
 $\Rightarrow 2 \times 1.3 \text{ kJ mol}^{-1} = 2.6 \text{ kJ mol}^{-1}$

40. (c) For cyclic process :  $\Delta U = 0 \Rightarrow q = -W$   
 Isothermal process:  $\Delta U = 0 \Rightarrow q = -W$   
 Adiabatic process:  $q = 0 \Rightarrow \Delta U = -W$   
 Isochoric process:  $q = 0 \Rightarrow \Delta U = q$   
 In Adiabatic process  $q = 0 \neq \Delta E$

### Exercise-3 (JEE Advanced Level)

1. (a,b,d)

Color, kinetic energy per mole and specific volume are intensive properties because it does not depend on mass.

2. (a,b,c)

The boundary may be real or imaginary which is separated to the system and surrounding perfectly isolated system can't be achieved. In reversible steps energy change in each step can be reversed.

3. (b,d)

$$W_{\text{irr}} > W_{\text{rev}}$$

$$\Delta E_{\text{rev}} = \Delta E_{\text{irr}} \text{ (Because } \Delta E \text{ is a state function)}$$

4. (a,b,c)

The isothermal expansion means a gas is expanding from initial volume to final volume at constant temperature. The internal energy and enthalpy depend upon the temperature only in case of ideal gas.

5. (b,c,d)

For adiabatic process,  $PV^\gamma = \text{constant}$

$$\frac{dP}{dV} = -\gamma \frac{P}{V}$$

From graph, slope (B) > slope (A)

$$\gamma_B > \gamma_A$$

For mono-atomic gas,  $\gamma = 1.67$  (He, Ar)

For diatomic and linear polyatomic gas,  $\gamma = 1.4$  ( $H_2$ ,  $N_2$  and  $CO_2$ )

For non-linear polyatomic,  $\gamma = 1.33$

6. (b,d)  $PV^\gamma = \text{constant}$  (for reversible adiabatic process)

$$\Delta H = C_p \Delta T$$

$\Delta T$  changes enthalpy changes.

7. (a,b,c,d)

Sublimation of a solid requires heat, it means system is absorbed heat ( $q > 0$ ). At low temperatures internal energy increases while at high temperature internal energy decreases.  $\Delta H > 0$

8. (b,d) Entropy is a measure of the disorder or randomness of the system. The greater the randomness in a system, greater is its entropy. The randomness is greater in liquid state as compared to solid state So the entropy increases when ice melts into water. Similarly, in vaporization of Camphor, it converts from solid to gas which increases randomness or entropy.

9. (a,b) Whenever a substance is transforming from a liquid state to a solid state, the change in enthalpy ( $\Delta H$ ) is negative. This process is commonly known as the freezing and results in the molecules within the substance becoming more ordered. In Other words randomness decreases.

10. (a,b,d)

Molar entropy is greater for heavier gas under identical conditions.

11. (a,b,d)

In adiabatic process, no heat exchange between the system and the surrounding.

$$\therefore \Delta S_{\text{surr}} = 0$$

For adiabatic reversible process,  $\Delta S_{\text{univ}} = 0$

$$\Delta S_{\text{sys.}} + \Delta S_{\text{surr}} = 0$$

$$\Rightarrow \Delta S_{\text{sys.}} = 0$$

$\therefore$  isoentropic process

For irreversible adiabatic compression,  $(\Delta S_{\text{sys.}})_{\text{rev.}} > 0$

For irreversible isothermal compression,

$$\Delta S_{\text{surr}} = \frac{-Q_{\text{irr}}}{T} > 0$$

12. (a,b,c)

The normal boiling point of a liquid X is 400K. At boiling point temperature equilibrium exist between liquid to vapor.

Thus,  $\Delta G = 0$

At 400K and 2 atm pressure, the liquid does not boil so that process is non-spontaneous and hence,  $\Delta G = +ve$ .

At 400K and 0.1 atm pressure, the liquid boil spontaneously and thus  $\Delta G = -ve$ .

13. (a,b,c,d)

For an isothermal expansion of ideal gas.

Isothermal means temperature is constant during whole process

$$\Delta H = 0$$

$$\Delta E = 0$$

$$\Delta G = \Delta H - T\Delta S$$

$$= 0 - T\Delta S$$

$$\Delta G = T\Delta S$$

14. (b,c,d)

Electrolysis of water is the decomposition of water ( $H_2O$ ) into oxygen ( $O_2$ ) and hydrogen ( $H_2$ ) due to an

electric current being passed through the water. Graphite is more stable than diamond. Hence, energy is required for graphite to convert into diamond. Dehydrogenation of ethane to ethylene is endothermic reaction because energy is required for removing hydrogen from ethane molecule.

15. (a,b,d)

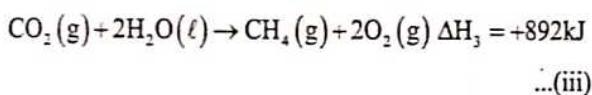
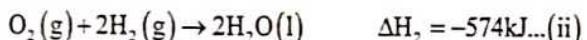
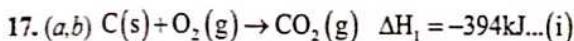
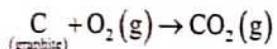
Heat of reaction depends on physical state of the reactants for example, some reactant may react only in certain physical state. Also heat may need to be supplied to change the state of state, like transforming it from liquid to gas.

Since, enthalpy is also a state function so the final product are obtained from reactant according to Kirchoff's law,  $\Delta H_2 = \Delta H_1 + C_p \Delta T$ . Kirchoff's law describes the enthalpy of a reaction's variation with temperature changes.

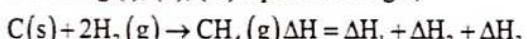
To study heat of reaction, whether the reaction is carried out at constant pressure or at constant volume, because heat is a path function, but when it is studied at constant pressure or volume it become state function.

16. (a,b,c)

The elemental form of carbon is graphite and diamond.



On adding (i), (ii), (iii) equations we get,

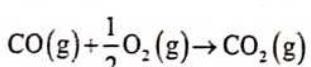
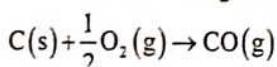


$$\begin{aligned} \Delta H &= -394 - 574 + 892 = -76 \text{ kJ} \\ &= -18.13 \text{ kcal.} \end{aligned}$$



19. (a,b,c)

The formation of  $CO_2$  is in two steps



$$\therefore H_f^\circ \neq \Delta H_{\text{reaction}}^\circ$$

Similarly for  $N_2O_3$  and  $CH_2Cl_2$  formation.

20. (b,c,d)

Molar heat of formation is the quantity of heat evolved or absorbed when one mole of substance is formed from its constituent elements under given conditions of temperature and pressure.

21. (a,b,c) Fact Based

22. (b) U is a state function so that  $\Delta U_{A \rightarrow B}$  is not depending on path.

$$\Delta U_{A \rightarrow B} = Q + W \quad (\text{1st law})$$

$$\Delta U_{A \rightarrow B} = (80 - 30) J = 50 J$$

$$\Delta U_{A \rightarrow B} = Q_{A \rightarrow D \rightarrow B} + W_{A \rightarrow D \rightarrow B}$$

$$50 J = Q_{ADB} + (-10 J)$$

$$Q_{ADB} = (60 J)$$

23. (a)  $\Delta U_{BA} = Q_{\text{curve}} + W$

$$-50 J = Q + (+20 J)$$

$Q = -70 J$ ; heat is liberated

24. (d)  $\Delta E_{A \rightarrow D} = Q + W$

$$-40 J = q_{AD} + (-10) \quad (\text{Given in question number 22})$$

$$q_{AD} = -30 J$$

$$25. (a) \Delta S = 2.303 n C_V \log \left( \frac{T_2}{T_1} \right) + 2.303 n R \log \left( \frac{V_2}{V_1} \right)$$

At same temperature,  $T_1 = T_2$

$$\Delta S = 2.303 \times 2 \text{ mol} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \log (50/5)$$

$$\Delta S = 38.23 \text{ JK}^{-1}$$

26. (b) Isobaric process,  $P_1 = P_2$

$$\Delta S = 2.303 n C_p \left( \frac{T_2}{T_1} \right)$$

$$23.03 \text{ JK}^{-1} = 2.303 \times 1 \text{ mol} \times C_p \log \left( \frac{600}{300} \right)$$

$$10 \text{ JK}^{-1} = 1 \text{ mol} \times C_p \times \log 2$$

$$C_p = \frac{10}{\log 2} \text{ JK}^{-1} \text{ mol}^{-1}$$

$$C_p - C_v = R$$

$$\frac{10}{\log 2} - C_v = R \Rightarrow C_v = -R + \frac{10}{\log 2}$$

27. (d)  $\Delta G = -ve$  (For spontaneous process)

$$\Delta H - T\Delta S < 0$$

$$30 \text{ kJ} - T \times 0.07 < 0$$

$$30 < T \times 0.07$$

$$T > \frac{30}{7} \times 100 \Rightarrow T > 428.6 \text{ K}$$

For non-spontaneous  $\Rightarrow T < 428.6 \text{ K}$ .

28. (b)  $CaCO_3 \xrightarrow{\Delta} CaO(s) + CO_2(g)$

$$\Delta G = \Delta H - T\Delta S$$

Heat is supplied to  $CaCO_3$  for decomposition into  $CaO$  and  $CO_2$ . Therefore, it is endothermic in nature.

Entropy also increases, therefore,  $\Delta S = +ve$  (small)

At high temperature  $T\Delta S$  term overweigh and it become more  $-ve$  so that  $\Delta G = -ve$  at high temperature.

29. (a)  $\Delta G = \Delta H - T\Delta S$

$$\Delta G = 2.1 \times 1000 - 298 \times 20$$

$$= 2100 - 5560 = -ve$$

Spontaneous

30. (c)  $\Delta G = \Delta H - T\Delta S < 0$

$$100 - T \times 0.05 < 0$$

$$100 < T \times 0.05$$

$$T > \frac{100}{0.05}$$

$$T > 2000 \text{ K.}$$

31. (d)  $\Delta G = \Delta H - T\Delta S$

$$0 = -40 \times 1000 - 400 \Delta S$$

$$-40000 = 400 \Delta S$$

$$\Delta S = -100 \text{ cal K}^{-1}$$

32. (a)  $\Delta G = \Delta H - T\Delta S$

$$= -15 \times 1000 + 300 \times 7.2$$

$$= -12.84 \text{ kcal mol}^{-1}$$

= -ve.

Spontaneous

33. (a)  $\Delta H^\circ_{\text{neu}} = \Delta H^\circ_{\text{ion}} + \Delta_r H^\circ$

$$-49.86 \text{ kJ mol}^{-1} = \Delta H^\circ_{\text{ion}} + (-55.84 \text{ kJ mol}^{-1})$$

$$\Delta H^\circ_{\text{ion}} = +5.98 \text{ kJ mol}^{-1}$$

34. (b) Diacidic base produce twice  $\text{OH}^-$  ions

$$\Delta H^\circ = 2 \times (-55.84 \text{ kJ mol}^{-1})$$

$$= -111.68 \text{ kJ}$$

35. (b)  $\text{NaOH} \rightarrow V_1$  volume (mL)

$$\text{H}_2\text{A} \rightarrow V_2$$
 volume (mL)

At complete neutralization,  $(\text{meq})_{\text{Acid}} = (\text{meq})_{\text{Base}}$

$$2 \times 0.05 V_2 = 0.1 \times V_1$$

$$\frac{V_1}{V_2} = 1$$

$$V_1 + V_2 = 100$$

$$2V_1 = 100$$

$$V_1 = 50$$

$$V_2 = 50$$

$$V_1 : V_2 = 50 : 50$$

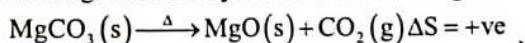
36. (a) Reversible isothermal expansion of an ideal gas work done,  $W = -2.303 nRT \log \left( \frac{V_2}{V_1} \right)$

$\Delta H = 0$  (for ideal gas) in case of reversible isothermal expansion.

37. (b) A process carried out infinitesimally slowly, then process is known as reversible.

38. (c)  $(\Delta G)_{T,P} \leq 0 \Rightarrow$  process is in equilibrium when it is equal to zero and spontaneous when it is negative. Therefore,  $\Delta G \leq 0$ , system is unable to do useful work.

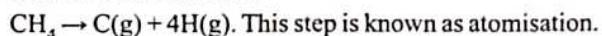
39. (a) Reversible adiabatic,  $\Delta S_{\text{surr}} = 0$  because there is no heat exchange between system and surrounding.



$$\Delta S_{\text{surr}} < 0$$

$$\Delta S_{\text{sys.}} > 0$$

40. (d)  $\text{C(s, graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ , this step is known as combustion, formation.



41. Faced Based

42. [7] Extensive property are those properties which depends on mass.

Free energy → extensive.

Vapour pressure → Intensive

Mole → extensive.

Kinetic energy → extensive

Entropy → extensive

Internal energy → extensive

Enthalpy → extensive

Specific heat capacity → Intensive

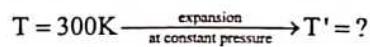
n → intensive

Total heat capacity → extensive

43. [8] Work and heat are path functions others are state functions.

$$\therefore 8$$

44. (c)  $n = 2 \quad n = 2$



$$V = 20 \text{ L} \quad V' = 40 \text{ L}$$

$$P = \frac{nRT}{V} \quad P = \frac{nRT'}{V'}$$

$$\frac{300}{20} = \frac{T'}{40}$$

$$T' = 600 \text{ K}$$

$$T' = 600\text{K} \xrightarrow[\text{adiabatic expansion}]{\text{Reversible}} T'' = ? \text{ (final temperature)}$$

$$V' = 40 \text{ L} \quad V'' = 110 \text{ L}$$

$$TV^{\gamma-1} = \text{constant}$$

$$600 \times (40)^{\gamma-1} = T (110)^{\gamma-1} \quad (\because T' = T)$$

$$6 \times \left( \frac{40}{110} \right)^{\gamma-1} = \frac{T}{100}$$

$$\Rightarrow \frac{T}{100} = 3$$

45. [-4] For reversible process,  $\int dW = -p \int_{V_i}^{V_f} dV$

$$W = -k \int_{V_i}^{V_f} V^3 dV$$

$$= -\frac{k}{4} [V_2^4 - V_1^4]$$

$$= -\frac{1}{5 \times 4} (3^4 - 1^4)$$

$$= \frac{-1}{5 \times 4} (3^4 - 1^4)$$

$$= -4 \text{ L atm}$$

46. [14] Work is done by the system during expansion.

$$W = -2.303 nRT \log\left(\frac{P_1}{P_2}\right)$$

$$= -2.303 P_1 V_1 \log\left(\frac{P_1}{P_2}\right)$$

$$= -2.303 \times 7 \times 1 \log\left(\frac{7}{1}\right)$$

$$= -13.6 \text{ L-atm}$$

∴ work is done on atmosphere = + 13.6 L atm

47. [10] 1<sup>st</sup> law  $\Delta U = Q + W$

$$60 \text{ J} = + 50 \text{ J} + W$$

$$W = 10 \text{ J}$$

48. [24] Heat absorbs = 20 Ca =  $20 \times 4.2 \text{ J} = 84 \text{ J}$

$$\text{Heat reject} = 60 \text{ J}$$

$$\text{Work done} = (84 - 60) = 24 \text{ J}$$

49. [80] Work done in an adiabatic compression,

$$W = nCv(T_2 - T_1)$$

$$W = 2 \text{ mol} \times \frac{3R}{2}(T_2 - 30 \text{ K})$$

$$W = 8.314(T_2 - 30) \text{ J}$$

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma$$

$$1^{1-\gamma} \cdot (30)^\gamma = 2^{1-\gamma} \cdot T_2^\gamma$$

$$(30)^\lambda = 2^{1-\gamma} \cdot T_2^\gamma$$

$$\frac{60^\gamma}{2} = T_2^\gamma$$

$$T_2 = 39.6 \text{ K}$$

$$W = 8.314(39.6 - 30) \text{ J}$$

$$= 8.314 \times 9.6$$

$$= 79.9 \text{ J}$$

50. Fact Based

51. [43]  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= -29.8 - 298(-0.1)$$

$$= -29.8 - 29.8$$

$$= -59.6 \times 1000$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$-59600 = -2 \times 298 \times 2.303 \times \log_{10} K_{eq}$$

$$\log_{10} K_{eq} = 43.42$$

52. Fact Based

53. [8]  $A + 3B \rightarrow 2C$

$$\Delta H^\circ_{rxn} = 2 \times (-10) - 3(0) - 3(0) = -20 \times 1000$$

$$\Delta S^\circ_{rxn} = 2 \times (45) - 3(30) - 40 = -40$$

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$$

$$= -20000 - 300(-40) = -8000 = -8 \text{ kcal}$$

54. [8]  $H_2(g) \rightarrow 2H(g)$

$$\Delta S^\circ_{rxn} = 2 \times 50 - 60 = 40 \text{ JK}^{-1}$$

$$\Delta G^\circ_{rxn} = 21.6 \times 1000 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - 300 \times 40$$

$$21600 = \Delta H^\circ - 300 \times 40$$

$$\Delta H^\circ = 21600 + 12000$$

$$= 33600 \text{ J mol}^{-1}$$

$$= 33.6 \text{ kJ mol}^{-1}$$

$$= 8 \text{ kCa mol}$$

55. [-50]  $X \rightleftharpoons{} Y$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = 25 \text{ kJ}$$

$$40.2 = 25 - 300 \times \Delta S^\circ$$

$$\Delta G^\circ = -RT \times 2.303 \log_{10} K_{eq} \quad \Delta S^\circ = -50.67 \text{ kJ}$$

$$= -8.314 \times 300 \times 2.303 \times \log_{10} 10^{-7}$$

$$= 40.2 \text{ kJ}$$

56. [40] At equilibrium,  $\Delta G = 0$

$$\Delta G = \Delta H - T\Delta S$$

$$0 = -30 \times 1000 - 750 \times \Delta S$$

$$\Delta S = -\frac{30,000}{750} = -40$$

$$S_{NH_3} - \frac{1}{2}S_{N_2} - \frac{3}{2}S_{H_2} = -40$$

$$50 - \frac{1}{2} \times 60 - \frac{3}{2}S_{H_2} = -40$$

$$20 - \frac{3}{2}S_{H_2} = -40$$

$$-\frac{3}{2}S_{H_2} = -60$$

$$S_{H_2} = 40$$

57. [9]  $C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O \quad \Delta H^\circ_1 = -3920$

$$C_6H_{10} + \frac{17}{2}O_2 + 6CO_2 + 5H_2O \quad \Delta H_2O = -3717$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H_3^\circ = -241$$

$$\Delta H^\circ_{Hydrogen} = \Delta H^\circ_2 + \Delta H_3^\circ - \Delta H_1^\circ = -3717 - 241 + 3920$$

$$= -38 \text{ kJ mol}^{-1}$$

$$= -9 \text{ kcal mol}^{-1}$$

58. [3] moles of glucose,  $n = \frac{0.36g}{180g \text{ mol}^{-1}} = 0.002 \text{ moles}$

$$= \frac{600 \times 10}{0.002} = 3 \times 10^6 \text{ J/mol}$$

$$= 3 \text{ MJ/mol}$$

59. Fact Based

60. [-86]  $\Delta_f H^\circ = \Delta_{sub} H^\circ + \frac{1}{2} \Delta_{diss} H^\circ + \Delta_i H^\circ + \Delta_{eg} H^\circ + \Delta_{lattice} H^\circ$

$$= 137 + \frac{1}{2} \times 144 + 496 + (-325) + (-742)$$

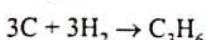
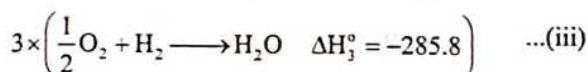
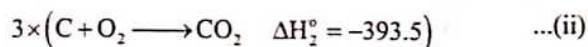
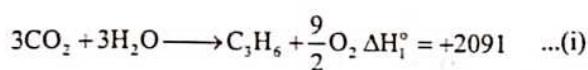
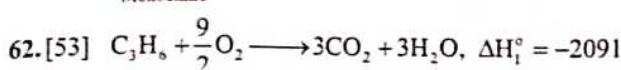
$$= -362 \text{ kJ mol}^{-1}$$

$$= -86 \text{ kcal mol}^{-1}$$



61. [8] Standard enthalpy of formation is zero for all elements in their standard states.

$\text{Br}_2(l)$ , C(graphite),  $\text{Cl}_2(g)$ ,  $\text{F}_2(g)$ ,  $\text{N}_2(g)$ ,  $P_{\text{Black}}$ ,  $P_{\text{red}}$ ,  $S_{\text{Monoclinic}}$



$$\Delta H_4^\circ = \Delta H_1^\circ + 3\Delta H_2^\circ + 3\Delta H_3^\circ$$

$$\Delta H_4^\circ = 53.1 \text{ kJ mol}^{-1}$$

63. [-87]  $\Delta H = \Delta U + P\Delta V$

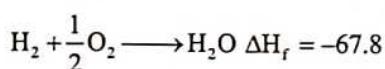
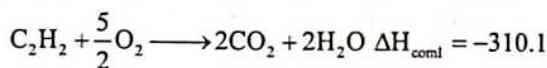
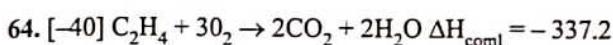
$$-92 = \Delta U + 40 \text{ bar} \times (-1.25) \text{ L}$$

$$-92 \text{ kJ} = \Delta U + (-50 \text{ L-bar})$$

$$-92 \text{ kJ} = \Delta U - 50 \times 101.26 \text{ J}$$

$$\Delta U = (-92 + 5.06) \text{ kJ}$$

$$\Delta U = -87 \text{ kJ}$$



$$\Delta H_{\text{Hydr}} = \Delta H_{\text{coml}}^1 + \Delta H_f - \Delta H_{\text{comf}} = -310.1 + (-67.8) + 337.2$$

$$\Delta H_{\text{Hyd}} = -40.7 \text{ kcal mol}^{-1}$$

$$\Delta H = \Delta U + P\Delta V$$

$$-40.7 = \Delta U + \Delta n g RT$$

$$-40.7 = \Delta U + (-1) \times 2 \times \frac{350}{1000}$$

$$\Delta U = -40.7 \text{ Cal mol}^{-1}$$

65. [78]  $-20 + 6 \times 99 + (\text{C} - \text{C})$  bond enthalpy =  $170 \times 2 + 6 \times 52$

$$(\text{C} - \text{C}) = 78 \text{ kcal}$$

66. [99.5]  $\Delta H = \Delta U + \Delta(PV)$

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1 \quad \dots(i)$$

$$P_1 = 1 \text{ atm} \quad P_2 = 1001 \text{ atm}$$

$$V_1 = 1 \text{ L} \quad V_2 = 0.99 \text{ L}$$

$$\text{Let } P = a + bV$$

$$\text{On finding } a = 100001, b = -10^5$$

$$W = - \int_{V_1}^{V_2} (100001 - 10^5 V) dV$$

$$W = 501 \text{ J}$$

$$\Delta U = W = 501 \text{ J}$$

In eqn (1) by using  $\Delta U = 501 \text{ J}$

$$\Delta U = 501 + (1001 \times 0.99 - 1 \times 1) \times 100$$

$$= 995005$$

$$\Delta H = 99.5 \text{ kJ}$$

67. [100]  $\Delta H = \Delta U + P\Delta V$

$$|\Delta H - \Delta U| = P\Delta V$$

$$|\Delta H - \Delta U| = P|V_{\text{graphite}} - V_{\text{diamond}}|$$

$$= 500 \times 10^3 \text{ bar} \left| \frac{12 \text{ g mol}^{-1}}{2 \text{ g cm}^{-3}} + \frac{12 \text{ g mol}^{-1}}{3 \text{ g cm}^{-3}} \right|$$

$$= 500 \times 10^3 \text{ bar} \times 2 \times 10^{-3} \text{ L mol}^{-1} = 1000 \text{ L bar mol}^{-1}$$

$$= 100 \text{ kJ mol}^{-1}$$

$$(\because 1 \text{ L bar} = 100 \text{ J})$$

68. [-1200] for adiabatic reversible process,  $T^Y P^{1-Y} = \text{constant}$

$$T_2 = T_1 \left( \frac{P_1}{P_2} \right)^{\left( \frac{1-4}{4} \right)} = 600 \text{ K}$$

$$W_1 = W_{\text{rev}} = nC_v(T_2 - T_1) = 2 \times \frac{3}{2} R \times 300$$

$$W_1 = 900R$$

$$W_2 = -2.303nRT \log \frac{P_1}{P_2} = -2 \times R \times 600 \times \ln \left( \frac{4\sqrt{2}}{1} \right)$$

$$W_2 = 600R$$

$$W_3 = -P\Delta V = -nRT = -\left( 200R \times \frac{5}{2} \times 0.7 \right)$$

$$W_3 = -2100R$$

$$W_{\text{Total}} = 900R - 2100R + 600R$$

$$= -600R = -1200 \text{ Cal}$$

69. [1020] In 1<sup>st</sup> Case,  $W_1 = -P\Delta V = -P - 0$  ( $\because \Delta V = 0$ )

$$W_1 = 0$$

$$\text{In 2<sup>nd</sup> Case, } W_2 = -2.303nRT \log \frac{P_1}{P_2}$$

$$P_1 = \frac{2 \times 300}{V_1}$$

$$P_2 = \frac{P_1 \times T_2}{T_1} = \frac{12000}{V_1}$$

$$W_2 = -2.303 \times 1 \times 2 \times 300 \times \log \left( \frac{1}{2} \right) = +420$$

$$\text{In 3rd case, } W_3 = -P_2 \times \Delta V$$

$$= -\left( \frac{1200}{V_1} \times \frac{V_1}{2} \right) = 600 \text{ cal}$$

$$W_{\text{Total}} = W_1 + W_2 + W_3$$

$$= 0 + 420 + 600$$

$$= 1.02 \text{ k Cal}$$



70. [32] For reversibly adiabatic process

$$TV^{\gamma-1} = \text{constant}$$

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

$$\frac{(u_{\text{rms}})_1}{(u_{\text{rms}})_2} = \sqrt{\frac{T_1}{T_2}} = \left( \frac{V_2}{V_1} \right)^{\frac{\gamma-1}{2}} = \left( \frac{V_2}{V_1} \right)^{\frac{7-1}{2}} = 2^5 = 32$$

$$71. [-2880] f_{\text{av}} = \frac{f_A n_A + f_B n_B}{n_A + n_B} = \frac{1 \times 6 + 2 \times 3}{1 + 2} = 4$$

$$\gamma_{\text{avg}} = 1 + \frac{2}{f_{\text{avg}}} = 1 + \frac{2}{4} = \frac{3}{2}$$

$$TV^{\gamma_{\text{avg}}-1} = \text{constant}$$

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\frac{\gamma-1}{2}} = 320 \left( \frac{1}{4} \right)^{\frac{1}{2}}$$

$$T_2 = 160 \text{ K}$$

$$\Delta U = n_T C_V \Delta T$$

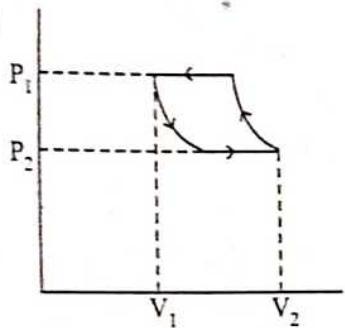
$$= 3 \times 2R \times (160 - 320)$$

$$= -960 \text{ J}$$

$$\Delta H = n_T C_P \Delta T$$

$$= 3 \times 3R \times (-160) = -2880 \text{ Cal}$$

72. [14]



$$W_{\text{net}} = P_2(V_2 - V_1) \ln \left( \frac{P_1}{P_2} \right)$$

$$= P_2(8 - 1)$$

$$= 2 \times 7 \text{ L-bar}$$

$$= 14 \text{ L-bar}$$

73. [20]  $\Delta G = -RT \ln K$

$$\Delta G_{300} = -8.314 \times 300 \times \ln 2 = -1746 \text{ J mol}^{-1}$$

$$\Delta G_{400} = -8.314 \times 400 \times \ln 8 = -6983 \text{ J mol}^{-1}$$

$$-1746 = \Delta H - 300 \Delta S \quad \dots(i)$$

$$-6983 = \Delta H - 373 \times \Delta S \quad \dots(ii)$$

$$\text{from (i) \& (ii), } \Delta S = \frac{\Delta H + 1746}{300}$$

$$-6983 = \Delta H - \frac{373}{300}(\Delta H + 1746)$$

$$\Delta H = 20 \text{ kJ mol}^{-1}$$

$$74. [16] \Delta S_{\text{system}} = nR \ln \left( \frac{P_1}{P_2} \right)$$

$$= 10 \times 8.314 \times \ln \left( \frac{2}{1} \right) = 56$$

$$\Delta S_{\text{surf}} = \frac{-Q}{T}$$

$$\Delta U = Q + W$$

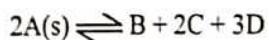
$$W = -P_{\text{ext}}(V_2 - V_1)$$

$$q = -W = nRTP_{\text{ext}} \left( \frac{1}{P_2} - \frac{1}{P_1} \right)$$

$$q = 10 \times 8 \times T \left( 1 - \frac{1}{2} \right) \Rightarrow \frac{-Q}{T} = -40$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surf}} = 56 - 40 = 16 \text{ J}$$

75. [-17.8]



$$\text{At equilibrium } (1 - 2x) \quad x \quad 2x \quad 3x$$

$$K_p = P_B^1 \cdot P_C^2 \cdot P_D^3$$

$$= (2)^1 \cdot (4)^2 \cdot (6)^3$$

$$= 32 \times 216$$

$$= 6912$$

$$\Delta G^\circ = -RT \ln K_p = -2 \times 1000 \times \ln 6912 = -17.68 \text{ kcal}$$

$$76. [10] dS = n \bar{C}_p \frac{dT}{T}$$

$$\Delta S = 1 \times \int_{300}^{600} (10 + 10^{-2}T) \frac{dT}{T}$$

$$= 10 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$77. [5] \Delta H_{\text{rxn}} = 2\Delta H_A + \Delta H_B - 3\Delta H_C$$

$$= 2 \times (-100) + (-60) - 3(-285)]$$

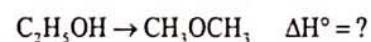
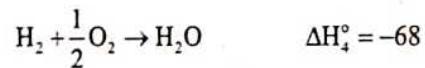
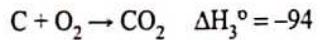
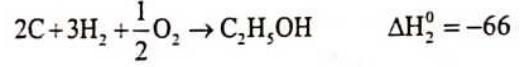
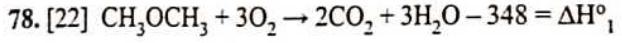
$$= 595 \text{ kJ mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

$$= 595 - 300 \times 2$$

$$= -5 \text{ kJ mol}^{-1}$$

$$|\Delta G| = 5 \text{ kJ mol}^{-1}$$



$$\Delta H^\circ = -\Delta H_2^\circ - \Delta H_1^\circ + 2\Delta H_3^\circ + 3\Delta H_4^\circ$$

$$= -(-66) - (-348) + 2 \times (-94) + 3 \times (-68)$$

$$= 22 \text{ kcal mol}^{-1}$$



79. [461]  $\Delta H_{r,n} = 2 \times \Delta_f H^\circ [\text{H(g)}] + \Delta_f H^\circ [\text{O(g)}] - \Delta_f H^\circ [\text{H}_2\text{O(g)}]$   
 $= (2 \times 218 + 249.2 + 241.8) \text{ kJ mol}^{-1}$   
 $= 927 \text{ kJ mol}^{-1}$

Average bond enthalpy of OH =  $\frac{\Delta H_{r,m}}{2} = \frac{927}{2}$   
 $= 463.5 \text{ kJ mol}^{-1}$

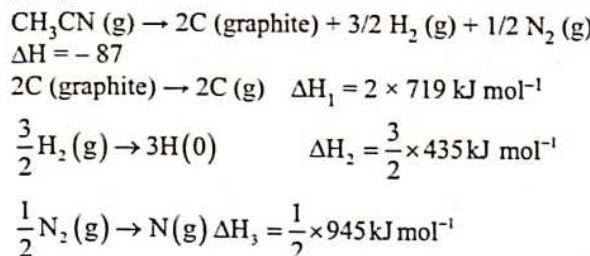
$U = H - nRT$   
 $= 463.5 - \left( \frac{1 \times 8.314 \times 298}{1000} \right)$

$U = 461 \text{ kJ mol}^{-1}$ .

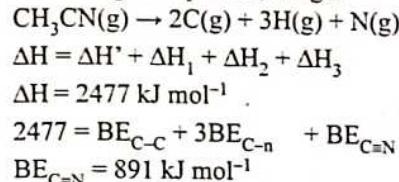
80. (i) [342]

$$\begin{aligned} 2\text{C(s)} + 3\text{H}_2\text{(g)} &\rightarrow \text{C}_2\text{H}_6\text{(g)} \quad \Delta_f H^\circ = -83 \text{ kJ mol}^{-1} \\ 2 \times (\text{C(s)} \rightarrow \text{C(g)}) \quad (\Delta_{\text{sub}} H^\circ = 719 \text{ kJ mol}^{-1}) \times 2 \\ 3 \times (\text{H}_2\text{(g)} \rightarrow 2\text{H(g)}) \quad (\Delta_{\text{diss}} H^\circ = 435 \text{ kJ mol}^{-1}) \times 3 \\ \text{Adding (2), (3) equation and subtract from (i) equation.} \\ 2\text{C(g)} + 6\text{H(g)} &\rightarrow \text{C}_2\text{H}_6\text{(g)} \quad \Delta H = -2826 \text{ kJ mol}^{-1} \\ \Delta H = 0 - (6(Eh) + (C-C)) \\ -2826 = -6 \times 414 + -(C-C) \\ -(C-C) = -342 \\ \text{BE (C-C)} = 342 \text{ kJ mol}^{-1} \end{aligned}$$

(ii) [891]



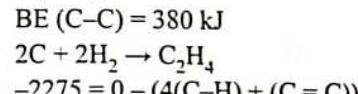
On adding all equation, we get



81. [26.5]  $2\text{C} + 3\text{H}_2 \rightarrow \text{C}_2\text{H}_6$

$$\begin{aligned} \Delta H_{\text{rxn}} &= +\Delta H_{\text{react}} + \Delta H_{\text{prod}} \\ -2840 &= 0 - (6(\text{C-H}) + 2(\text{C-C})) \\ -2840 &= -(410 \times 6 + 2 \times (\text{C-C})) \\ 2(\text{C-C}) &= -380 \end{aligned}$$

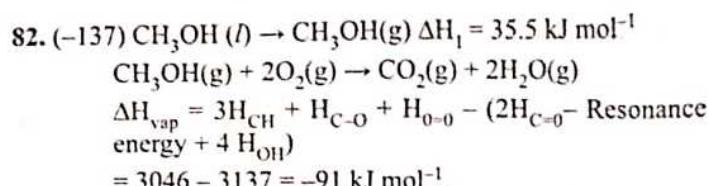
$\text{BE (C-C)} = 380 \text{ kJ}$



$\text{BE (C=C)} = 635 \text{ kJ}$

In benzene,  $= 6(\text{C-C}) + 3(\text{C=C}) + 6(\text{C-H})$   
 $= 6 \times 380 + 3 \times 635 + 6(410)$   
 $= 6645 \text{ kJ}$

Resonance energy = Actual – Theoretical  
 $= 6645 - 5530$   
 $= 1115 \text{ kJ mol}^{-1}$   
 $= 26.5 \text{ kCal mol}^{-1}$



Latent heat of vaporisation of water is  $40.6 \text{ kJ mol}^{-1}$   
 $2 \text{ moles of water, } \Delta H_3 = 2 \times 40.6 = 81.2 \text{ kJ mol}^{-1}$   
 $\Delta H = \Delta H_{\text{vap}} + \Delta H_2 + (-\Delta H_3)$   
 $= 35.5 - 91 - 81.2$   
 $= -136.7 \text{ kJ mol}^{-1}$ .  
 $\Delta H = -137 \text{ kJ mol}^{-1}$ .

## Exercise-4 (Past Year Questions)

### JEE MAIN

1. (d) As the heat is absorbed

$$\therefore q = +2085$$

Now for reversible isothermal process,  
 $q = -w$

$$\therefore w = -q = -2085$$

2. (a)  $\Delta E = -1364.47 \text{ kJ mol}^{-1}$

$$T = 298 \text{ K}, \Delta n_g = -1$$

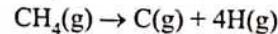
$$\because \Delta H = \Delta E + P\Delta V$$

$$\text{but } P\Delta V = \Delta n_g RT$$

$$\Delta H = -1364.47 + [(-1) \times 0.0083 \times 298]$$

$$\Delta H = -1366.95 \text{ kJ mol}^{-1}$$

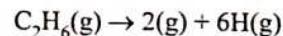
3. (b) For methane



$$\text{So, } 4 \times E_{\text{C-H}} = 360 \text{ kJ mol}$$

$$E_{\text{C-H}} = 90 \text{ kJ mol}$$

For ethane,



$$E_{\text{C-C}} + 6 \times E_{\text{C-H}} = 620 \text{ kJ/mol}$$

$$E_{\text{C-C}} = 80 \text{ kJ/mol}$$

$$\text{Therefore, } NA \frac{hc}{\lambda} = 80 \times 1000 \text{ J}$$

$$\lambda = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-34} \times 3 \times 10^8}{80000}$$

$$\lambda = 1.49 \times 10^3 \text{ nm}$$

4. (b)  $\underline{\Delta G}_{r,n}^\circ = -RT \ln k_p$  ... (i)

$$\Delta G_{r,n}^\circ = 2\Delta G_F^\circ(\text{NO}_2) - 2FG_F^\circ(\text{NO})$$
 ... (ii)

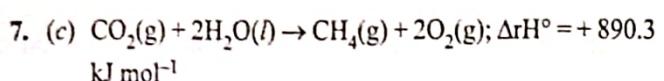
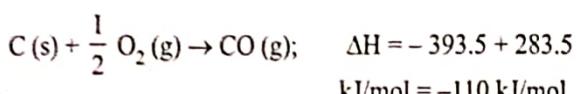
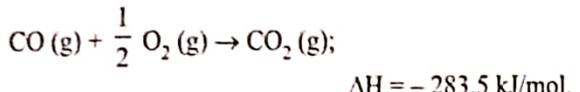
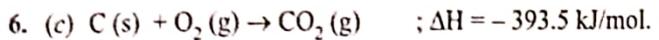
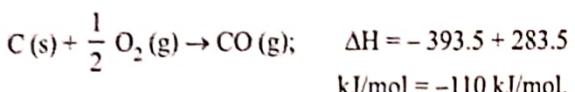
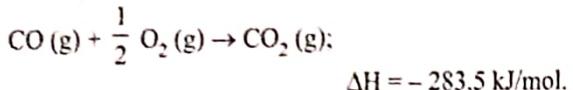
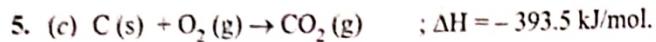
$$2\Delta G_F^\circ(\text{NO}_2) - 2\Delta G_F^\circ(\text{NO}) = -RT \ln k_p$$

$$\Delta G_F^\circ(\text{NO}_2) = 0.5 \times (2\Delta G_F^\circ(\text{NO}) - RT \ln k_p)$$

$$\Delta G_F^\circ(\text{NO}_2) = 0.5 \times (2\Delta G_F^\circ(\text{NO}) - RT \ln k_p)$$

$$\Delta G_F^\circ(\text{NO}_2) = 0.5 \times [2 \times 86600 - R(298) \ln 1.6 \times 10^{12}] \text{ J/mol}^{-1}$$





$$-393.5 - 285.8 \quad ? \quad 0$$

$$\Delta_r H^\circ = \sum (\Delta_f H^\circ)_{\text{Products}} - \sum (\Delta_f H^\circ)_{\text{Reactants}}$$

$$890.3 = [1 \times (\Delta_f H^\circ)_{CH_4} + 2 \times 0] - [1 \times (-393.5) + 2 \times (-285.8)]$$

$$(\Delta_f H^\circ)_{CH_4} = 890.3 - 965.1 = -74.8 \text{ kJ/mol}$$

8. (c) From 1st law :

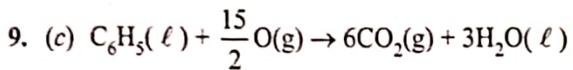
$$\Delta U = q + w$$

For adiabatic process:

$$q = 0$$

$$\therefore \Delta U = w$$

Work involve in adiabatic process is at the expense of change in internal energy of the system.



$$\Delta ng = 6 - \frac{15}{2} = -\frac{3}{2}$$

$$\Delta U = -3263.9 \text{ kJ mol.}$$

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

$$\Delta H = -3263.9 - \frac{3}{2} \times 8.314 \times 298$$

$$\Delta H = -3265.9 \text{ kJ/mol.}$$

10. (a)  $C_p$  does not changes with change in pressure

11. (c) (A)  $q + w = \Delta U = \text{state function}$

(B)  $Q \Rightarrow \text{path function}$

(C)  $H - TS = G \Rightarrow \text{state function}$

12. (c)  $q = P\Delta V$

$$q = 16$$

$$C_p = 24$$

$$C_p = \frac{q_p}{\Delta T} \Rightarrow \Delta T = \frac{16}{24} K = \frac{2}{3} K$$

13. (a)  $w = -nRT \ln \frac{V_2}{V_1}$

$$w = -nRT \ln \frac{V_b}{V_i}$$

$$|w| = nRT \ln \frac{V_b}{V_i}$$

$$|w| = nRT(\ln V_b - \ln V_i)$$

$$y = mx - c$$

Slope of curve 2 is more than curve 1 and intercept of curve 2 is more negative than curve.

14. (a) As  $PV = nRT$ , where  $n$  &  $T$  are constant

$$PV = k = nRT$$

isothermal expansion  $PVm = k$  (graph  $\rightarrow$  c)

$$P = \frac{k}{V_m} \rightarrow (\text{Graph A})$$

15. (c) In order to be spontaneous  $\Delta G^\circ$  should be  $-ve$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$0 = 491.1 \times 10^3 - T \times 198$$

$$T = \frac{491100}{198} = 2480$$

If temp is above 2480 K, the reaction will be spontaneous.

16. (a) At the thermal equilibrium,

$$\text{final temperature } T_f = \frac{T_1 + T_2}{2}$$

$$\Rightarrow \text{for the 1st block, } \Delta S_I = C_p \ln \frac{T_f}{T_1}$$

$$\Rightarrow \text{for the 2nd block, } \Delta S_{II} = C_p \ln \frac{T_f}{T_2}$$

When brought in contact with each other,

$$\Delta S = \Delta S_I + \Delta S_{II} = C_p \ln \frac{T_f}{T_1} + C_p \ln \frac{T_f}{T_2}$$

$$= C_p \ln \left( \frac{T_f}{T_1} \times \frac{T_f}{T_2} \right) = C_p \ln \left[ \frac{T_f^2}{T_1 T_2} \right]$$

$$= C_p \ln \left[ \frac{\left( \frac{T_1 + T_2}{2} \right)}{T_1 T_2} \right] = C_p \ln \left[ \frac{(T_1 + T_2)^2}{4 T_1 T_2} \right]$$

17. (a)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta G^\circ = A - BT$$

In endothermic reaction  $\Delta H = +ve$ . Hence,  $A = +ve$

18. (d)  $H_2O(s) \rightarrow H_2O(l) \rightarrow H_2O(l) \rightarrow H_2O(g) \rightarrow H_2O(g)$

$$1 \text{ kg} \quad 1 \text{ kg} \quad 1 \text{ kg}$$

at 273 K at 273 K at 373 K at 373 K at 383 K

$$\Delta s = \Delta s_1 + \Delta s_2 + \Delta s_3 + \Delta s_4$$

$$= \frac{334}{273} + 4.2 \ln \frac{373}{273} + \frac{2491}{373} + 2 \ln \frac{383}{373} = 9.267 \text{ kJ kg}^{-1} \text{ K}^{-1}$$



19. (c)  $\Delta G = \Delta H - T\Delta S < 0$

$$T = \frac{\Delta H}{\Delta H} = \frac{200}{40} = 5 \text{ K}$$

20. (d) Four moles of gas

$(N_2 + 3H_2) \rightarrow 2NH_3$  reacts to give only two moles of gas the hence entropy decreases.

21. (c)  $\Delta G^\circ = -2.303RT \log K_{eq}$   
 $= -2.303 \times 8.314 \times 298 \log 10^{-14}$   
 $= -2.303 \times 8.314 \times 298 \times -14$   
 $= 79,881.87$   
 $= 80 \text{ kJ mol}^{-1}$

22. (b)  $\Delta G = \Delta H - T\Delta S$

for spontaneous process at all temp.  $\Delta G < 0$  and it is possible when  $\Delta H < 0$  and  $\Delta S > 0$ .

23. (c) For cyclic process :  $\Delta U = 0 \Rightarrow q = -w$   
 For isothermal process :  $\Delta U = 0 \Rightarrow q = -w$   
 For adiabatic process :  $q = 0 \Rightarrow \Delta U = w$   
 For isochoric process :  $w = 0 \Rightarrow \Delta U = q$

24. (d)  $\Delta H = n \int_{T_1}^{T_2} C_{p,m} dT = 3 \times \int_{300}^{1000} (23 + 0.01T) dT$   
 $= 3[23(1000 - 300) + \frac{0.01}{2}(1000^2 - 300^2)]$   
 $61950 \text{ J} \approx 62 \text{ kJ}$

25. (a)  $n = 5; T_i = 100 \text{ K}; T_f = 200 \text{ K};$   
 $C_V = 28 \text{ J/mol K}; \text{ Ideal gas}$

$$\begin{aligned}\Delta U &= nC_V\Delta T \\ &= 5 \text{ mol} \times 28 \text{ J/mol K} \times (200 - 100) \text{ K} \\ &= 14,000 \text{ J} = 14 \text{ kJ} \\ \Rightarrow C_p &= C_v + R = (28 + 8) \text{ J/mol K} \\ &= 36 \text{ J/mol K} \\ \Rightarrow \Delta H &= nC_p\Delta T = 5 \text{ mol} \times 36 \text{ J/mol K} \times 100 \text{ K} \\ &= 18000 \text{ J} = 18 \text{ kJ} \\ \Delta H &= \Delta U + \Delta(PV) \\ \Rightarrow \Delta(PV) &= \Delta H - \Delta U = (18 - 14) \text{ kJ} = 4 \text{ kJ}\end{aligned}$$

26. (a)  $\Delta U = q + w$   
 $q = -2 \text{ kJ}, W = 10 \text{ kJ}$   
 $\Delta U = 8 \text{ kJ}$

27. (c)  $W = -P_{ext}(V_2 - V_1)$   
 $= -1 \text{ bar} \times (10 - 1) \text{ lit}$   
 $= -9 \text{ bar} \cdot \text{lit} = -900 \text{ J}$   
 $= -0.9 \text{ kJ}$

28. (d)  $\Delta G = 120 - \frac{3}{8}T$

At equilibrium  $\Delta G = 0$   
 $\therefore T = 320 \text{ K}$

$X \rightleftharpoons{Y}$ , if  $T > 320 \text{ K}$ , then  $\Delta G$  becomes negative.  
 Thus, the reaction will proceed in the forward direction and the amount of  $Y$  will be higher than its amount on equilibrium.

Here only at  $T = 350 \text{ K}$  is greater than 320 K.

29. (a) (ii) + (iii) = (i)

$$Y + Z = X$$

30. (d)  $I_{2(s)} \rightarrow I_{2(g)} : \Delta H_1 = 24 \text{ cal/g at } 200^\circ \text{ C}$

$$\begin{aligned}\Delta H_2 &= \Delta H_1 + \Delta C_{Prxn}(T_2 - T_1) \\ &= 24 + (0.031 - 0.055) \times 50 = 24 - 1.2 \\ &= 22.8 \text{ cal/g}\end{aligned}$$

31. (c)  $C_7H_{16(l)} + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(l)$

$$\Delta n_g = n_p - n_r = 7 - 11 = -4$$

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

$$\therefore \Delta H - \Delta U = -4 RT$$

32. [48.00]

$$|W| = \frac{1}{2}(6+10) \times 6 = 48 \text{ J}$$

33. [6.25 to 6.25]

$$\Delta U = nC_v\Delta T$$

$$5000 = 4 \times C_v (500 - 300)$$

$$C_v = 6.25 \text{ JK}^{-1} \text{ mol}^{-1}$$

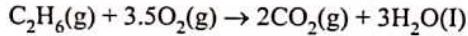
34. [-2.70 to -2.70]

$$\begin{aligned}\Delta H &= \Delta U + \Delta ngRT = 2.1 \times 10^3 + 2(2)(300) \\ &= 2100 + 1200 = 3300 \text{ cal}\end{aligned}$$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S = 3300 - (300)(20) = 3300 - 6000 \\ &= -2700 \text{ cal} = -2.7 \text{ kcal}\end{aligned}$$

35. (c) Fact based

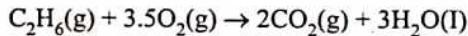
36. [-192.50 or -85.00]



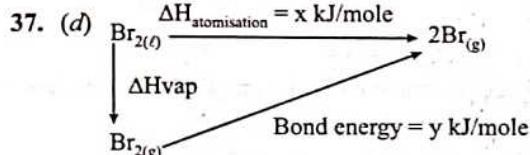
From the given data

$$2 \times (-286) + 3 \times (-393.5) - (-1560) = -572 - 1180.5 + 1560 = -192.50 \text{ kJ/mol.}$$

or



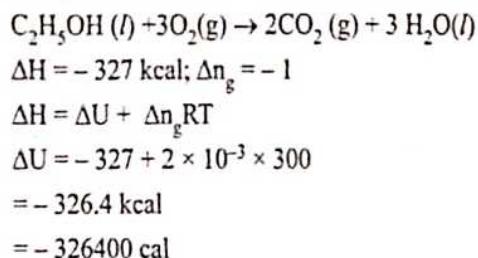
$$2 \times (-393.5) + 3 \times (-286) - (-1560) = -85 \text{ kJ/mol}$$



$$\Delta H_{atomisation} = \Delta H_{vap} + \text{Bond energy}$$

Hence  $x > y$

38. [-326400]

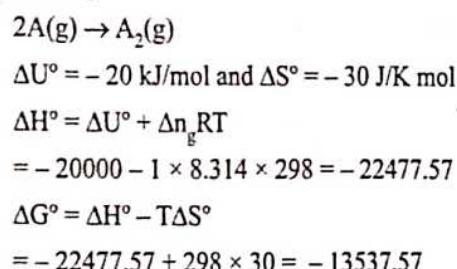


39. (d)  $\Delta_{\text{Sol}}H^\circ = \Delta_{\text{lattice}}H^\circ + \Delta_{\text{Hyd}}H^\circ$

$$4 = 788 + \Delta_{\text{Hyd}}H^\circ$$

$$\Delta_{\text{Hyd}}H^\circ = -784 \text{ kJ/mol}$$

40. [-13537.57]



41. (a)  $\Delta G^\circ = -RT \ln K$

$$T_1 = 25^\circ\text{C} \quad K_1 = 10$$

$$\Delta G^\circ \text{ at } T_1 = -8.314 \times 298 \times 2.303 \times \log 10$$

$$= -5.71 \text{ kJ/mol}$$

$$\Delta G^\circ \text{ at } T_2 = -8.314 \times 373 \times 2.303 \times \log(100)$$

$$= -14.29 \text{ kJ/mol}$$

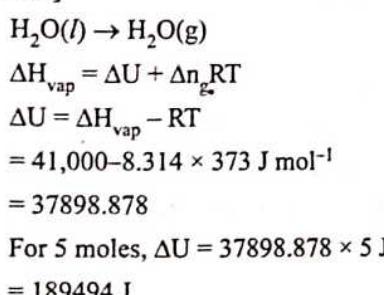
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-5.71 = \Delta H^\circ - 298 (\Delta S^\circ)$$

$$-14.29 = \Delta H^\circ - 373 (\Delta S^\circ)$$

$$\Delta H^\circ = 28.4 \text{ kJ/mol}$$

42. [189494]



43. (a)  $P_{\text{ext}} = 0$

$$W = -P_{\text{ext}} \Delta V$$

$$= 0$$

44. (b) For 1 mole of ideal gas.

- Both internal energy (U) and Enthalpy (H) depends on temperature
  - Compressibility factor Z = 1
  - $C_{P,m} - C_{V,m} = R$
- and  $dU = C_{V,m} dT$

45. [15] Moles(n) = 5, T = 293 K

Process  $\rightarrow$  Isothermal  $\rightarrow$  Irreversible

$$W = -P_{\text{ext}} \Delta V$$

$$= -4.3 \times \left( \frac{5 \times 293 R}{1.3} - \frac{5 \times 293 R}{2.1} \right) = -15.34 \text{ kJ}$$

$$\Delta V = 0, W = -Q = 15.34 \text{ kJ/mol}$$

$$Q = 15.34 \text{ kJ/mol}$$

So, the answer is 15.

46. [50]

$$\text{Mass organic compound} = 1.6 \text{ gm}$$

$$\text{Mass of AgBr} = 1.88 \text{ gm}$$

$$\text{Moles of Br} = \text{Moles of AgBr} = \frac{1.88}{188} = 0.01$$

$$\text{Mass of Br} = 0.01 \times 80 = 0.80 \text{ gm}$$

$$\% \text{ of Br} = \frac{0.80 \times 100}{1.60} = 50\%$$

47. [31]

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

$$\Delta n_g = 1 - 0 = 1$$

$$\Delta H - \Delta U = 1 \times 8.31 \times 373$$

$$= 30.99 \times 10^2 \text{ J/mol} = 31 \times 10^2 \text{ J/mol}$$

48. [-741.5]

For given reaction

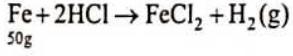
$$\Delta n = 1 + 1 - 1.5 = 0.5$$

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

$$= -742.7 + 0.5 \times 8.314 \times 10^{-3} \times 298$$

$$= -741.5 \text{ kJ mol}^{-1}$$

49. [-2218]



$$n = \frac{50}{55.85}$$

$$W = -P_{\text{ext}} \Delta V, PV = nRT$$

$$W = -\Delta n_g RT$$

$$W = -1 \times 8.314 \times 298$$

$$W \text{ for } \frac{50}{55.85} \text{ mole} = -8.314 \times 298 \times \frac{50}{55.25}$$

$$= -2218.059 \text{ J}$$

50. [101]

$$\Delta_{\text{sub}}H = \Delta_{\text{Fus}}H + D_{\text{Vap}}H$$

$$\Delta_{\text{sub}}H = 98.2 + 2.8$$

$$\Delta_{\text{sub}}H = 101 \text{ kJ/mol}$$

51. [200]

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G < 0 \quad (\text{spontaneous})$$

$$\Delta H^\circ - T\Delta S^\circ < 0$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$



$$T > \frac{80000}{2T}$$

$$2T^2 > 80000$$

$T > 200$  (minimum T for spontaneous)

52. (b)  $\Delta G = \Delta G^\circ + RT \ln K$

At equilibrium,

$$\Delta G = \Delta G^\circ + RT \ln K = 0$$

$$\Delta G^\circ = -RT \ln K$$

$$-RT \ln K < 0$$

$$RT \ln K > 0$$

$$K > 1$$

53. [1380]

$$\Delta G^\circ = -RT \ln K_p$$

$$= -R(300)\ln(100)$$

$$\Delta G^\circ = -1380R$$

$$x = 1380$$

54. [336]

$$\Delta G = -43.4 \text{ kJ/mol}$$

$$\Delta H = 51.4 \text{ kJ/mol}$$

$$\Delta G = \Delta H - T\Delta S$$

$$-49400 = 51400 - 300 \Delta S$$

$$\Delta S = \frac{+100800}{300}$$

$$\Delta S = 336 \text{ J K}^{-1} \text{ mol}^{-1}$$

55. [5]

Given,  $\Delta H = -57.8 \text{ kJ mol}^{-1}$

$$\Delta S = -176 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

Using Gibb's free energy relation

$$\Delta G = \Delta H - T\Delta S$$

Where, = change in Gibb's free energy

$\Delta H$  = Change in enthalpy

T = Temperature

$\Delta S$  = Change in entropy

$$\Delta G = 57.8 \text{ kJ/mol} - \left[ 298 \text{ K} \times (-176 \text{ J K}^{-1} \text{ mol}^{-1}) \right]$$

$$= 57.8 \text{ kJ/mol} - \left( 298 \times \frac{-175}{1000} \text{ kJ} \right) [\because 1 \text{ kJ} = 1000 \text{ J}]$$

$$= -5.352 \text{ kJ/mol}$$

$$|\Delta G| = 5.352$$

56. [964]

57. (c)  $\Delta G^\circ = -RT \ln K$  ... (i)

$$\Delta G = \Delta H^\circ - T\Delta S^\circ$$
 ... (ii)

From (i) and (ii)

$$-(\Delta H^\circ + T\Delta S^\circ) = RT \ln K$$

$$\ln K = \frac{-(\Delta H^\circ + T\Delta S^\circ)}{RT}$$

58. (a) Fact based

59. [964]

$$T_{\text{rain}} = \left( \frac{\Delta H^\circ}{\Delta S^\circ} \right)$$

$$\Delta H_{\text{rem}}^\circ = [\Delta_f H^\circ(\text{Fe}) + \Delta_f H^\circ(\text{CO})] -$$

$$= [\Delta_f H^\circ(\text{FeO}) + \Delta_f H^\circ(\text{C}_{(\text{graphite})})]$$

$$= [0 - 110.5] - [-266.3 + 0]$$

$$= 155.8 \text{ kJ/mol}$$

$$[\Delta S^\circ(Fe') + \Delta S^\circ(C_{(\text{graphite})})]$$

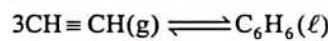
$$= [27.28 + 197.6] - [57.49 + 5.74]$$

$$= 161.65 \text{ J / mol - K}$$

$$T_{\text{rain}} = \frac{155.8 \times 10^3 \text{ J / mol}}{161.65 \text{ J / mol - K}} = 963.8 \text{ K}$$

$$= 964 \text{ K (Nearest integer)}$$

60. [855]



$$\Delta G^\circ = \Delta G_F^\circ(\text{C}_6\text{H}_6) - 3\Delta G_F^\circ(\text{CH} \equiv \text{CH})$$

$$= -1.24 \times 10^5 - 3(-2.04 \times 10^5)$$

$$= 4.88 \times 10^5 \text{ J/mol}$$

$$\Delta G^\circ = -RT \ln K = -2.303RT \log K$$

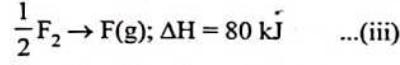
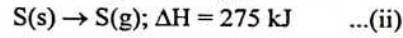
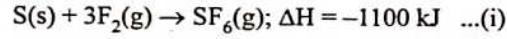
$$\log K = \frac{-4.88 \times 10^5}{2.303 \times 8.314 \times 298}$$

$$|\log K| = 85.5$$

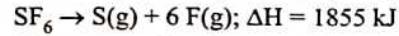
$$x \times 10^{-1} = 85.5$$

$$x = 855$$

61. [309]



Equation (ii) + 6 equation (iii) – equation (i)



Thus average bond energy for S – F bond

$$= \frac{1855}{6} = 309.16 \text{ kJ}$$

62. [336]

$$\Delta G = -43.4 \text{ kJ/mol}$$

$$\Delta H = 51.4 \text{ kJ/mol}$$

$$\Delta G = \Delta H - T\Delta S$$

$$-49400 = 51400 - 300 \Delta S$$

$$\Delta S = \frac{+100800}{300}$$

$$\Delta S = 336 \text{ J K}^{-1} \text{ mol}^{-1}$$



63. [230]



Al and Ca are in its standard state so enthalpy of formation of these is zero.

$$\therefore \Delta H_f^\circ = \Delta H_f^\circ(\text{Al}_2\text{O}_3) - 3\Delta H_f^\circ(\text{CaO})$$

$$\Delta H_f^\circ = -1675 - 3(-635)$$

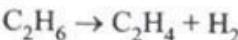
$$\Delta H_f^\circ = 230 \text{ kJ}$$

64. [21] Heat of combustion per mol for 12 g =  $-2.48 \times 10^2 \text{ kJ}$ 

For 1g of graphite:

$$\text{Heat of combustion} = \frac{-2.48 \times 10^2}{12} = -2066 \text{ kJ} = -21$$

65. [131]



$$\Delta H = [(E_{\text{C-C}} + 6E_{\text{C-H}}) - (E_{\text{C=C}} + 4E_{\text{C-H}} + E_{\text{H-H}})]$$

$$\Delta H = [(347 + 6 \times 414) - (611 + 4 \times 414 + 433)]$$

$$= 2831 - 2700$$

$$= 131 \text{ kJ/mol}$$

Hence, the reaction enthalpy  $\Delta_r H$  is  $131 \text{ kJ mol}^{-1}$ .

66. [5]

$$\text{Given, } \Delta H = -57.8 \text{ kJ mol}^{-1}$$

$$\Delta S = -176 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

Using Gibb's free energy relation

$$\Delta G = \Delta H - T\Delta S$$

Where, = change in Gibb's free energy

 $\Delta H$  = Change in enthalpy

T = Temperature

 $\Delta S$  = Change in entropy

$$\Delta G = 57.8 \text{ KJ/mol} - \left[ 298 \text{ K} \times (-176 \text{ Jk}^{-1} \text{ mol}^{-1}) \right]$$

$$= 57.8 \text{ KJ/mol} - \left( 298 \times \frac{-175}{1000} \text{ kJ} \right) [\because 1 \text{ kJ} = 1000 \text{ J}]$$

$$= -5.352 \text{ kJ/mol}$$

$$|\Delta G| = 5.352$$

67. [82] Milli moles of HCl =  $200 \times 0.2 = 40$ 

$$\Rightarrow \text{Milli moles of NaOH} = 300 \times 0.1 = 30$$

$$\Rightarrow \text{Heat released} = \left( \frac{30}{1000} \times 57.1 \times 1000 \right) = 1713 \text{ J}$$

$$\Rightarrow \text{Mass of solution} = 500 \text{ mL} \times 1 \text{ gm/mL} = 500 \text{ gm}$$

$$\Rightarrow \Delta T = \frac{Q}{m \times 0} = \frac{1713 \text{ J}}{500 \text{ g} \times 4.18 \frac{\text{J}}{3-\text{K}}} = 0.8196 \text{ K}$$

$$= 81.96 \times 10^{-2} \text{ K}$$

68. [38]  $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}$ ,  $\Delta H_{\text{vap}} = 41 \text{ kJ/mol}$ 

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

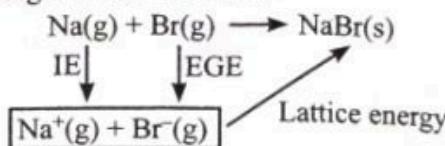
 $\Delta E$  is internal energy change $\Delta n_g$  is change in gaseous moles =  $1 - 0 = 1$ 

$$41 = \Delta E + 1 \times 8.3 \times 10^{-3} \times 373$$

$$\Delta E \approx (41 - 3) = 38 \text{ kJ mol}^{-1}$$

69. [-5576]

The total enthalpy change is the sum of the enthalpy changes of each reaction.



the enthalpy of reaction of :

$$\text{NaBr} = \text{IE} + \text{EGE} + \text{lattice energy}$$

$$\Delta rH = 495.8 - 325 - 728.4$$

$$= -557.6 \text{ kJ/mol}$$

$$= -5576 \times 10^{-1} \text{ kJ/mol}$$

70. [131]



$$\Delta H = [(E_{\text{C-C}} + 6E_{\text{C-H}}) - (E_{\text{C=C}} + 4E_{\text{C-H}} + E_{\text{H-H}})]$$

$$\Delta H = [(347 + 6 \times 414) - (611 + 4 \times 414 + 433)]$$

$$= 2831 - 2700$$

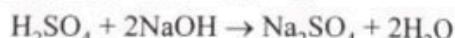
$$= 131 \text{ kJ/mol}$$

Hence, the reaction enthalpy  $\Delta_r H$  is  $131 \text{ kJ mol}^{-1}$ .

71. [82]

$$\text{Millimoles of H}_2\text{SO}_4 = 400 \times 0.2 = 80$$

$$\text{meq of NaOH} = 600 \times 0.1 = 60$$



$$t = 0 \quad 80 \quad 60 \quad --$$

$$50 \quad - \quad 30 -$$

30 m moles of product formed.



$$\text{Moles of H}^+ \& \text{OH}^- \text{ neutralised} = \frac{60}{1000}$$

$$\therefore \Delta H = \frac{60}{1000} \times (-57.1) = 3426 \text{ J/mol}$$

Total volume = 1 L, mass = 1000 g

$$mS\Delta T = \Delta H$$

$$1000 \times 4.18 \times \Delta T = 3426$$

$$\Delta T = 0.8196 = 81.9 \times 10^2 \text{ K} = 82 \times 10^{-2} \text{ K}$$

$$x = 82$$

72. [718]

$$\Delta_f H_{\text{KCl}}^\circ = \Delta_{\text{Sub}} H_{(\text{K})}^\circ + \Delta_{\text{ionisation}} H_{(\text{K})}^\circ$$

$$+ \Delta_{\text{EGE}} H_{(\text{Cl})}^\circ = \Delta_{\text{lattice}} H_{(\text{KCl})}^\circ + \frac{1}{2} \Delta_{\text{bond}} H_{(\text{Cl})}^\circ$$

$$-436.7 = 89.2 + 419 + (-348.6) + \Delta_{\text{lattice}} H_{(\text{KCl})}^\circ$$

$$+ \frac{1}{2} (243.0)$$

$$\Delta_{\text{lattice}} H_{(\text{KCl})}^\circ = -717.8 \text{ kJ/mol}$$

73. [38]  $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}$ ,  $\Delta H_{\text{vap}} = 41 \text{ kJ/mol}$ 

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

 $\Delta E$  is internal energy change $\Delta n_g$  is change in gaseous moles =  $1 - 0 = 1$ 

$$41 = \Delta E + 1 \times 8.3 \times 10^{-3} \times 373$$

$$\Delta E \approx (41 - 3) = 38 \text{ kJ mol}^{-1}$$

74. [667]

$$\text{Molar mass of glucose } (\text{C}_6\text{H}_{12}\text{O}_6) = 180 \text{ g/mol}$$

$$\text{moles of glucose required per day} = \frac{1000 \text{ kJ/day}}{2700 \text{ kJ/mol}}$$

$$= \frac{100}{27} \text{ mol/day}$$

Gram of glucose required by the body in a day

$$= \frac{100}{27} \times 180 \left( \frac{\text{g}}{\text{day}} \right) = 666.67 \text{ g/day} \approx 667 \text{ g/day}$$

75. (b) Fact based

76. [300]

$$\Delta G = \Delta H - T\Delta S = 0 \text{ at equilibrium}$$

$$\Rightarrow -165 \times 10^3 - T \times (-505) = 0$$

$$T = 300 \text{ K}$$

77. (a)  $\Delta H = \Delta U - P\Delta V$ 

if  $U + PV$  (by definition)

$$\Delta H = \Delta U + P\Delta V$$

78. [195]

$$\text{N}_2\text{O} \text{ moles} = \frac{22}{44} = \frac{1}{20}$$

$$\Delta H = nC_p\Delta T = \frac{1}{20} \times 100(-40) = -200 \text{ J}$$

$$\Delta U = q_p + W$$

$$W = -P_{ext}\Delta V$$

$$W = -1 \frac{(167.75 - 217.1)}{1000} \times 101.35$$

$$W = +5 \text{ J}$$

$$\Delta U = -200 + 5 = -195 \text{ J}$$

79. [0] For free expansion:

$$P_{ext} = 0, W = 0$$

$$q = 0, \Delta U = 0$$

80. [8630]

$$n = 5 \text{ mol}, T = 300 \text{ K}$$

$$v_1 = 10 \text{ L}, v_2 = 20 \text{ L}$$

$$W = -nRT \ln \frac{v_2}{v_1}$$

$$= -5 \times 8.3 \times 300 \times \ln \frac{20}{10} = -8630.38 \text{ J}$$

81. [38]  $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ 

$$n = \frac{36}{18} = 2 \text{ mol}$$

$$\Delta U = \Delta H - \Delta_n g RT$$

$$41.1 - \frac{1 \times 8.31 \times 373}{1000} \text{ kJ/mol} = 38 \text{ kJ/mol}$$

82. [2]  $C_{p,m} = C_{v,m} + R$ 

$$\Rightarrow C_{v,m} = 20.785 - 8.314 = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta U = nC_v m \Delta T$$

$$n = \frac{5000}{12.471 \times 200} = \frac{25}{12.471} \approx 2$$

83. [3] Internal energy, volume enthalpy are state variable.

84. [57]

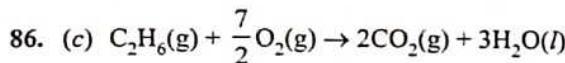
$$\Delta H = \Delta U + \Delta_{ng} RT$$

$$\Delta H = -59.6 + 1 \times 8.314 \times 300 \times 10^{-3}$$

$$\Delta H = -57.10$$

$$85. (c) \Delta H = \sum \Delta H_{\text{combustion}}(\text{Reactant}) - \sum \Delta H_{\text{combustion}}(\text{product})$$

$$= 3 \times (-1300) - (-3268) = -632 \text{ kJ/mol}$$



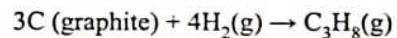
$$\Delta_C H(\text{C}_2\text{H}_6) = 2\Delta_F H(\text{CO}_2)(g) + 3\Delta_F H(\text{H}_2\text{O})(l) - \Delta_F H(\text{C}_2\text{H}_6)(g)$$

$$-1560 = 2(-394) + 3(-286) - \Delta_F H(\text{C}_2\text{H}_6)(g)$$

$$\Delta_F H(\text{C}_2\text{H}_6) = -86 \text{ kJ/mole.}$$

87. [104]

The desired reaction is:



$$\Delta H_F = 3\Delta H_2 + 4\Delta H_3 + \Delta H_1$$

$$= 3(-393.5) + 4(-285.8) - (-2220) = -103.7 \text{ kJ/mol}$$

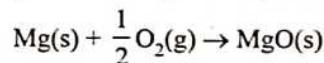
$$|\Delta H_F| = 104 \text{ kJ/mol.}$$

88. [117]

Given data is for 1 moles and asked for 5 moles

So value is  $23.4 \times 5 = 117 \text{ kJ}$ 

89. [600]



$$\Delta H = \Delta U + \Delta_{ng} RT$$

$$-601.70 \times 10^3 = \Delta U - \frac{1}{2} \times 8.3 \times 300$$

$$-601.7 \text{ kJ} = \Delta U - 1.245 \text{ kJ}$$

$$\Delta U = -600.455 \text{ kJ} \approx 600$$

90. [-727]

$$\Delta U = -726 \text{ kJ/mol}$$

$$\Delta_{ng} = 1 - \frac{3}{2} = -\frac{1}{2}$$

$$\Delta H = \Delta U + \Delta_{ng} RT$$

$$= -726 - \frac{1}{2} \times \frac{8.3 \times 300}{1000} = -727.245$$

91. [2]  $\Delta H_{\text{ionisation}}$  of  $\text{CH}_3\text{COOH}$ 

$$= [-57.3 - (-55.3)] = 2 \text{ kJ/mol}$$

92. [35]

Let  $X_g$  is burnt

$$\text{moles} = \frac{X}{280}$$

$$\text{Heat released by } \frac{X}{280} \text{ moles} = 2.5 \times 0.45$$



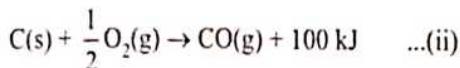
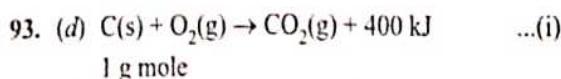
$$\text{Heat released by 1 mole} = \frac{2.5 \times 0.45 \times 280}{X} \text{ kJ}$$

$$\Delta H = \Delta U + \Delta_{ng} T$$

$$\Delta H = \Delta U$$

$$9 = \frac{2.5 \times 280 \times 0.45}{X}$$

$$X = 35 \text{ g}$$



$$0.6 \times 1000 = 600 \text{ gm}$$

$$600 \times \frac{60}{100} \text{ (pure carbon)}$$

$$= 360 \text{ gm} = \frac{360}{12} = 30 \text{ mole}$$

$$\text{Carbon converted into CO}_2 = \left( 30 - 30 \times \frac{60}{100} \right) = 12 \text{ mole}$$

$$\& \text{carbon converted in CO} = 30 \times \frac{60}{100} = 18 \text{ mole}$$

$$\text{Energy generated} = 18 \times 100 = 1800 \text{ kJ}$$

$$\text{Energy generated during 1st reaction} = 12 \times 400 = 4800$$

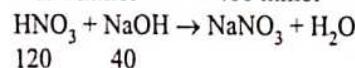
$$\text{Total} = 4800 + 1800 = 6600 \text{ kJ}$$

94. [54]



$$600 \text{ mL} \times 0.2 \text{ M} \quad 400 \text{ ml} \times 0.1 \text{ M}$$

$$= 120 \text{ mmol} \quad = 40 \text{ mmol}$$



$$80 \ 0 \quad 40 \text{ mmol}$$

$$\Delta H = 40 \text{ mmol} \times (57 \times 10^3) \frac{\text{J}}{\text{mol}}$$

$$= 40 \times 10^{-3} \text{ mol} \times 57 \times 10^3 \frac{\text{J}}{\text{mol}} = 2280 \text{ J}$$

$$mS\Delta T = 2280$$

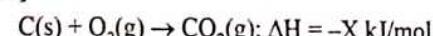
$$1000 \text{ mL} \times \frac{1 \text{ gm}}{\text{mL}} \times 4.2 \times \Delta T = 2280$$

$$\Delta T = 542.86 \times 10^{-3}$$

$$\Delta T = 54.286 \times 10^{-2} \text{ K}$$

$$\Delta T = 54.286 \times 10^{-2} \text{ }^\circ\text{C}$$

95. [200]



$$Q = C\Delta T = 20 \text{ kJ} \times 2$$

40 kJ heat is released for 2.4 g of C

$$\text{for 1 mole 'C': } Q = \frac{40}{2.4} \times 12$$

$$= \frac{400}{24} \times 12 = 200 \text{ kJ/mol}$$

$$Q = \Delta E = \Delta H = 200 \text{ kJ} \quad (\because \Delta_{ng} = 0)$$

$$X = 200$$

## JEE ADVANCED

96. [2] Work done along dashed path

$$-W = \sum P \Delta V$$

$$= 4 \times 1.5 + 1 \times 1 + \frac{2}{3} \times 2.5 = 8.65 \text{ atm}$$

Work done along solid path

$$W = nRT \ln \frac{V_2}{V_1} = P_1 V_1 \ln \frac{V_2}{V_1}$$

$$= 2 \times 2.3 \log \frac{5.5}{0.5}$$

$$= 2 \times 2.3 \log 11 = 4.79$$

$$= \frac{W_d}{W_s} = \frac{8.65}{4.79} = 1.80 \approx 2$$

97. (A)  $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$

It is phase transition. The process is endothermic (sublime)

Gas is produced, so entropy increase.

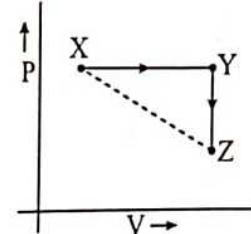
(B) On heating  $\text{CaCO}_3$  decomposed. So, process is endothermic. The entropy increases as gaseous product is formed.

(C)  $2\text{H} \rightarrow \text{H}_2(\text{g})$

Entropy decrease as number of gaseous particles decrease.

(D) It is phase transition. White and red P are allotropes since red P is polymeric form  
So  $\Delta S$  is -ve.

98. (a,c)



$$(a) \Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$$

(Correct)

$$(b) W_{x \rightarrow y} = W_{x \rightarrow y} + W_{y \rightarrow z}$$

(Incorrect)

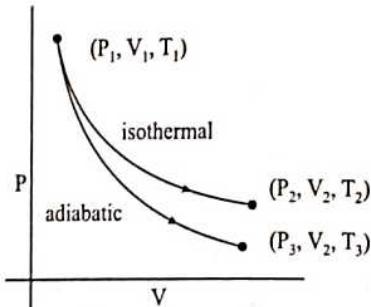
$$(c) W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow z}$$

(Correct)

$$(d) \Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow z}$$

(Incorrect)

99. (a,d)



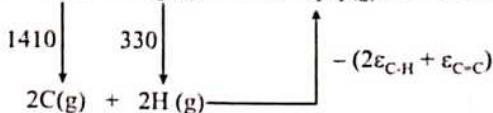
$$(a) T_1 = T_2 \text{ (due to isothermal)}$$

(b)  $T_3 > T_1$  (incorrect) cooling will take place in adiabatic expansion)

(c)  $W_{\text{isothermal}} > W_{\text{adiabatic}}$  {with sign, this is incorrect}

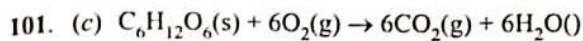
(d)  $\Delta U_{\text{isothermal}} = 0 > \Delta U_{\text{adiabatic}} = -\text{ve}$

So, answer is (a,d)



$$\therefore \Delta H = +1410 + 330 - (350 \times 2) - \varepsilon_{\text{C-C}} = +225$$

$$\therefore \varepsilon_{\text{C-C}} = 1740 - 700 - 225 = +815 \text{ KJ/mol.}$$



$$\begin{aligned} \Delta_C H &= 6 \times \Delta_f H (\text{CO}_2) + 6 \Delta_f H (\text{H}_2\text{O}) - \Delta_f H (\text{C}_6\text{H}_{12}\text{O}_6) \\ &\quad - 6\Delta_f (\text{O}_2, \text{g}) \end{aligned}$$

$$= 6 \times (-400 - 300) - (-1300) - 0$$

$$= -4200 + 1300$$

$$= -2900 \text{ KJ/mol}$$

For one gram of glucose, enthalpy of combustion

$$= -\frac{2900}{180} = -16.11 \text{ KJ/g.}$$

102. (a,b,c)

Since the vessel is thermally insulated so

$$q = 0$$

$$P_{\text{ext}} = 0, \text{ so } w = 0$$

so  $\Delta U = 0$  (ideal gas)

Hence  $\Delta T = 0$

$$\Rightarrow \Delta T = 0$$

$$\Rightarrow T_2 = T_1$$

$$\Rightarrow P_2 V_2 = P_1 V_1$$

The process is however adiabatic irreversible.

So we cannot apply  $P_2 V_2^\gamma = P_1 V_1^\gamma$

103. (b) For  $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O(g)}$  at  $T = 100^\circ\text{C}$ , 1atm equilibrium exists.  $\therefore \Delta G = 0, \Delta H - T\Delta S = 0$   
 $\Delta H = T\Delta S > 0$  for system, since evaporation is endothermic

$$\therefore (\Delta S)_{\text{system}} > 0, \text{ also } (\Delta S)_{\text{surrounding}} = \frac{q_{\text{sur}}}{{T_{\text{sur}}}}$$

Heat gained by system = heat lost by surroundings

$$\therefore q_{\text{sur}} < 0 \therefore (\Delta S)_{\text{sur}} < 0$$

104. (a) Let the heat capacity of insulated beaker be C.

$$\begin{aligned} \text{Mass of aqueous content in expt. 1} &= (100 + 100) \times 1 \\ &= 200 \text{ g} \end{aligned}$$

$$\Rightarrow \text{Total heat capacity} = (C + 200 \times 4.2) \text{ J/K}$$

Moles of acid, base neutralised in expt. 1 =  $0.1 \times 1 = 0.1$

$$\Rightarrow \text{Heat released in expt 1} = 0.1 \times 57 = 5.7 \text{ KJ}$$

$$\Rightarrow 5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T.$$

$$5.7 \times 1000 = (C + 200 + 4.2) \times 5.7$$

$$\Rightarrow (C + 200 \times 4.2) = 1000$$

In second experiment,  $n_{\text{CH}_3\text{COOH}} = 0.2, n_{\text{NaOH}} = 0.1$

Total mass of aqueous content = 200 g

$$\Rightarrow \text{Total heat capacity} = (C + 200 \times 4.2) = 1000$$

$$\Rightarrow \text{Heat released} = 1000 \times 5.6 = 5600 \text{ J.}$$

Overall, only 0.1 mol of  $\text{CH}_3\text{COOH}$  undergo neutralization.

$$\Rightarrow \Delta H_{\text{neutralization}} \text{ of } \text{CH}_3\text{COOH} = \frac{-5600}{0.1}$$

$$= -56000 \text{ J/mol}$$

$$= -56 \text{ KJ/mol.}$$

$$\Rightarrow \Delta H_{\text{ionization}} \text{ of } \text{CH}_3\text{COOH} = 57 - 56 = 1 \text{ KJ/mol}$$

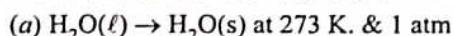
105. (b) Final solution contain 0.1 mole of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  each.

Hence it is a buffer solution.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$= 5 - \log 2 + \log \frac{0.1}{0.1} = 4.7$$

106. (a) -R,T (b)-P,Q,S (c)-P,Q,S (d)-P,Q,S,T



$$\Delta H = -\text{ve} = q$$

$$\Delta S_{\text{sys}} < 0, \Delta G = 0.$$

w ≠ 0 (as water expands on freezing),  $\Delta U \neq 0$

(b) Free expansion of ideal gas.

$$q = 0 \quad w = 0$$

$$\Delta U = 0 \quad \Delta S_{\text{sys}} > 0$$

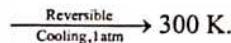
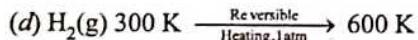
$$\Delta G < 0$$

(c) Mixing of equal volume of ideal gases at constant pressure & temp in an isolated container

$$q = 0, w = 0,$$

$$\Delta U = 0, \Delta S_{\text{sys}} > 0$$

$$\Delta G < 0$$



$$q = 0, w = 0, \Delta U = 0, \Delta G = 0, \Delta S_{\text{sys}} = 0$$

107. (c) ∵ Process is done against const. External P, process will be irreversible.

$$\therefore "S_{\text{sur}} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$$

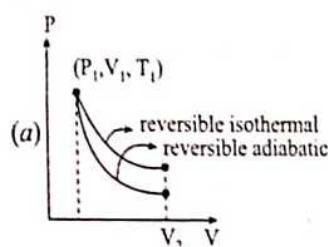
$$= \frac{-3 \times (2-1) \times 101.3}{300} = -1.013 \text{ J/K}$$

108. (a,b)

$$\Delta S_{\text{sur}} = \frac{-\Delta H}{T_{\text{sur}}}$$

For endothermic, if  $T_{\text{sur}}$  increases,  $\Delta S_{\text{sur}}$  will increase.  
For exothermic, if  $T_{\text{sur}}$  increases,  $\Delta S_{\text{sur}}$  will decrease.

109. (a,c,d)



Area under curve in reversible isothermal is more. So, more work will be done by gas.

$$(b) T_1 = T_2 \Rightarrow \Delta U = nC_V \Delta T = 0$$

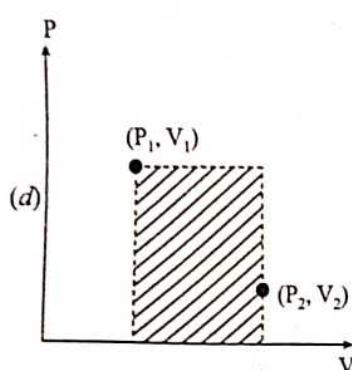
In reversible adiabatic expansion,  $T_2 < T_1$

$$\therefore \Delta T = -ve \therefore \Delta U = -ve$$

$$(c) \text{In Free expansion, } P_{\text{ext}} = 0 \therefore W = 0$$

If carried out isothermally ( $\Delta U = 0 \Rightarrow q = 0$  (Adiabatic);  
From I law

If carried out adiabatically ( $q = 0 \Rightarrow \Delta U = 0$  (isothermal));  
From I law



During irreversible compression, maximum work is done on the gas (corresponding to shaded area)

$$110. (c) dG = VdP - SdT$$

$$\text{At } 298 \text{ K, } SdT = 0$$

$$\therefore dG = VdP$$

$$\int_1^P dG = \int_1^P VdP \therefore G - G^\circ = V(P - 1)$$

[ $\because$  Solids involved  $\therefore V$  almost constant]

$$\therefore \Delta_f G = [G^\circ_{\text{diamond}} + V_d(P - 1)] - [G^\circ_{\text{graphite}} + V_g(P - 1)]$$

$$0 = 2.9 \times 10^3 + (P - 1) 10^5 (-2 \times 10^{-6})$$

$$\therefore P = 14501 \text{ bar}$$

111. (a,c)



given  $T_2 > T_1$

$$\frac{\ln k_1}{\ln k_2} > \frac{T_2}{T_1}$$

$$T_1 \ln k_1 > T_2 \ln k_2$$

$$-\Delta G_1^\circ > -\Delta G_2^\circ$$

$$(-\Delta H^\circ + T_1 \Delta S^\circ) > (-\Delta H^\circ + T_2 \Delta S)$$

$$T_1 \Delta S^\circ > T_2 \Delta S^\circ$$

$$\Delta S^\circ < 0$$

112. [-14.6]

From the given data



$$\Delta G^\circ = 1,00,000$$

$$\Delta G^\circ = 1,00,000 = -RT \ln k_p$$

$$k_p = \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} (P_{\text{H}_2\text{O(g)}}) = 0.01 \text{ bar}$$

$$100000 = -RT \ln \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

$$P_{\text{H}_2} = -14.6$$

113. (b,c)

AC  $\rightarrow$  Isochoric

AB  $\rightarrow$  Isothermal

BC  $\rightarrow$  Isobaric

$$\# q_{\text{AC}} = \Delta U_{\text{BC}} = nC_V(T_2 - T_1)$$

$$W_{\text{AB}} = nRT_1 \ln \left( \frac{V_2}{V_1} \right) \text{ A (wrong)}$$

$$q_{\text{BC}} = \Delta H_{\text{AC}} = nC_p(T_2 - T_1)$$

$$W_{\text{BC}} = -P_2(V_1 - V_2) \text{ B (correct)}$$

$$nC_p(T_1 - T_2) < nC_V(T_1 - T_2) \text{ C (correct)}$$

$$\Delta H_{\text{CA}} < \Delta U_{\text{CA}}$$

D (wrong)

114. (a,b)

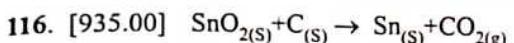
Enthalpy of formation is defined as enthalpy change for formation of 1 mole of substance from its elements, present in their natural most stable form.

115. (a,b,c)

For 1 mole Vander Waal's gas

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

If  $P_{ext} = P$ , means process is reversible. For Vanderwaal gas, expression is correct for all reversible process.

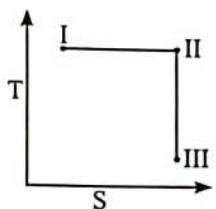


$$\Delta H^\circ_{rxn} = [-394] - [-581] = 187 \text{ kJ/mole}$$

$$\Delta S^\circ_{rxn} = [52+210] - [56+6]$$

$$= 200 \text{ J/k-mole}$$

117. (a,b,d)



(I)  $\xrightarrow[\text{Reversible Isothermal expansion}]{} \text{(II)} \xrightarrow[\text{Rev. Adiabatic Expansion}]{} \text{(III)}$

Isoenthalpic process is isoenthalpic while reversible adiabatic process is isoentropic

118. [10] 1<sup>st</sup> process is adiabatic since entropy is constant.

$$W_1 = \Delta U$$

$$\Delta U = 450R - 2250R = -1800R \quad \dots(i)$$

In 2<sup>nd</sup> process

$$W_2 = -2.303 nRT \log \frac{v_3}{v_2} \quad \dots(ii)$$

$$= -nRT \ln \frac{v_3}{v_2}$$

$U = nC_v T$  for process II

$$450R = 1 \times \frac{5}{2} RT$$

$$T = \frac{450 \times 2}{5} = 180 \text{ K}$$

$$W_1 = W_2$$

$$-1800R = -1 \times R \times 100 \ln \frac{v_3}{v_2}$$

$$\ln \frac{v_3}{v_2} = \frac{1800}{180} = 10$$



# CHAPTER

# 5

# Equilibrium

## Exercise-1 (Topicwise)

1. (c) When rate of forward reaction is equal to rate of backward reaction the reaction is said to be in equilibrium.

2. (b) At equilibrium, the rate of forward & backward reaction become equal.

$$3. (d) [HI] = \frac{64 \text{ gm}}{128 \times 2 \text{ litre}} = 0.25$$

4. (b) As conc. of reactant increases, rate of reaction increases.

5. (d) Fact Based

6. (a) As we increase the concentration of substance, then speed of the reaction increases.

7. (d) Equilibrium constant for the reaction

$$3A + 2B \rightleftharpoons C \text{ is } K = \frac{[C]}{[A]^3[B]^2}$$

8. (d) Suppose 1 mole of A and B each taken then 0.8 mole/litre of C and D each formed remaining concentration of A and B will be  $(1 - 0.8) = 0.2$  mole/litre each.

$$K_c = \frac{[C][D]}{[A][B]} = \frac{0.8 \times 0.8}{0.2 \times 0.2} = 16.0$$



$$\text{Initial conc. } \begin{matrix} 4 & 4 & 0 & 0 \end{matrix}$$

$$\text{After T time conc. } \begin{matrix} (4-2) & (4-2) & 2 & 2 \end{matrix}$$

$$\text{Equilibrium constant} = \frac{[C][D]}{[A][B]} = \frac{2 \times 2}{2 \times 2} = 1$$

10. (a) For reaction  $A + 2B \rightleftharpoons C$

$$K = \frac{[C]}{[A][B]^2} = \frac{0.216}{0.06 \times 0.12 \times 0.12} = 250$$

11. (b)  $A + 2B \rightleftharpoons C + 3D$

$$K = \frac{[P_C][P_D]^3}{[P_A][P_B]^2} = \frac{0.30 \times 0.50 \times 0.50 \times 0.50}{0.20 \times 0.10 \times 0.10} = 18.75$$



$$K_c = \frac{[C]}{[A][B]^2}$$



Moles	2	0	0
At eq <sup>m</sup>	$\frac{2 \times 60}{100}$	$\frac{2 \times 40}{100}$	$\frac{2 \times 40}{100}$

Volume of container = 2 litre.

$$K_c = \frac{\frac{2 \times 40}{100 \times 2} \times \frac{2 \times 40}{100 \times 2}}{\frac{2 \times 60}{100 \times 2}} = 0.266$$

14. (d) Unit of  $K_p = (\text{atm})^{\Delta n}$

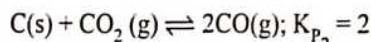
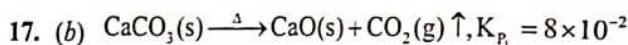
$$\text{Unit of } K_c = (\text{mole/litre})^{\Delta n}$$

$$= [\text{mole / litre}]^0 = 1 \text{ (unitless)}$$

15. (b) For  $A + B \rightleftharpoons C + D$

$$K = \frac{[C][D]}{[A][B]} = \frac{0.4 \times 1}{0.5 \times 0.8} = 1$$

$$16. (a) K_p = \frac{[P_{CO}]^2[P_{O_2}]}{[P_{CO_2}]^2} = \frac{[0.4]^2 \times [0.2]}{[0.6]^2} = 0.0888$$



$$K_{p_2} = \frac{[P_{CO}]^2}{[P_{CO_2}]}; P_{CO} = \sqrt{[K_{p_1} \times K_{p_2}]}$$

$$P_{CO} = \sqrt{[8 \times 10^{-2} \times 2]} = \sqrt{16 \times 10^{-2}} = 4 \times 10^{-1} = 0.4$$

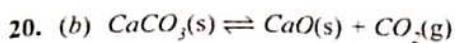


$$\text{Initial conc. } \begin{matrix} 1 & 1 & 0 & 0 \end{matrix}$$

$$\text{At equili} \quad \begin{matrix} (1-x) & (1-x) & x & x \end{matrix}$$

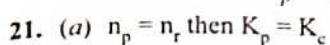
$$K_p = \frac{P_{CO} \cdot P_{H_2O}}{P_{H_2} \cdot P_{CO_2}} = \frac{x \cdot x}{(1-x)(1-x)} = \frac{x^2}{(1-x)^2}$$

$$19. (c) K_p = \frac{[P_{CO}]^2}{[P_{CO_2}]} = \frac{4 \times 4}{2} = 8$$



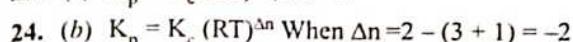
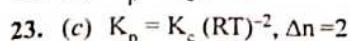
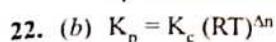
$$K_p = P_{\text{CO}_2}$$

Solid molecule does not have partial pressure so in calculation of  $K_p$  only  $P_{\text{CO}_2}$  is applicable.

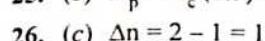


where  $n_p$  = no. of moles of product in gas

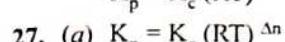
$n_r$  = no. of moles of reactant in gas



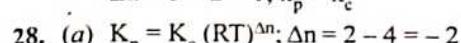
i.e. negative =  $K_p < K_c$



$$K_p = K_c (\text{RT})$$



$\Delta n = 3 - 2 = 1; k_p > k_c$



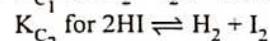
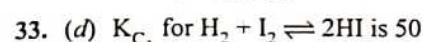
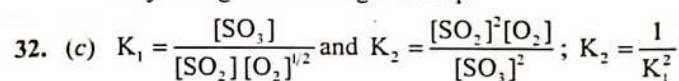
$$K_p = 6 \times 10^{-2} \times (0.0812 \times 773)^{-2}$$

$$K_p = \frac{6 \times 10^{-2}}{(0.0812 \times 773)^2} = 1.5 \times 10^{-5}$$

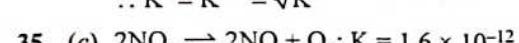
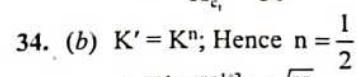
29. (a) Those reaction which have more values of K proceeds towards completion.

30. (c) For this reaction, there is no change in equilibrium constant by change of volume (as  $\Delta n = 0$ ).

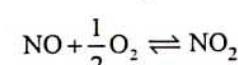
31. (d)  $K_f$  is a characteristic constant for the given reaction its only change with change in temp.



$$K_{C_2} = \frac{1}{K_{C_1}} = \frac{1}{50} = 0.02$$



$$K = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2} \quad \dots(\text{i})$$

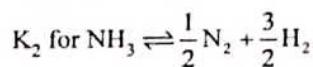
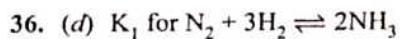


$$K = \frac{[\text{NO}_2]}{[\text{NO}][\text{O}_2]^{1/2}} \quad \dots(\text{ii})$$

On multiplying (i) and (ii)

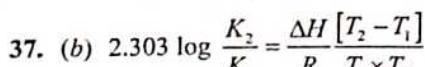
$$K \times K' = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2} \times \frac{[\text{NO}_2]}{[\text{NO}][\text{O}_2]^{1/2}} = \frac{[\text{NO}][\text{O}_2]^{1/2}}{[\text{NO}_2]} = \frac{1}{K}$$

$$K \times K' = \frac{1}{K} ; K = \frac{1}{K'^2} ; K' = \frac{1}{\sqrt{K}}$$

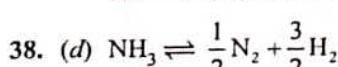


$$K_1 \times K_2 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \times \frac{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}{[\text{NH}_3]}$$

$$K_1 \times K_2 = \frac{1}{K_2} ; K_2 = \frac{1}{\sqrt{K_1}}$$



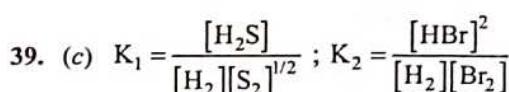
$\Delta H = + \text{ve}$  for the reaction



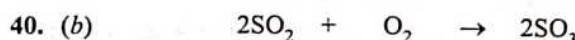
$$K_c = \frac{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}{[\text{NH}_3]} \text{ and } \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftharpoons \text{NH}_3$$

$$K_d = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}$$

$$\text{So for dissociation} = \frac{1}{K_c}$$



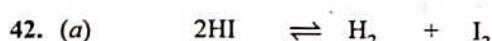
$$K_3 = \frac{[\text{HBr}]^2 \times [\text{S}_2]^{1/2}}{[\text{Br}_2] \times [\text{H}_2\text{S}]} ; \frac{K_2}{K_1} = K_3$$



at eq.      5-3      5-1.5      3

total moles =  $2 + 3.5 + 3 = 8.5$

$$41. (c) K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.1)^2}{0.05} = 0.2$$

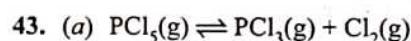


t = 0      3.2

$$\text{At eq}^m \quad 3.2 - 3.2\alpha \quad \frac{3.2\alpha}{2} \quad \frac{3.2\alpha}{2}$$

$$\alpha = \frac{22}{100} = 0.22$$

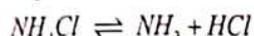
$$\text{So, } n_{\text{HI}} = 3.2 - 3.2 \times 0.22 = 2.496$$



For this reaction  $\Delta n = 2 - 1 = 1$

value of  $\Delta n$  is positive so the dissociation of  $\text{PCl}_5$  take forward by decrease in pressure & by increase in pressure the dissociation of  $\text{PCl}_5$  decrease.

44. (b)  $\frac{\text{Normal molecular weight}}{\text{experimental molecular wt.}} = 1 + \alpha$



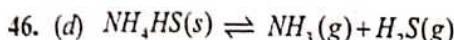
for complete dissociation

$$\therefore \alpha = 1$$

$$\therefore \text{Experimental Molecular wt} = \frac{\text{nor. mol. wt.}}{2}$$

$$45. (b) K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left[\frac{20}{100}\right] \times \left[\frac{20}{100}\right]}{\left[\frac{80}{100}\right]}$$

$$= \frac{0.2 \times 0.2}{0.8} = \frac{0.04}{0.8} = 0.05$$



$$\begin{array}{ll} a & 0.5\text{atm} \\ a-x & 0.5+x \\ & x \end{array}$$

$$\text{Total pressure} = 0.5 + 2x = 0.84$$

$$\text{i.e., } x = 0.17$$

$$K_p = P_{NH_3} \cdot P_{H_2S} = (0.67) \cdot (0.17) = 0.1139$$

$$47. (b) K_p = (P_{NH_3})(P_{H_2S})$$

$$P_{NH_3} = 0.5 + x$$

$$0.11 = (0.5 + x)(x)$$

$$0.11 = 0.5x + x^2$$

$$x^2 + 0.5x - 0.11 = 0$$

$$x = 0.165$$

48. (a) For this reaction  $\Delta n$  is negative &  $\Delta H$  is negative so it take forward by decrease in temperature.

49. (c) According to Le-chatelier principle when concentration of reactant increases, the equilibrium shift in favour of forward reaction.

50. (d) We know that

$$P \text{ become } \frac{1}{2} P \text{ & V become } 2V \text{ so,}$$

$$\frac{1}{2} P \times 2V = PV = nRT$$

So there is no effect in equation

51. (d) Equilibrium constant depends upon temperature.

52. (a) According to Le-Chatelier principle exothermic reaction is forwarded by low temperure, in forward direction number of moles is less, hence pressure is high.

53. (d) Equilibrium constant changes only with temperature, not with pressure and the concentration of either reactant or product.

54. (a)  $N_2 + O_2 \rightleftharpoons 2NO; Q \text{ cal}$

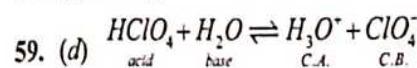
The above reaction is endothermic so for higher production of  $NO$ , and the temperature should be high.

55. (d) According to Le-chatelier's principle.

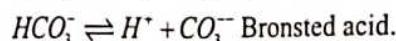
56. (c) At low pressure, reaction proceeds where volume is increasing. This is the favourable condition for the reaction.  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ .

57. (a) T & P.

58. (b) At equilibrium  $\Delta G = 0$ .

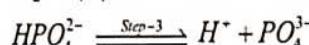
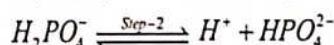
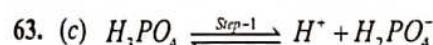


60. (b) Those substance which accept the proton are called Bronsted base and which donate the proton are called Bronsted acid.



61. (c) Because it is an electron pair acceptor as central atom have a vacant d-orbital.

62. (b) The basic character of hydride decreases down the group.



64. (d) Water is a neutral, protic solvent and act as both acid as well as Base.

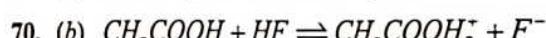
65. (b) According to Bronsted principle  $HNO_3$  is acid so they give  $H^+$  in aqueous solution and form  $NO_3^-$ .

66. (c)  $BF_3$  have vaccant orbital, so it can accept lone pair of  $e^-$ , but can not donate proton.

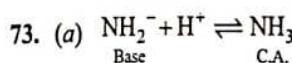
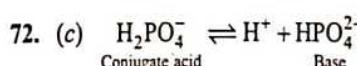
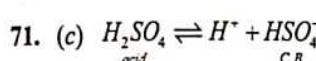
$$67. (d) K_w = [H^+] \times [OH^-] = \text{mol}^2 \text{L}^{-2}$$

$$68. (b) \text{For pure water } [H^+] = [OH^-], \therefore K_w = 10^{-12}$$

69. (a) Because pure water has a 7 pH.



HF gives  $H^+$  to the  $CH_3COOH$ . So it is a conjugate base of  $F^-$



74. (d) Conjugate acid is obtained from the base by means.  $Cl^-$  is a weak base

$$75. (c) \text{pH} = 4 \text{ means; } [H^+] = 10^{-4} \text{ mol}$$

$$76. (d) 10^{-3} \text{N KOH will give } [OH^-] = 10^{-3} \text{M}$$

$$\text{pOH} = 3$$

$$\therefore \text{pH} + \text{pOH} = 14, \text{pH} = 14 - 3 = 11$$

$$77. (b) \text{pH} + \text{pOH} = \text{p}K_w = 14$$

$$78. (a) [OH^-] = 10^{-2} \text{ M; pOH} = 2$$

$$\text{pH} + \text{pOH} = 14; \text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 2 = 12$$

$$79. (b) \frac{N}{100} = 0.01 \text{ N HCl; } [H^+] = 10^{-2} \text{ M; pH} = 2$$

$$[\text{OH}] = 10^{-2} \text{ M for NaOH}$$

$$\text{pH} + \text{pOH} = 14; \text{pH} = 14 - 2; \text{pH} = 12$$



80. (c)  $\text{H}_2\text{O} \rightleftharpoons [\text{H}^+] [\text{OH}^-]$   
 $\text{HC}_l \rightleftharpoons [\text{H}^+] [\text{Cl}^-]$   
 $\text{Total } [\text{H}^+] = [\text{H}^+]_{\text{H}_2\text{O}} + [\text{H}^+]_{\text{HC}_l} = 10^{-7} + 10^{-8}$   
 $= 10^{-7} [1 + 10^{-1}]$   
 $[\text{H}^+] = 10^{-7} \times \frac{11}{10}$   
 $\text{pH} = -\log [\text{H}^+] = -\log \left( 10^{-7} + \frac{11}{10} \right); \text{pH} = 6.958$

81. (c)  $\text{H}_2\text{SO}_4$  ionized in two step  
 $1^{\text{st}} \text{ H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^-$   
 $2^{\text{nd}} \quad \text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-}$

82. (b)  $[\text{H}^+] = 2 \times 10^{-2} \text{ M}$   
 $\therefore \text{pH} = -\log [2 \times 10^{-2}];$   
 $\text{pH} = 1.7 \text{ i.e. in between 1 and 2.}$

83. (b)  $[\text{NaOH(aq)}] = 10^{-3}, \quad \text{pOH} = 3, \text{pH} = 11$   
 $[\text{HCl(aq)}] = 10^{-3}, \quad \text{pH} = 3$   
 $[\text{NaCl(aq)}] = \text{neutral}, \quad \text{pH} = 7$

84. (b)  $10^{-10} \text{ M HC}_l = 10^{-10} \text{ M } [\text{H}^+]$ . But  $\text{pH} \neq 10$  because solution is acidic. This is because  $\text{H}^+$  from  $\text{H}_2\text{O}$  ( $10^{-7} \text{ M}$ ) cannot be neglected.  
 $\text{Total } [\text{H}^+] = 10^{-7} + 10^{-10}$   
 $= 10^{-7} [1 + 10^{-3}] = 10^{-7} (1.001)$   
 That is why  $\text{pH} = 7$  (slightly less than 7)

85. (b) Because the degree of dissociation is inversely proportional to the concentration of the electrolyte.

86. (b) Electrolytes are those substances which dissociates in water to give ions.

87. (a)  $K = \frac{\alpha^2 C}{1-\alpha}; \alpha = \frac{0.01}{100}; \therefore K = \alpha^2 C = \left[ \frac{0.01}{100} \right]^2 \times 1$   
 $= 1 \times 10^{-8}.$

88. (a) NaCl, being a salt, is a strong electrolyte.

89. (c) According to the Ostwald's dilution formula  
 $\alpha^2 = \frac{K(1-\alpha)}{C}$ . But for weak electrolytes  $\alpha$  is very small. So that  $(1-\alpha)$  can be neglected. So that  $\alpha = \sqrt{\frac{K_a}{C}}$ .

90. (b)  $\alpha \propto \text{dilution of solution}$

91. (d) Mathematical form of Ostwald's dilution law.

92. (c)  $[\text{CN}^-] = \sqrt{K_a C} = \sqrt{4 \times 10^{-10} \times 10^{-1}} = \sqrt{4 \times 10 \times 10^{-12}}$   
 $= 6.3 \times 10^{-6}$

93. (d)  $[\text{H}^+] = \alpha \cdot C = \frac{2}{100} \times .02; [\text{H}^+] = 4 \times 10^{-4} \text{ M}$   
 $\text{pH} = -\log [\text{H}^+] = 4 - \log 4; \text{pH} = 3.3979$

94. (b)  $\text{pH} = 3, [\text{H}^+] = 10^{-3} \text{ M} \quad \therefore [\text{H}^+] = \sqrt{K \times c}$   
 $[10^{-3}]^2 = K \times c ; \frac{[10^{-6}]}{0.1} = K = 10^{-5}$

95. (c) For  $\text{NH}_4\text{OH}$ .  
 $[\text{OH}^-] = C \cdot \alpha ; C = \frac{1}{10} \text{ M}, \alpha = 0.2$   
 $[\text{OH}^-] = \frac{1}{10} \times 0.2 = 2 \times 10^{-2} \text{ M}$   
 $\text{pOH} = -\log [\text{OH}^-] = \log [2 \times 10^{-2}] ; \text{pOH} = 1.7$   
 $\text{pH} = 14 - \text{pOH} = 14 - 1.7 = 12.30.$

96. (b)  $\text{NH}_4\text{CN}$  is a salt of weak acid and weak base and thus for it.  
 $K_H = \frac{K_w}{K_a \times K_b}$

97. (b) Alkaline,  
 $\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightleftharpoons \underset{\substack{\text{Weak} \\ \text{acid}}}{\text{CH}_3\text{COOH}} + \underset{\substack{\text{Strong} \\ \text{base}}}{\text{NaOH}}$

98. (c) Because salt of S.A + S.B. does not undergo hydrolysis.

99. (c)  $\text{Fe}^{3+}$  ions are hydrolysed to develop acidic nature

100. (c) 0.001 M of NaOH means  $[\text{OH}^-] = .001 = 10^{-3} \text{ M} \Rightarrow \text{pOH} = 3$   
 $\text{pH} + \text{pOH} = 14 \Rightarrow \text{pH} = 14 - 3 = 11$

101. (c)  $\text{pK}_a = -\log K_a, \text{pK}_b = -\log K_b$   
 $\text{pH} = -\frac{1}{2} [\log K_a + \log K_w - \log K_b]$   
 $= -\frac{1}{2} [-5 + \log (1 \times 10^{-14}) - (-5)]$   
 $= -\frac{1}{2} [-5 - 14 + 5] = -\frac{1}{2} (-14) = 7$

102. (a)  $\text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2 \text{ HCl}$

103. (b) It contains replacable H atom.

104. (a) An acid buffer solution consists of solution of weak acid with strong base of its salt.

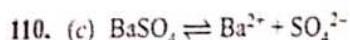
105. (b)  $[\text{Salt}] = 0.1 \text{ M}, [\text{Acid}] = 0.1 \text{ M}$   
 $K_a = 1.8 \times 10^{-5}; \text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$   
 $= -\log (1.8 \times 10^{-5}) + \log \frac{0.1}{0.1} = -(\log 1.8 \times 10^{-5})$   
 $\text{pH} = 4.7$

106. (c)  $\text{CH}_3\text{COONH}_4$  is a simple buffer and called salt of weak acid.

107. (c) A strong acid is not used to make a buffer

108. (a)  $\text{NH}_4\text{OH}$  is a weak acid and  $\text{NH}_4\text{Cl}$  is a strong base salt.

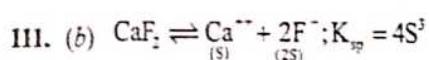
$$109. (a) \text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = (-\log 2 \times 10^{-5}) + \log \frac{10 \times 1}{50 \times 2} = 4.$$



$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

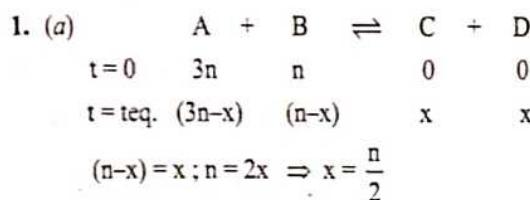
$$K_{sp} = 10^{-9}, [\text{Ba}^{2+}] = 0.01$$

$$[\text{SO}_4^{2-}] = \frac{K_{sp}}{[\text{Ba}^{2+}]} = \frac{10^{-9}}{10^{-2}} = 10^{-7}$$



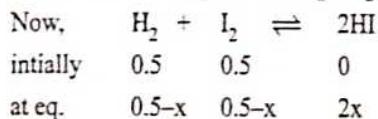
$$112. (d) K_{sp} \text{ for } \text{CaF}_2 = 4s^3 = 4 \times [2 \times 10^{-4}]^3 = 3.2 \times 10^{-11}.$$

## Exercise-2 (Learning Plus)



2. (b) Given: Volume = 20.0 lit

0.50 mole of each gas that is  $\text{H}_2$  &  $\text{I}_2$



$$K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$49 = \frac{(2x)^2}{(0.5-x)^2} \quad (\text{as } K_{eq} = 49)$$

$$7 = \frac{2x}{0.5-x}$$

$$2x = 3.5 - 7x$$

$$9x = 3.5$$

$$x = 0.39$$

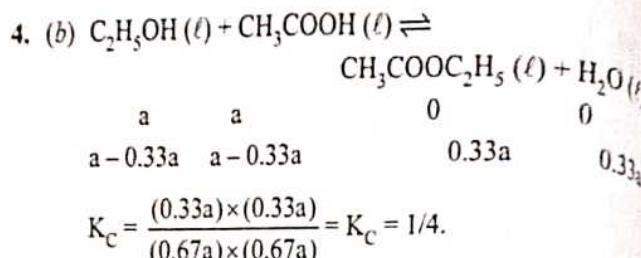
$$[\text{HI}] = \frac{2x}{20} = \frac{x}{10} \Rightarrow \frac{3.9}{10} = 0.039$$

3. (a) Given: Equilibrium constant,  $K_C = 2.5$

We know:

$$\frac{K_f}{K_b} = 2.5$$

$$K_f = 2.5 \times 3.2 \times 10^{-2} = 8 \times 10^{-2}$$



5. (a) Given:  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

At equilibrium

$$\text{conc. of } \text{N}_2\text{O}_4 = 4.8 \times 10^{-2} \text{ mol/lit}$$

$$[\text{NO}_2] = 1.2 \times 10^{-2} \text{ mol/lit}$$

$$\therefore K_C = \frac{(1.2 \times 10^{-2})^2}{(4.8 \times 10^{-2})} = 3 \times 10^{-3}$$

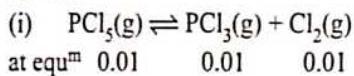
6. (b) Given:  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g); K_C = 4 \times 10^{-4}$

$$\text{Now, } \text{NO}(g) \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g)$$

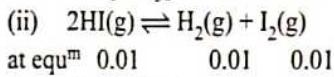
$$K'_C = ?$$

$$K_C \frac{1}{[K_C]^{1/2}} \Rightarrow \frac{1}{(4 \times 10^{-4})^{1/2}} \Rightarrow \frac{1}{2 \times 10^{-2}} \Rightarrow 50$$

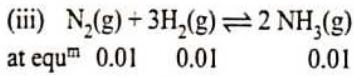
7. (b) Given:



$$K_{ci} = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \Rightarrow \frac{0.01 \times 0.01}{0.01} = 0.01$$



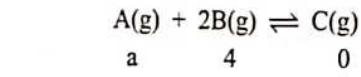
$$K_{ci} = \frac{0.01 \times 0.01}{(0.01)^2} = 1$$



$$K_{ci} = \frac{(0.01)^2}{(0.01)(0.01)^3} = \frac{1}{10^{-4}} = 10^4$$

Extent of reaction  $K_C \rightarrow (iii) > (ii) > (i)$

8. (c) Given: reaction



as  $x = 1$

$$n_{A(g)} = a-1, \quad n_{B(g)} = 2, \quad n_{C(g)} = 1$$

$$[A] = \frac{a-1}{5}, \quad [B] = \frac{2}{5}, \quad [C] = \frac{1}{5}$$

$$K_C = \frac{(1/5)}{\left(\frac{2}{5}\right)^2 \left(\frac{a-1}{5}\right)} ; K_c = \frac{25}{4(a-1)} \quad ... (i)$$

as  $K_C = 0.25$

from (i) & (ii)

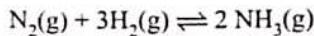
$$0.25 = \frac{25}{4(a-1)}$$

$$\Rightarrow 4(a-1) = 100$$

$$a-1 = 25 \Rightarrow a = 26$$



9. (b) Given 1 mole N<sub>2</sub>, 3 mole H<sub>2</sub>  
total pressure = 4 atm



initially	1	3		
at equilibrium	1-x	3-3x	2x	

$$P_{\text{total}} = 1 - x + 3 - 3x + 2x \\ = 4 - 2x$$

as given in question

P<sub>total</sub> fall to 3 atm

$$\therefore P_{\text{total}} = 3$$

from (i) & (ii)

$$3 = 4 - 2x \Rightarrow x = \frac{1}{2}$$

$$P_{N_2} = \frac{1}{2}; P_{H_2} = 3 - \frac{3}{2} = \frac{3}{2}; P_{NH_3} (\text{eq.}) = 2 \times \frac{1}{2} = 1$$

$$(\text{for formation of } NH_3) K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{(1)^2}{\frac{1}{2} \times \left(\frac{3}{2}\right)^3} \\ = \frac{1}{0.5 \times (1.5)^3}$$

$$K_p \text{ for dissociation of } NH_3 \Rightarrow (0.5) \times (1.5)^3$$

10. (a) 2H<sub>2</sub>O(g) + 2Cl<sub>2</sub>(g) ⇌ 4HCl(g) + O<sub>2</sub>(g)

$$K_p = 0.03, T = 427^\circ C = 700 \text{ K}$$

$$K_p = K_C (RT)^{\Delta n_g}$$

$$K_C = \frac{K_p}{RT} = \left[ \frac{0.03}{0.082 \times 700} \right]$$

$$K_C = 5.23 \times 10^{-4}$$

11. (b) Using  $K_p = K_C (RT)^{\Delta n_g}$

$$\text{so, } \log \frac{K_p}{K_c} = \Delta n_g \log RT$$

so,  $\Delta n_g = -1$ , this is for (b).

12. (d) Given: N<sub>2</sub>O<sub>4</sub>(g) ⇌ 2NO<sub>2</sub>(g)

$$K_p = K_C$$

$$K_p = K_C (RT)^{\Delta n_g}$$

$$\Delta n_g = 2 - 1 \Rightarrow 1$$

$$K_p = K_C \times RT$$

$$RT = 1 \text{ T} = \frac{1}{R}$$

$$\Rightarrow \frac{1}{0.082} \Rightarrow 12.19 \text{ K}$$

$$T = 12.19 \text{ K}$$

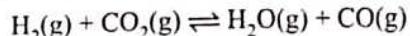
13. (c) Given: CO(g) +  $\frac{1}{2}$ O<sub>2</sub>(g) ⇌ CO<sub>2</sub>(g)

$$\Delta n_g = 1 - \left( \frac{1}{2} + 1 \right), \Delta n_g = -\frac{1}{2}$$

as we know

$$K_p = K_C (RT)^{\Delta n_g} \Rightarrow \frac{K_p}{K_c} = (RT)^{-1/2}$$

14. (b) Given: Reaction as



$$\text{Here } K_p = K_C$$

$$\text{initially } 0.25 \quad 0.25 \quad 0 \quad 0$$

$$\text{at eq. } 0.25-x \quad 0.25-x \quad x \quad x$$

$$K_C = \frac{[CO][H_2O]}{[H_2][CO_2]} \Rightarrow \frac{x^2}{(0.25-x)^2}$$

$$\Rightarrow 0.16 = \frac{x^2}{(0.25-x)^2}$$

$$[\text{as } K_p = K_C = 0.16]$$

$$\Delta n_g = 0$$

$$\frac{x}{(0.25-x)} = 0.4$$

$$x = 0.1 - 0.4x$$

$$x = \frac{0.1}{1.4} = \frac{1}{14}$$

$$\% \text{ mole of CO} = \frac{(1/14)}{\text{total mole}} \times 100$$

$$\text{total mole} = 0.5 \text{ mole}$$

$$\% \text{ mole of CO} = \frac{(1/14)}{0.5} \times 100 \\ = 14.28\%$$

15. (c) Given: H<sub>2</sub>(g) + I<sub>2</sub>(g) ⇌ 2HI(g); K<sub>p</sub> = 50

$$K_p = K_C (RT)^{\Delta n_g}$$

now,

$$\Delta n_g = 2 - 2 = 0$$

$$\therefore K_p = K_C$$

$$K_C = 50$$

16. (a) PCl<sub>5</sub> dissociation in a closed container



$$1 \quad 0 \quad 0$$

$$1 - \alpha \quad \alpha \quad \alpha$$

$$\text{Total mole} = 1 - \alpha + \alpha + \alpha$$

$$\Rightarrow 1 + \alpha$$

$$\chi_{PCl_3} = \frac{\alpha}{1 + \alpha}$$

$$\therefore (\text{partial pressure}) P_{PCl_3} = P \left[ \frac{\alpha}{1 + \alpha} \right]$$

17. (a)  $\alpha = \frac{D-d}{d} \Rightarrow \alpha = \frac{D}{d} - 1; \alpha + 1 = \frac{D}{d}$

$$1 + \alpha = \frac{D}{d}$$

y = mx + c, By comparing we get

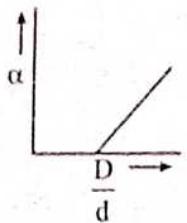
$$m = 1, c = 0$$

18. (b)  $\alpha = \frac{D-d}{(n-1)d}; \alpha = \frac{D-d}{d}$

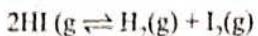
$$\alpha = \left[ \frac{D}{d} - 1 \right]; \left( \frac{D}{d} \right) = \alpha + 1$$

$$\alpha = \left( \frac{D}{d} \right) - 1.$$

Comparing with  $y = mx + c$   
 $m = +ve, c = -ve$



19. (d) Given: Reacion



$$1 \quad 0 \quad 0$$

$$1-\alpha \quad \frac{\alpha}{2} \quad \frac{\alpha}{2}$$

$$\text{C}(1-\alpha) \quad \frac{\text{Ca}}{2} \quad \frac{\text{Ca}}{2}$$

(where  $\alpha$  is degree of dissociation)

$$\text{as } K_C = K_p = \frac{\alpha^2}{4(1-\alpha)^2}$$

$$\sqrt{K_p} = \frac{\alpha}{2(1-\alpha)}, 2\sqrt{K_p} = \frac{\alpha}{1-\alpha}$$

$$\frac{1-\alpha}{\alpha} = \frac{1}{2\sqrt{K_p}} \Rightarrow \frac{1}{\alpha} - 1 = \frac{1}{2\sqrt{K_p}}, \frac{1}{\alpha} = 1 + \frac{1}{2\sqrt{K_p}}$$

$$\frac{1}{\alpha} = \frac{2\sqrt{K_p} + 1}{2\sqrt{K_p}} \Rightarrow \alpha = \frac{2\sqrt{K_p}}{2\sqrt{K_p} + 1}$$

20. (a)  $(\text{VD})_{\text{mix}} = \frac{M_{\text{mix}}}{2} = \frac{M}{2(1+\alpha)}$

so, as  $\alpha$  increases  $(\text{VD})_{\text{mix}}$  decreases.

21. (a) Given: V.D of  $\text{N}_2\text{O}_4 = 30$



$$1 \quad 0$$

$$1-\alpha \quad 2\alpha$$

$$\text{Total mole} = 1 + 2\alpha - \alpha \Rightarrow 1 + \alpha$$

Mass conservation

(wt. of  $\text{N}_2\text{O}_4$  at  $t = 0$ ) = (wt. of mixture.)

$$1 \times (92) = (1 + \alpha) 2 \times 30$$

$$\Rightarrow \frac{92}{60} = 1 + \alpha, \alpha = \frac{32}{60} \Rightarrow \frac{8}{15}$$

$$\alpha \% = \frac{8}{15} \times 100 = 53.3\%$$

22. (a) Given:



$$1 \quad 1 \quad 0 \quad 0$$

$$1-\alpha \quad 1-\alpha \quad \alpha \quad \alpha$$

$$K = \frac{[\text{C}][\text{D}]}{[\text{B}][\text{A}]}, K = \frac{\alpha^2}{(1-\alpha)^2}$$

$$\sqrt{K} = \frac{\alpha}{1-\alpha}, \frac{1-\alpha}{\alpha} = \frac{1}{\sqrt{K}}$$

$$\frac{1}{\alpha} = \frac{1+\sqrt{K}}{\sqrt{K}}$$

Now,

$$\alpha = \frac{\sqrt{K}}{1+\sqrt{K}}$$

23. (a) Given:  $\text{A(g)} \rightleftharpoons \text{B(g)} + \text{C(g)} + \text{D(g)}$

$$\text{initially} \quad 1 \quad 0 \quad 0 \quad 0$$

$$\text{at eq.} \quad 1-x \quad x \quad x \quad x$$

$$\text{Total mole} = 1 + 2x$$

Apply mass conservation

(Wt. of A at  $t = 0$ ) = (wt of mixture at eq.)

$$1 \times M_{\text{wt.}} = [1 + 2x] 2 \times 50$$

$$M_{\text{wt.}} = (1 + 0.2) \times 100 \text{ (as } x = 0.1)$$

$$M_{\text{wt.}} = 120$$

24. (c) Given:  $\text{N}_2\text{O}_4$  dissociated



$$1 \quad 0$$

$$\text{at eq.} \quad (1-x) \quad 2x$$

$$\text{Total mole} = 1 - x + 2x = 1 + x$$

Mass conservation

(wt. of  $\text{N}_2\text{O}_4$  at  $t = 0$ ) = (wt. of  $\text{NO}_2$  at eq.)

$$1 \times 92 = (1 + x) \times 82$$

$$\frac{92}{82} - 1 = x$$

$$x = \frac{10}{82}$$

$$x \% = \frac{10}{82} \times 100 = 12.2\%$$

25. (b) We know that  $d = \frac{D}{1 + (n-1)\alpha}$

where  $n$  is number of mole of gases produced from one mole of a gas.

26. (b)  $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$

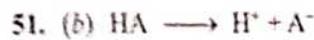
$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{50}{66.9} = \frac{\Delta H}{2.303R} \left[ \frac{1}{623} - \frac{1}{721} \right]$$

After calculation negative value of  $\Delta H$  is obtained.

27. (a)  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \Delta n_g = 0$   
 If we change the volume the ultimate effect will be due to change in pressure.  
 $\Rightarrow$  If  $\Delta n_g = 0$   
 no effect of change in volume.
28. (d) On adding any reactant equilibrium shifts in forward direction, so amount of product increases.
29. (b) On adding inert gas at constant pressure effect on equilibrium will be similar to as if volume of container has been increased.
30. (b) For any physical equilibrium on increasing pressure equilibrium shifts in the direction of higher density.
31. (c) Solubility of gas is directly proportional to the pressure of gas above liquid.
32. (a)  $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$   
 Volume of container is constant  
 so no effect of addition of inert gas.
33. (d) Exothermic  
 $\Rightarrow$  low yield at high temperature  
 $\Delta n_g < 0$   
 $\Rightarrow$  low yield at low pressure
34. (a)  $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$   
 $\Delta n_g = 2 - 1 \Rightarrow 1$   
 $\Delta n_g > 0$   
 $\Rightarrow$  so on increasing the pressure equilibrium shifted left (or backward direction)  
 as pressure increases volume decreases.
35. (a)  $\ln k_p = \frac{-\Delta H}{RT} + \ln A$   
 For exothermic  $\Delta H < 0$   
 so, slope +ve
36. (c) Amphiprotic: can accept and Release  $H^+$   
 Only  $H_2PO_4^-$  &  $HCO_3^-$
37. (d) Fact based
38. (a)  $[OH^-] = 10^{-7}$  in pure water.  
 So as temperature increases  $K_w$  increases  $\Rightarrow [OH^-]$  decreases.
39. (c) Factual.
40. (b) In this solution, source of  $OH^-$  is water  
 $\therefore C\alpha = [OH^-]$ , C(molarity) of  $H_2O = 55.55$   
 $\alpha = 1.8 \times 10^{-11} M$   
% ionisation =  $1.8 \times 10^{-9} M$
41. (d)  $[H^+]_1 = 10^{-2}; [H^+]_2 = 10^{-6}$ ; Factor =  $10^4$
42. (c)  $[H^+] = 0.016 M$   
 $[H^+] [OH^-] = 10^{-14} \Rightarrow [OH^-] = 6.25 \times 10^{-13} M$
43. (a) Initial Final  
 $pH = 12$   $pH = 11$   
 $[H^+] = 10^{-12} M$   $[H^+] = 10^{-11} M$   
 $[OH^-] = 10^{-2} M$   $[OH^-] = 10^{-3} M$   
 Initial No. of mole of  $OH^- = 10^{-2}$  Final No. of mole of  $OH^- = 10^{-3}$   
 So no. of mole of  $OH^-$  removed =  $[0.01 - 0.001] = 0.009$

44. (d)	HCl c × v	NaOH c × v	$[H^+]_{\text{remaining}}$	pH
(a)	$\frac{1}{10} \times 100$	$\frac{1}{10} \times 100$	neutral	7
(b)	$\frac{1}{10} \times 55$	$\frac{1}{10} \times 45$	$\frac{1}{100}$	2
(c)	$\frac{1}{10} \times 10$	$\frac{1}{10} \times 90$	Basic as $OH^-$ $pH > 7$ are more	
(d)	$\frac{1}{5} \times 75$	$\frac{1}{5} \times 25$	$\frac{10}{100}$	1
45. (c)	$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$  $0.01$ $0.01 - 0.01\alpha$	$0.01\alpha$	$0.01\alpha$	
	$[HCl^-] = 0.01$			
	$[H^+]_T = 0.01 + 0.01\alpha$			
	as $\alpha$ is small, so			
	$0.01 + 0.01\alpha = 0.01$			
	$K_d = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$			
	$K_d = \frac{(0.01\alpha)(0.01)}{0.01 - 0.01\alpha}$			
	as $\alpha$ is small so			
	$0.01 - 0.01\alpha \approx 0.01$			
	$1.69 \times 10^{-5} = \frac{(0.01\alpha)(0.01)}{0.01 - 0.01\alpha}$			
	on solving we get			
	$\alpha = 1.69 \times 10^{-3}$			
46. (c)	$pH = pK_a + \log \left[ \frac{\text{salt}}{\text{acid}} \right]$			
	50% ionised $\Rightarrow [Salt] = [Acid]$			
	$\Rightarrow pH = pK_a = 4.5 \Rightarrow pOH = 9.5$			
47. (a)	$M_{eq}$ of HCl = $25 \times 0.5 = 12.5$			
	$M_{eq}$ of NaOH = $10 \times 0.5 = 5$			
	$M_{eq}$ of HCl remaining $12.5 - 5 = 7.5$			
	$[H^+] = 0.15$			
	$pH = -\log(0.15)$			
	$= 0.8239$			
48. (a)	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$			
	$P^{OH} = 3, [OH^-] = 10^{-3}, \% \text{ dissociation} = \frac{10^{-3}}{0.05} \times 100 = 2\%$			
49. (d)	As concentration of solution decreases, degree of dissociation of weak electrolyte increases.			
50. (c)	$HF \longrightarrow H^+ + F^-$			
	$pK_w = pK_a + pK_b$ [For conjugate Acid-Base]			
	$\Rightarrow pK_a = 14 - 10.87 = 3.17$			
	$K_a = 6.76 \times 10^{-4}$			



$$\begin{array}{ccc} 1-x & x & x \\ x = 1\% = 0.01 & & \end{array}$$

$$\Rightarrow [\text{H}^+] = 0.01$$

$$\Rightarrow \text{pH} = 2$$



$$[\text{H}^+] = \frac{0.1}{100} = 10^{-3}$$

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

$$\text{pH} = -\log[10^{-3}]$$

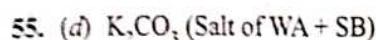
$$\text{pH} = 3$$

53. (b) % Hydrolysis does not depend on the conc. in case of "Weak acid + weak base : Salt"

54. (a) % h =  $\sqrt{\frac{K_b}{C}}$ ,  $K_b = \frac{K_w}{K_a}$

$$\% h = \sqrt{\frac{K_w}{K_a \cdot C}} = \sqrt{\frac{10^{-14} \times 80}{1.3 \times 10^{-9} \times 1}}$$

$$\% h = 2.48\%$$



56. (c) Salt of weak acid & weak base

$$\text{pH} = [\text{pK}_w + \text{pK}_a - \text{pK}_b] = [14 + 4.8 - 4.78]$$

$$\text{pH} = 7.01$$

57. (b) Solution of HCl &  $\text{NH}_4\text{Cl}$  will be acidic, solution of NaCl neutral whereas solution of NaCN will be basic.

58. (a)  $\text{NaCl} + \text{HCl}$  : Not the Buffer

and Solution is acidic due to HCl.  
 $\Rightarrow \text{pH} < 7$ .

59. (d) m. equivalent of KOH = 8

m. equivalent of HCOOH = 16

Remaining m. eq. after reaction (HCOOH) = 8

Formed m. eq. (HCOOK) = 8

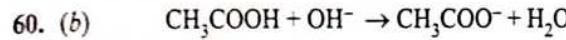
$\Rightarrow$  Acidic Buffer

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

As [salt] = [acid]

$$\text{pH} = \text{p}K_a = 3.7$$

$$\text{pOH} = 10.3$$



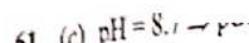
$$\begin{array}{ccccc} t=0 & 20 \text{ m} & 20 \text{ m} & & \\ & - & - & & \end{array}$$

$$t = \text{eq} \quad 20 \text{ m}$$

$$\text{So, } [\text{CH}_3\text{COO}^-] = \frac{20}{200} = 0.1 \text{ M}$$

$$\text{pH} = \frac{1}{2}[14 + 4.74 + \log(0.1)]$$

$$\text{pH} = 8.87$$



Basic Buffer

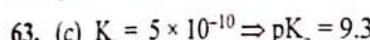
$$\Rightarrow \text{pOH} = \text{p}K_b + \log \left[ \frac{\text{salt}}{\text{base}} \right]$$

If volume of salt = V ml

$$\Rightarrow 5.3 = 4.7 + \log \left[ \frac{0.2 \times V}{10} \right]$$

$$\Rightarrow V = 200 \text{ ml}$$

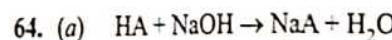
62. (d) Because it is an acidic buffer.



$$\text{pH} = \text{p}K_b + \log \left[ \frac{\text{salt}}{\text{acid}} \right]$$

$$9 = 9.3 + \log \frac{5 \times V}{10 \times 2}$$

$$V = 8 \text{ ml}$$



$$\begin{array}{ccccc} 10 & x & 10 & & \\ 10-x & - & 10+x & & \end{array}$$

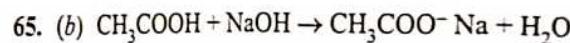
$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$5.5 = 5 + \log \left[ \frac{10+x}{10-x} \right] \quad 5 = \log \left[ \frac{10+x}{10-x} \right]$$

on solving

$$x = 5.192 \text{ mmol}$$

$$\text{wt of NaOH} = 40 \times 5.192 = 0.208 \text{ g}$$



$$\begin{array}{ccccc} 40 & 20 & & & \\ 20 & - & & & 20 \\ & & & & 20 \end{array}$$

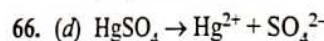
pH for acidic buffer

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log(1.8 \times 10^{-5}) + \log \left[ \frac{20/200}{20/200} \right]$$

$$\text{pH} = 4.74$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.74} \Rightarrow [\text{H}^+] = 1.81 \times 10^{-5}$$



$$- \quad \text{S} \quad \text{S}$$

$$\text{Ksp} = \text{S}^2$$

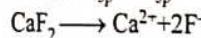
$$\Rightarrow 6.4 \times 10^{-5} = \text{S}^2$$

$$\Rightarrow \text{S} = 8 \times 10^{-3} \text{ mole/L}$$

$$\text{S} = 8 \times 10^{-3} \times 10^3 \text{ mole/m}^3$$

$$\Rightarrow \text{S} = 8 \text{ mole/m}^3$$

67. (b) For ppt  $Q_{sp} > K_{sp}$



$$Q_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

$$(a) Q_{sp} = 12.5 \times 10^{-14} \quad (b) Q_{sp} = 12.5 \times 10^{-10}$$

$$(c) Q_{sp} = 12.5 \times 10^{-13} \quad (d) Q_{sp} = 12.5 \times 10^{-15}$$

Only (b) option will get precipitate.

68. (d) WA Vs SB end point > 7, Phenolphthalein

69. (a) Ppt. occurs only when

$$K_{sp} > K_{sp}$$

$$K_{sp} = [Ag^+] [Cl^-]$$

$$= \frac{10^{-4} \times 10^{-4}}{4} = \frac{10^{-8}}{4} = 2.5 \times 10^{-9}$$

70. (c)  $Q_{sp}(AgBr) = [Ag^+] [Br^-]$

$$\Rightarrow Q_{sp} = 2 \times 10^{-16}$$

$$Q_{sp} < K_{sp}$$

$\Rightarrow$  No precipitation

$$[Ag^+] = 10^{-7} M$$

71. (c)  $HIn \rightleftharpoons H^+ + In^-$

$$P^H = P^{Ka} + \log \left[ \frac{\text{Ionised}}{\text{Unionised}} \right]$$

$$6 = 5 + \log \left[ \frac{\text{Ionised}}{\text{Unionised}} \right]$$

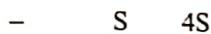
$$1 = \log \left[ \frac{\text{Ionised}}{\text{Unionised}} \right]$$

$$\frac{\text{Ionised}}{\text{Unionised}} = \frac{10}{1}$$

Ionised = 10, Unionised = 1

$$\frac{\text{Ionised}}{\text{Ionised} + \text{Unionised}} = \frac{10}{10+1} = \frac{10}{11}$$

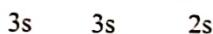
72. (a)  $MX_4 \rightarrow M^{4+} + 4X^-$



$$K_{sp} = [S][4S]^4$$

$$\Rightarrow K_{sp} = 256S^5 \Rightarrow S = \left( \frac{K_{sp}}{256} \right)^{1/5}$$

73. (d)  $Li_3Na_3(AlF_6)_2 \rightarrow 3Li^+ + 3Na^+ + 2[AlF_6]^{3-}$

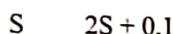


$$K_{sp} = (3s)^3 (3s)^3 (2s)^2 = 2916 s^8.$$

74. (c)  $CaF_2 \rightarrow Ca^{2+} + 2F^-$



On adding 0.1 M NaF



As S is small so  $2S + 0.1 \approx 0.1$

$$K_{sp} = [Ca^{2+}] [F^-]^2$$

$$3.4 \times 10^{-11} = S \times (0.1)^2$$

$$S = 3.4 \times 10^{-9}$$

75. (a)  $Ag_2CO_3 \rightarrow 2Ag^+ + CO_3^{2-}$



Here  $[Ag^+] = 2s = 2 \times 10^{-4} M \Rightarrow s = 1 \times 10^{-4}$

$$\therefore K_{sp} = 4s^3 = 4(1 \times 10^{-4})^3 = 4 \times 10^{-12}$$

76. (c)  $Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$

$$2 \times 0.01 \quad 0.01$$

$Ag_2CO_3 \rightarrow 2Ag^+ + CO_3^{2-}$

$$2x \quad (x+0.01)$$

$$x + 0.01 \approx 0.01$$

$$K_{sp} = 4x^2 (0.01)$$

$$K_{sp} = 4 \times 10^{-12} = 4x^2 (0.01) = x = 10^{-5}$$

77. (c) order of solubility: Complex formation > Pure water > Common ion effect.

So,  $s_1 > s_3 > s_2 > s_4$

78. (a)  $K_{sp}(BaCrO_4) = 2.4 \times 10^{-10} M^2$

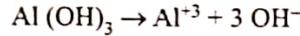
$$[CrO_4^{2-}] = 6 \times 10^{-4}$$

$$K_{sp}(BaCrO_4) = [Ba^{2+}] [CrO_4^{2-}] = 2.4 \times 10^{-10}$$

$$\Rightarrow [Ba^{2+}] \times 6 \times 10^{-4} = 2.4 \times 10^{-10}$$

$$[Ba^{2+}] = 4 \times 10^{-7} M \text{ Ans.}$$

79. (a)  $pH = 4 \Rightarrow [H^+] = 10^{-4} M \Rightarrow [OH^-] = 10^{-10} M$



$$K_{sp}(Al(OH)_3) = [Al^{3+}] [OH^-]^3$$

$$[Al^{3+}] [OH^-]^3 = 1 \times 10^{-33}$$

$$[Al^{3+}] (10^{-10})^3 = 1 \times 10^{-33} \Rightarrow [Al^{3+}] = 10^{-3} M$$

80. (d) Higher the concentration of  $H^+$ , higher is the solubility of  $Fe(OH)_3$ .

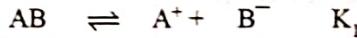
solubility of  $Fe(OH)_3$  is maximum in 0.1 M  $H_2SO_4$

81. (a) order of solubility: Complex formation > Pure water > Common ion effect.

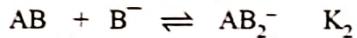
$AgBr$  form complex  $[Ag(NH_3)_2]^+$  in  $NH_3$ , so solubility is maximum in  $NH_3$  (aq).

### Exercise-3 (JEE Advanced Level)

1. (a,c)



$$y \quad y-x$$



$$y-x \quad x$$

$$\Rightarrow K_1 = (y-x)y, K_2 = \frac{x}{y-x}$$

$$\Rightarrow \frac{k_1}{k_2} = \frac{y}{x}(y-x)^2$$

$$[B^-] = y-x$$

2. (a,c)

(a) An irreversible reaction goes to almost completion.

(b) At equilibrium, the rate of forward reaction becomes equal to that of backward reaction

3. (a,b,c)

4. (c,d) Based on theory

5. (b,c) Based on theory

6. (c,d)

Addition of solids have no effect on equilibrium and temperature favours endothermic direction while increasing pressure will shift equilibrium in backward direction as  $\Delta n_g$  is +ve.

7. (b,c)

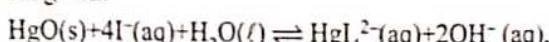
Exothermic  $\Rightarrow$  low temp

$\therefore$  forward reaction favoured

High temp backward

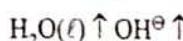
8. (c,d)

As given:



$$K = \frac{[\text{HgI}_4^{2-}][\text{OH}^-]^2}{[\text{I}^-]^4}$$

as,  $\text{OH}^{\ominus} \uparrow \text{HgI}_4^{2-} \downarrow$



9. (c,d)

Introduction of inert gas at constant Pressure have effect of decrease in Pressure & addition of reactant amount always take place forward reactions.

$\Rightarrow$  equilibrium shifted forward

10. (c,d)

As few moles of  $\text{CO(g)}$  are introduced into the vessel second equilibrium shifts backward, decreasing the concentration of  $\text{Cl}_2$ . So, first equilibrium will go forward.

11. (a,c)

Addition of solids have no effect on equilibrium and temperature favours endothermic direction while increasing pressure will shift equilibrium in backward direction as  $\Delta n_g$  is +ve.

12. (a,b,c)

Addition of inert gas at constant volume has no effect on equilibrium concentrations.

13. (b,d)

$$\text{pK}_a(\text{H}_3\text{O}^+) = -1.74 = \text{pK}_b \text{ of } \text{OH}^-$$

$$\text{pK}_a + \text{pK}_b = 14 \text{ only for conjugate acid base pair.}$$

$$\alpha = 1.8 \times 10^{-9} \text{ or } 1.8 \times 10^{-7} \% \text{ for H}_2\text{O.}$$

14. (a,b,c)

$$(a) \text{pK}_w = -\log K_w = -\log(1 \times 10^{-12}) = 12.$$

$$(b) K_w = [\text{H}^+][\text{OH}^-] = 10^{-12}.$$

$$[\text{H}^+] = [\text{OH}^-]$$

$$\Rightarrow [\text{H}^+]^2 = 10^{-12}; [\text{H}^+] = 10^{-6}; \text{pH} = -\log[\text{H}^+]$$

$$= -\log 10^{-6} = 6.$$

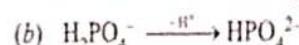
(c)  $\text{H}_2\text{O}$  is neutral because  $[\text{H}^+] = [\text{OH}^-]$  at 373 K even when pH = 6.

(d) is not correct at 373 K. Water cannot become acidic.

15. (b,c)

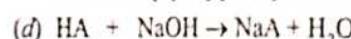
(a) pH of  $10^{-8}$  m sol. of HCl is 6.97

(consider the  $\text{H}^+$  from  $\text{H}_2\text{O}$  also)



$$(c) \text{K}_w = [\text{H}^+][\text{OH}^-]$$

On  $\uparrow$  temp  $[\text{H}^+][\text{OH}^-]$  both  $\uparrow \Rightarrow \text{K}_w \uparrow$



C C

C-C/2 C-C/2 C/2 C/2

$$\text{pH} = \text{pK}_a + \log \frac{\text{salt}}{\text{acid}}$$

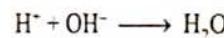
$$\text{pH} = \text{pK}_a \text{ as [salt]} = \text{[acid]}$$

16. (b,c,d)

(b), (c) and (d) are the mixture of conjugate acid-base pairs.

17. (a,d)

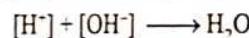
$$(a) [\text{H}^+] = 10^{-2} \text{ and } [\text{OH}^-] = 10^{-2}$$



This leads complete neutralisation

$$\text{so, pH} = \frac{2+12}{2} = 7$$

$$(d) [\text{H}^+] = 10^{-5} \text{ and } [\text{OH}^-] = 10^{-5}$$



This leads complete neutralisation

$$\text{so, pH} = \frac{5+9}{2} = 7$$



0.09 0.09

- 0.09 0.09 0.09-x x

$$[\text{H}^+]_T = [\text{H}^+]_{\text{HCl}} + [\text{H}^+]_{\text{Cl}_2\text{HCCOOH}}$$

$$= 0.09+x = 0.09+x$$

$$\text{At pH} = 1; \text{pH} = -\log[\text{H}^+] \Rightarrow [\text{H}^+] = 10^{-1} = 0.1$$

Now

$$0.09+x = 0.1 \Rightarrow x = 0.01$$

$$Ka(\text{CHCl}_2\text{COOH}) = \frac{[\text{CHCl}_2\text{COO}^-][\text{H}^+]}{[\text{CHCl}_2\text{COOH}]}$$

$$= \frac{0.1 \times 0.1}{(0.09-0.01)} = 1.25 \times 10^{-2}$$

19. (a,c,d)

$$[\text{H}^+]_{\text{CH}_3\text{COOH}} = \sqrt{\text{Ka} \cdot \text{c}} = \sqrt{1.8 \times 10^{-5} \times 0.1}$$

$$= 1.34 \times 10^{-3}\text{M}$$

The solution which have  $[\text{H}^+]$  range  $1.34 \times 10^{-3}$  will not change pH.

Sol. A, C, D provide,  $[\text{H}^+]$  in this range.



20. (a, b, c)

$$\text{Total } [\text{H}^+] = \sqrt{K_a C_1 + K_b C_2}$$

$$= \sqrt{\left(3.6 \times 10^{-4} \times \frac{0.5}{500} \times 100\right) + \left(8 \times 10^{-4} \times \frac{0.1}{500} \times 400\right)}$$

$$\therefore [\text{H}^+] = 10^{-2} \text{ M.}$$

$$\text{For HN}_3, [\text{N}_3^-] = \frac{K_a [\text{HN}_3]}{[\text{H}^+]} = \frac{3.6 \times 10^{-4} \times 0.5}{0.01 \times 500} \times 100$$

$$= 3.6 \times 10^{-3} \text{ M.}$$

$$\text{For HOCl, } [\text{OCN}^-]$$

$$= \frac{K_b [\text{HOCl}]}{[\text{H}^+]} = \frac{8 \times 10^{-4} \times 0.1 \times 400}{0.01 \times 500} = 6.4 \times 10^{-3} \text{ M.}$$

21. (a,c)

As  $K_a$  of acid increases,  $K_b$  of its conjugate base decreases.

22. (b,c)

On the basis of Ostwald dilution law, number of  $\text{H}^+$  ions will increase but increase in volume will be more. Therefore,  $[\text{H}^+]$  decreases, pH increases.

23. (b,c,d)

$$\% h = \sqrt{\frac{K_w}{K_a C}}, \text{ from given formula}$$

(a) depends on concentration

(b)  $h \propto \frac{1}{\sqrt{C}}$  with dilution C decrease so h increase

(c)  $h \propto \frac{1}{K_h}$

(d)  $h \propto K_w \& K_w \propto T$

24. (a,d)

$$(a) \frac{[\text{H}_3\text{AsO}_4]}{[\text{H}_2\text{AsO}_4^-]} = \frac{[\text{H}^+]}{K_1} = \frac{10^{-8}}{2.5 \times 10^{-4}} = \frac{1}{25000}$$

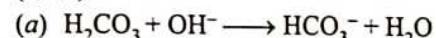
$\therefore [\text{H}_3\text{AsO}_4] \ll [\text{H}_2\text{AsO}_4^-]$ .

$$(b) \frac{[\text{H}_2\text{AsO}_4^-]}{[\text{HAsO}_4^{2-}]} = \frac{[\text{H}^+]}{K_2} = \frac{10^{-8}}{5 \times 10^{-8}} = \frac{1}{5}$$

$$(c) \frac{[\text{AsO}_4^{3-}]}{[\text{HAsO}_4^{2-}]} = \frac{K_3}{[\text{H}^+]} = \frac{2 \times 10^{-13}}{10^{-8}} = \frac{1}{50000}$$

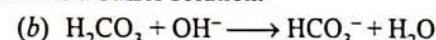
$\therefore [\text{AsO}_4^{3-}] \ll [\text{HAsO}_4^{2-}]$ .

25. (a,b,c)



moles 1.5	1
0.5	-

so it is a buffer solution.

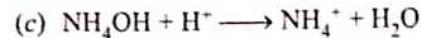


moles 1.5	2
-	0.5



moles 1.5	0.5
1	-

so it is a buffer solution.



moles 5 4

1 - 4

so it is a buffer solution.

26. (a,b)

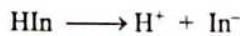
(a) A buffer solution is a solution which contains weak acid and its conjugate base. It is acidic buffer.

(b) Basic buffer contains weak base and its conjugate acid.

(c) is wrong because it does not show change in pH on adding small amount of acid or base.

(d) is wrong; all the above statements are not correct.

27. (a,d)



$$K_{in} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \Rightarrow \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{in}}{[\text{H}^+]} = \frac{10^{-9}}{10^{-9.6}} = 10^{0.6} = 4$$

$\therefore \% \text{ of } [\text{In}^-] \text{ in solution} = \frac{4}{5} \times 100 = 80\%$   
so pink colour will be visible.



$$\text{pOH} = \text{p}^{K_b} + \log \frac{\text{Salt}}{\text{Base}}$$

(a) as  $\frac{1}{5}$  neutralised so,

$$\text{pH} = 9, \Rightarrow \text{p}^{OH} = 5$$

$$5 = \text{p}^{K_b} + \log \frac{1/5}{4/5}$$

$$\Rightarrow K_b = 2.5 \times 10^{-6}$$

(b) At equivalence point

$$\text{pH} = \frac{1}{2} [\text{p}^{K_w} - \text{p}^{K_D} - \log c]$$

$$4.5 = \frac{1}{2} [14 - 5.6 - \log c] \Rightarrow C = 0.25 \text{ M}$$

$$(c) C_{\text{HCl}} = \frac{n_{\text{HCl}}}{V_f} = 0.25 = \frac{0.5 \times V_L}{V_L + 0.1} \Rightarrow V_L = 0.1 \text{ L} = 100 \text{ mL}$$

(d) at equivalence point  $n_{\text{WB}} = n_{\text{HCl}}$

$$M/45 = 0.5 \times 0.1$$

$$M = 2.25 \text{ g}$$

$$\% \text{ weight of base} = \frac{2.25}{2.5} \times 100 = 90\%$$

29. (c, d)

In  $\text{AgNO}_3$  solution, the solubility of  $\text{AgCN}$  will decrease as compared to pure water because of common ion effect of  $\text{Ag}^+$  ion.

In  $\text{NH}_3$  solution and buffer of  $\text{pH} = 5$ , the solubility of  $\text{AgCN}$  will increase due to complex formation in case of  $\text{NH}_3$  solution and hydrolysis of  $\text{CN}^-$  ions in case of buffer of  $\text{pH} = 5$ .



30. (a,b)

$$K_{sp} = 1.1 \times 10^{-11} = (1.4 \times 10^{-4})^x \cdot y \quad x^x \cdot y^y$$

so we have  $x + y = 3$  (by comparing values)

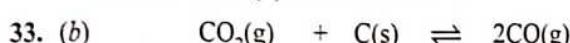
$$\text{so, } x^x \cdot y^y = \frac{1.1 \times 10^{-11}}{1.4 \times 1.4 \times 1.4 \times 10^{-12}} = \frac{110}{1.96 \times 1.4}$$

Hence  $x = 1, y = 2$  or  $y = 1, x = 2$

31. (b,d) Factual

32. (a,b)

$\text{H}_2\text{SO}_4$  is a strong acid and it completely dissociated in  $\text{H}_2\text{O}$ . Hence its and are determined in  $\text{CH}_3\text{COOH}$ . Also  $\text{H}_2\text{SO}_4$  is neutral while  $\text{HSO}_4^-$  because the -ve charge has more affinity towards  $\text{H}^+$  ion. Hence choices (a) and (b) are correct while (c) is incorrect. As  $\text{H}_2\text{SO}_4$  is completely dissociated in water so a 0.01 M  $\text{H}_2\text{SO}_4$  is completely dissociated and its  $[\text{H}^+]$  ion conc. will be equal to 0.02 M. Hence choice (d) will be incorrect.



$$t=0 \quad 0.1$$

$$t=t_{\text{eq.}} \quad 0.1-x \quad 2x$$

$$\frac{(0.1-x)44 + (2x \times 28)}{0.1+x} = 36 \Rightarrow x = \frac{1}{30}$$

$$\text{Total moles} = 0.1 + \frac{1}{30} = \frac{2}{15} = 0.1+x$$

34. (a) Moles of  $\text{CO}_2$  at eq. =  $0.1 - x = \frac{1}{15}$

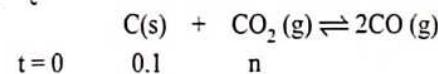
$$\text{Moles of CO at eq.} = 2x = \frac{2}{30} = \frac{1}{15}$$

$$P_{\text{CO}} = \frac{0.082 \times 900}{15 \times 0.82} = 6 \text{ atm}$$

$$P_{\text{CO}_2} = \frac{1}{15} \times \frac{0.082}{0.82} \times 900 = 6 \text{ atm}$$

$$\therefore K_p = \frac{6 \times 6}{6} = 6 \text{ atm}$$

35. (b)  $n_c = 0.1$



$$t=0 \quad 0.1 \quad n$$

$$t=t_{\text{eq.}} \quad - \quad n-0.1 \quad 0.2$$

$$P_{\text{CO}} = \frac{0.2 \times 0.082 \times 900}{0.82} = 18 \text{ atm}$$

$$K_p = 6 = \frac{(18)^2}{P_{\text{CO}_2}}; P_{\text{CO}_2} = 54 \text{ atm}$$

$$\therefore \frac{(n-0.1)(0.082)(900)}{0.82} = 54$$

$$n = 0.7$$

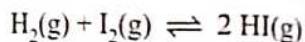
36. (d) Solubility of gas is favourable at high pressure and this process is exothermic hence solubility will be more at low temperature.

37. (c) Since density of gold decreases after melting therefore it is favourable at low pressure and high temperature.

38. (a,b)

Number of moles will remain unchanged but decreased volume pressure will get increased and the concentrations.

39. (c) Given as:



$$\text{initially} \quad 1 \quad 3$$

$$\text{At equilibrium} \quad 1-x/2 \quad 3-x/2 \quad x$$

Addition of 2 mole  $\text{H}_2$ ,

$$\Rightarrow \frac{(x)^2}{\left(1-\frac{x}{2}\right)\left(3-\frac{x}{2}\right)} = \frac{(2x)^2}{(3-x)(3-x)}$$

$$\Rightarrow 2x = 3 \Rightarrow x = \frac{3}{2}$$

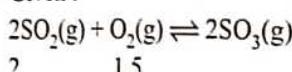
$$x = 1.5$$

40. (c)  $K_c = \frac{(2x)^2}{(3-x)(3-x)} = \frac{9}{\left(\frac{9}{4}\right)} = 4$

$K_c = K_p$  because  $\Delta n_g = 0$

$$K_c = K_p = 4$$

41. (b) Given :



$$\text{at equ.} \quad 2-2x \quad 1.5-x \quad 2x$$

$$\text{conc.} = \frac{2-2x}{5} \quad \frac{1.5-x}{5} \quad \frac{2x}{5}$$

$\text{SO}_2 \rightarrow \text{SO}_3$  (nf of  $\text{SO}_2 = 2$ )

m.eq of  $\text{KMnO}_4$  = m.eq of  $\text{SO}_2$

$$0.4 \times 5 = (2.2x) \times 2$$

$$2 = 2(1-x) \times 2$$

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

$$[\text{SO}_2] = \frac{1}{5}; [\text{O}_2] = \frac{1}{5}$$

$$[\text{SO}_3] = \frac{1}{5}$$

$$K_c = 5$$

42. (d) Based on theory

43. (a) Since  $K_a$  of  $\text{CH}_3\text{COOH}$  &  $K_b$  of  $\text{NH}_4\text{OH}$  are same degree of hydrolysis of  $\text{CH}_3\text{COO}^-$  &  $\text{NH}_4^+$  are same.

44. (c) Consider equal behaviour of acid & base

45. (a) For  $\text{SrF}_2$  in pure water

$$4s_1^3 = K_{sp}$$

For  $\text{SrF}_2$  in 0.1 M NaF solution

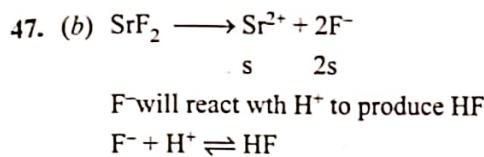
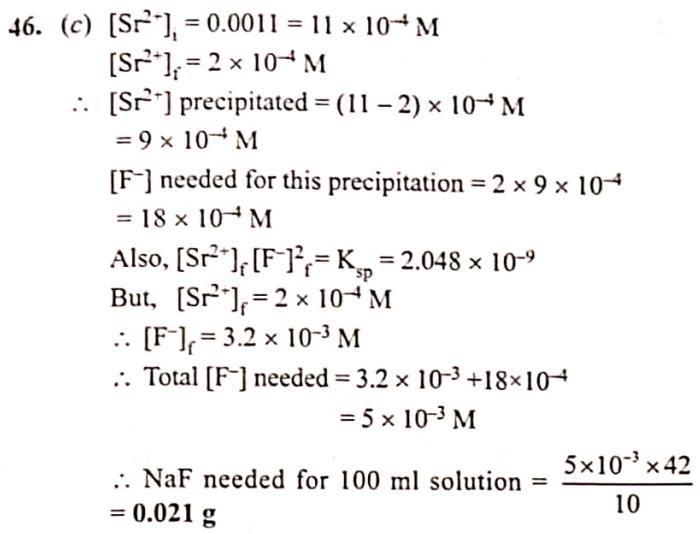
$$s_2(0.1)^2 = K_{sp}$$

$$\Rightarrow 4s_1^3 = s_2(0.01)$$

$$\Rightarrow 4s_1^3 = s_1 \times \frac{256}{10^6}(0.01)$$

$$\Rightarrow s_1 = 8 \times 10^{-4} \text{ M}$$

$$\therefore K_{sp} = 4s_1^3 = 2.048 \times 10^{-9}$$



$$K = \frac{1}{K_s} = \frac{[HF]}{[H^+][F^-]} = \frac{7}{10^{-5}}$$
 $\therefore [HF] = 7 \times 10^5 [F^-] [H^+] (\because [H^+] = 10^{-5}; pH=5)$ 
 $= 7 \times 10^5 [F^-] \times 10^{-5} = 7 [F^-]$

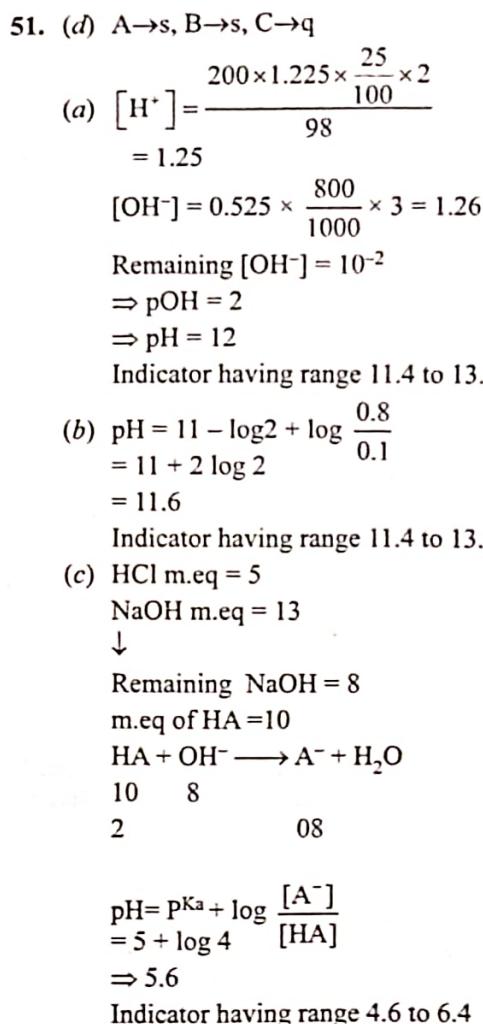
Here  $[F^-] + [HF] = 2s$

$$\therefore [F^-] = \frac{s}{4}$$
 $K_{sp} = s \left( \frac{s}{4} \right)^2 = 2.048 \times 10^{-9}$ 
 $\therefore s = 3.2 \times 10^{-3} \text{ mol/L}$

48. (b) A  $\rightarrow$  q,s; B  $\rightarrow$  p; C  $\rightarrow$  p; D  $\rightarrow$  r
- (a)  $\Delta n_g = 2 - 4 = -2$  and  $K_p = K_c (RT)^{\Delta n_g}$   
(b)  $\Delta n_g = 2 - 1 = 1$  and  $K_p = K_c (RT)^{\Delta n_g}$   
(c)  $\Delta n_g = 2 - 1 = 1$  and  $K_p = K_c (RT)^{\Delta n_g}$   
(d)  $K_p$  is not defined as all are in liquid state.

49. (a) A  $\rightarrow$  p; B  $\rightarrow$  q; C  $\rightarrow$  s; D  $\rightarrow$  r  
 $K_p = K_c (RT)^{\Delta n_g}$   
(a)  $\Delta n_g = -2$       (b)  $\Delta n_g = 0$   
(c)  $\Delta n_g = -1/2$       (d)  $\Delta n_g = 1/2$

50. (c) A  $\rightarrow$  p,t; B  $\rightarrow$  q,r; C  $\rightarrow$  q,s
- (a)  $\Delta n_g = 0$   
(b)  $\Delta n_g = -1$   
(c)  $\Delta n_g = 2$   
if reaction is exothermic then T  $\uparrow$  se then reaction goes forward.  
 $\Delta n_g = 0$ , no effect on pressure  
 $\Delta n_g < 0$ , P high then reaction goes forward.  
 $\Delta n_g > 0$ , P low then reaction goes forward.



52. [50]  
Given:  $-H_2(g) + I_2(g) \rightleftharpoons 2HI(g); K_p = 0.5$   
 $K_p = K_c (RT)^{\Delta n_g}$   
now,  
 $\Delta n_g = 2 - 2 = 0$   
 $\therefore K_p = K_c$   
 $K_c = 50$

53. [64]  
For this reaction there is no change in equilibrium constant by change of volume.

54. [16]  
 $K_p$  remain constant on change in volume.

55. [120]  
Given:

	$A(g) \rightleftharpoons B(g) + C(g) + D(g)$			
initially	1	0	0	0
at eq.	1-x	x	x	x

Total mole = 1 + 2x

Apply mass conservation

(Wt. of A at t = 0) = (wt of mixture at eq.)

$$1 \times M_w = [1 + 2x] 2 \times 50$$

$$M_w = (1 + 0.2) \times 100 \text{ (as } x = 0.1\text{)}$$

$$M_w = 120$$

56. [1]

$$\text{If } \Delta G^\circ = 0$$

$$\Delta G^\circ = -2.303 RT \log K_p$$

$$\log K_p = 0$$

$$(\because \log 1 = 0)$$

$$K_p = 1.$$

57. [4.0%]

$$\% h = \sqrt{\frac{kw}{ka.c}}$$

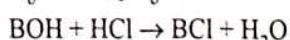
$$= \sqrt{\frac{10^{-14}}{6.2 \times 10^{-10} \times 10^{-2}}}$$

$$\% h = 0.04$$

$$\text{Percent hydrolysis} = 4\%$$

58. [10]

$$\frac{\alpha_2}{\alpha_1} = \sqrt{\frac{K_a \cdot C_2}{K_a \cdot C_1}} = \sqrt{\frac{C_2}{C_1}} = 10$$

59. [9]  $K_b = 10^{-5}$ ,  $pK_b = 5$ 

At half neutralization, 50% of the base is converted to its salt, with strong acid HCl, it forms a basic buffer.

$$\text{pOH} = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

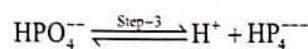
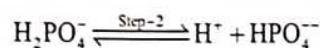
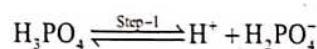
$$\text{pOH} = 5 + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$[\text{salt}] = [\text{base}]$$

$$\text{pOH} = 5$$

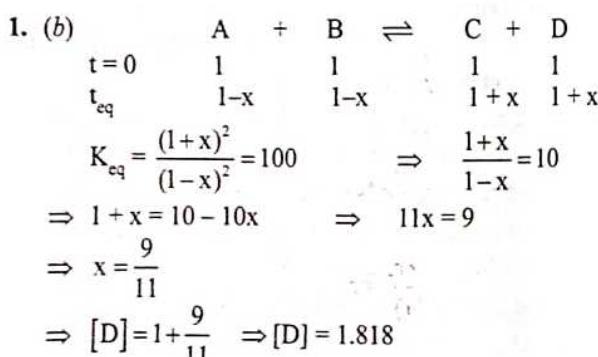
$$\text{pH} = 14 - \text{pOH} = 9$$

60. [3]



## Exercise-4 (Past Year Questions)

### JEE MAIN



2. (d) From thermodynamics

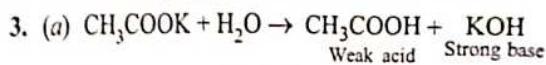
$$\ln k = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

for exothermic reaction,

$$\Delta H = -ve$$

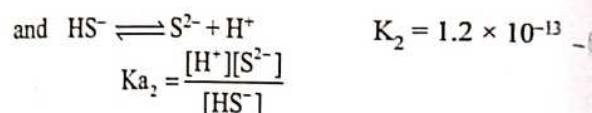
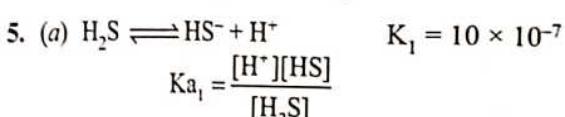
$$\text{slope} = \frac{-\Delta H^\circ}{R} = +ve$$

So from graph, line should be A &amp; B.



Hence nature of solution is basic.

4. (b) Methyl orange shows Red (pinkish) color in acidic medium & yellow color in basic medium since orange solution is basic so

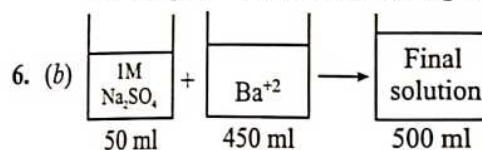
initial color  $\Rightarrow$  yellow & Titrated with acid soFinal color  $\Rightarrow$  pinkish (red)

$$\therefore \text{H}_2\text{S} \rightleftharpoons \text{S}^{2-} + 2\text{H}^+ \quad K_{\text{overall}} = \times K_1 \times K_2 = 1.2 \times 10^{-20}$$

So,

$$[\text{S}^{2-}] = \frac{1.2 \times 10^{-20} \times [\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{1.2 \times 10^{-20} \times 10^{-1}}{4 \times 10^{-2}}$$

$$= 3 \times 10^{-20} \text{ M}$$

\*All the  $[\text{H}^+]$  will come from strong acid  $[\text{HCl}]$  onlyConcentration of  $\text{SO}_4^{2-}$  in  $\text{Ba}^{+2}$  solution

$$M_1 V_1 = M_2 V_2$$

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

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

for just precipitation

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

$$[\text{Ba}^{+2}][\text{SO}_4^{2-}] = K_{sp} (\text{BaSO}_4)$$

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

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

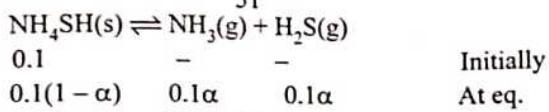
For calculation of  $[\text{Ba}^{+2}]$  in original solution (450 ml)

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

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

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

7. (d) Moles of  $\text{NH}_4\text{SH} = \frac{5.1}{51} = 0.1$  mol



given  $\alpha = 30\% = 0.3$

Therefor number of moles equilibrium due

$$= 0.1 \times 0.3 + 0.1 \times 0.3$$

$$= 0.03 + 0.03 = 0.06$$

as we know  $PV = nRT$

At equilibrium,

$$P_{\text{total}} \times 3L = 0.06 \times .082 \times 600$$

$$P_{\text{total}} = 0.984 \text{ atm}$$

At equilibrium,

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = \frac{P_{\text{total}}}{2} = 4.492$$

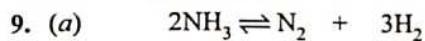
$$K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = 0.492 \times 0.492$$

$$K_p = 0.242 \text{ atm}^2$$

8. (d)  $\Delta G^\circ = 120 - \frac{3}{8} = 315$

$$= 1.875$$

X is maximum



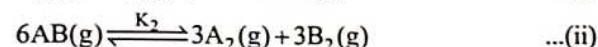
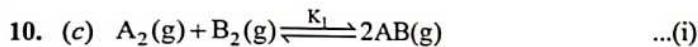
$$\begin{array}{ccccc} t=0 & P_1 & - & - & \\ t=\text{eq} & P_{\text{NH}_3} & \frac{P_1}{2} & \frac{3P_1}{2} & \end{array}$$

$$P = P_{\text{total}} = \frac{P_1}{2} + \frac{3P_1}{2} = 2P_1$$

$$\therefore P_1 = \frac{P}{2}$$

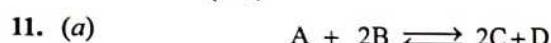
$$k_{\text{eq}} = \frac{1}{K_p} = \frac{\left(\frac{P_1}{2}\right)\left(\frac{3P_1}{2}\right)^3}{(P_{\text{NH}_3})^2}$$

$$P_{\text{NH}_3} = \frac{(K_p)^{\frac{1}{2}} 3^{\frac{3}{2}} P^2}{16}$$



Reaction (ii) =  $-3 \times$  reaction (i)

$$\therefore K_2 = \left(\frac{1}{K_1}\right)^3 \Rightarrow K_2 = K_1^{-3}$$



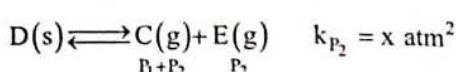
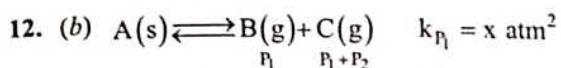
Initially conc a 1.5a

$$\text{at eq. } a-x \quad 1.5a-2x \quad 2x \quad x$$

$$\text{at equilibrium, } a-x = 1.5a - 2x$$

$$\text{or } a = 2x$$

$$K_C = \frac{(2x)^2 x}{(a-x)(1.5a-2x)^2} = \frac{4x^2 \cdot x}{(x)(x)^2} = 4$$



$$x = k_{p_1} = P_1 (P_1 + P_2) \quad \dots (i)$$

$$y = k_{p_2} = P_2 (P_1 + P_2) \quad \dots (ii)$$

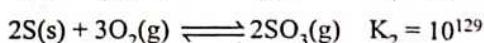
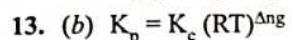
$$k_{p_1} + k_{p_2} = (P_1 + P_2)^2$$

on addition equation (i) and (ii)

$$x+y = (P_1 + P_2)^2$$

$$\text{or } P_1 + P_2 = \sqrt{x+y}$$

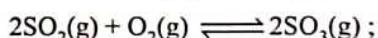
$$\text{or } P_{\text{Total}} = P_B + P_C + P_E = 2(P_1 + P_2) = 2\sqrt{x+y}$$



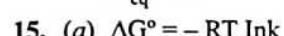
multiplying equation (i) by (ii) ;



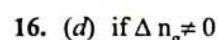
$\Rightarrow$  Subtracting (iii) from (ii); we get



$$K_{\text{eq}} = 10^{(129-104)} = 10^{25}$$



if  $K < 1 \Rightarrow \Delta G^\circ > 0$



$$K_p \neq K_c$$

17. (a)  $K_c = 1.7 \times 10^{16}$  i.e. reaction goes to completion. catalyst won't affects the equilibrium it only affect rate of reaction.

18. (a) The pH of NaOH is more than 7 and during the titration it decreases.



$$400 \times .1 = 40 \quad 400 \times .1 = 40$$

$$20 \quad 0$$

$$\therefore [\text{H}^+] = \frac{20 \times 20}{800} = \frac{1}{20} \Rightarrow \text{pH} = -\log\left(\frac{1}{20}\right)$$

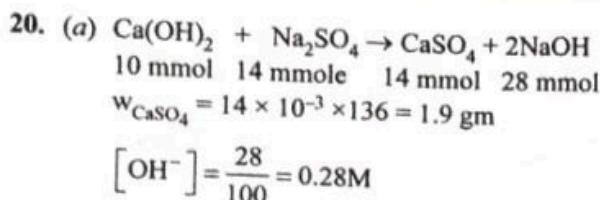
$$\therefore \text{pH} = 1.3$$

$$(b) \log\left(\frac{K_w_2}{K_w_1}\right) = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

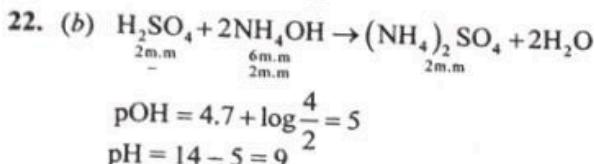
$$(c) K_a = 10^{-5}, \text{pH} = 5 \Rightarrow [\text{H}^+] = 10^{-5}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \Rightarrow K_a = \frac{[\text{H}^+]\alpha}{(1-\alpha)}$$

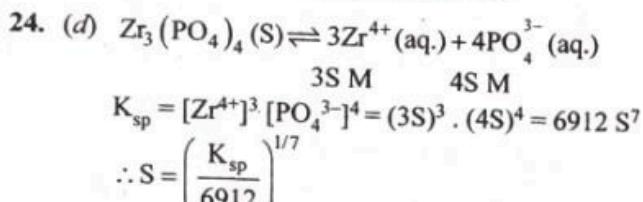
$$10^{-5} = \frac{10^{-5} \times \alpha}{(1-\alpha)} \text{ or } \alpha = 50\%$$



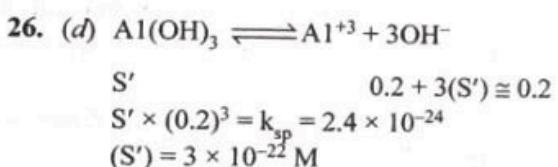
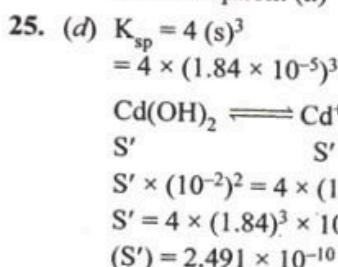
21. (c)  $8 \times 10^{-12} = (2S' + 0.1)^2 S'$   
 $\text{or } S' = 8 \times 10^{-10} \text{ M}$



23. (a) Rainwater becomes acidic because gases present in the environment are dissolved so its pH will be less than 7. pH of rainwater is approximate 5.6.



Correct option: (d)



27. (b) For the salt of strong acid and weak base

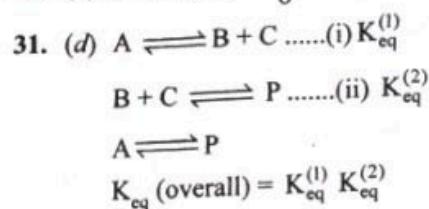
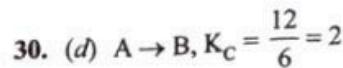
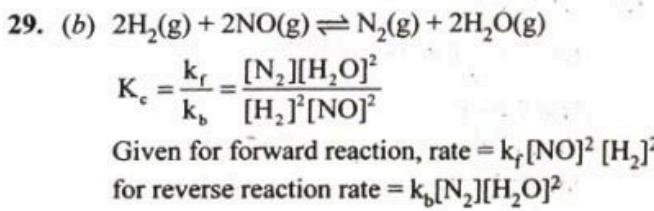
$$[\text{H}^+] = \sqrt{\frac{K_w \times C}{K_b}}$$

$$[\text{H}^+] = \sqrt{\frac{10^{-14} \times 2 \times 10^{-2}}{10^{-5}}}$$

$$-\log[\text{H}^+] = 6 - \frac{1}{2}\log 20$$

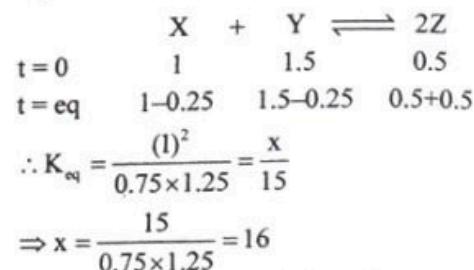
$$\therefore \text{pH} = 5.35$$

28. (d) on increasing temperature pH decreases and the reaction endothermic

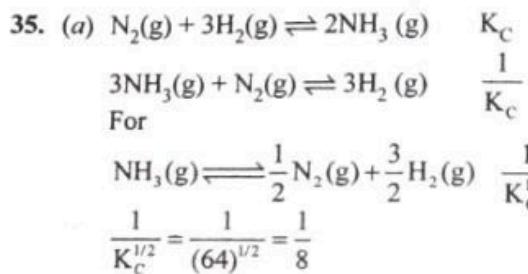


32. (b) At equilibrium,  
 rate of forward reaction = Rate of backward reaction

33. [16.00]



34. (b)  $\because$  Given reaction is endothermic  
 $\therefore$  On decreasing temperature backward reaction will be favoured. On adding  $\text{N}_2$ , pressure is increased at constant T, and volume would also be constant so no change is observed.



36. (a)  $K_p = K_C (RT)^{\Delta n_p}$   
 $= K_C (RT)^{1-3/2}$   
 $= K_C (RT)^{-1/2}$   
 $\Rightarrow K_C = K_p (RT)^{1/2}$

37. (c) Catalyst will effect the  $R_f$  &  $R_b$  at some extent, so  $K_{eq}$  won't change.

38. [3]  $K_c = \frac{1.5 \times 0.5}{0.5 \times 0.5} = 3$

39. [10.60 to 10.60]

$$M_{\text{H}_2\text{SO}_4} \Rightarrow \frac{9.8}{98 \times 100} = 10^{-3}$$

$$M_{\text{NaOH}} \Rightarrow \frac{4}{40 \times 100} = 10^{-3}$$

$$= \frac{40 \times 10^{-3} - 10 \times 10^{-3} \times 2}{50} = \frac{20}{50} \times 10^{-3}$$

$$[\text{OH}^-] = \frac{2}{5} \times 10^{-3}$$

$$\text{pOH} = 3.397$$

$$\text{pH} = 10.603$$

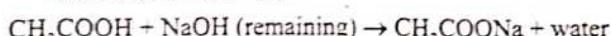


40. [5.22 to 5.24]

m mole of acetic acid in 20 mL = 2

m mole of HCl in 20 ml = 1

m mole of NaOH = 2.5



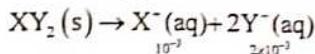
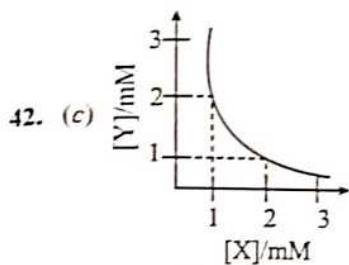
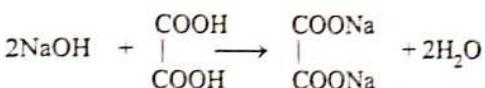
2	3/2	0	0
0.5	0	3/2	

$$\text{pH} = \text{pK}_a + \log \frac{3/2}{1/2}$$

$$= 4.75 + \log 3 = 4.75 + 0.4771 = 5.2271 \approx 5.23$$

$$= 4.74 + 0.48 = 5.22$$

41. (b) The strength of NaOH measured by titrating against oxalic by taking NaOH in the burette and oxalic acid in the conical flask.



$$K_{sp} = [\text{X}^+][\text{Y}^-]^2$$

$$\text{or } K_{sp} = 10^{-3} \times (2 \times 10^{-3})^2 \text{ or } k_{sp} = 4 \times 10^{-9} \text{ M}^3$$

43. (b)  $Q = [\text{Pb}^{2+}][\text{Cl}^-]^2$

$$= \frac{300 \times 0.134}{400} \times \left[ \frac{100 \times 0.4}{400} \right]^2$$

$$= \frac{3 \times 0.134}{4} \times (0.1)^2$$

$$= 0.105 \times 10^{-2}$$

$$= 1.005 \times 10^{-3}$$

$Q > K_{sp}$

44. [4]  $\text{Cr(OH)}_3 \rightarrow \text{Cr}^{+3} + 3\text{OH}^-$

s 3s

$$k_{sp} = s \cdot (3s)^3$$

$$\Rightarrow 6 \times 10^{-31} = 27s^4$$

$$\Rightarrow s = \left( \frac{6}{27} \times 10^{-31} \right)^{1/4}$$

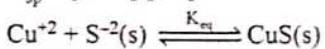
$$[\text{OH}^-] = 3s$$

$$= 3 \times \left( \frac{6}{27} \times 10^{-31} \right)^{1/4} = (18 \times 10^{-31})^{1/4} \text{ M}$$

45. (b)  $K_{sp}$  value of CuS is very low =  $10^{-36}$  ( $36 \times 10^{-36}$ ) due to low  $K_{sp}$  value  $\text{Cu}^{+2}$  ion gets precipitated very quickly even with very low concentration of  $\text{S}^{2-}$  ion.



$$K_{sp} = [\text{Cu}^{+2}][\text{S}^{2-}]$$



$$K_{eq} = \frac{1}{K_{sp}} = \frac{1}{3.6 \times 10^{-36}} = \frac{10^{36}}{3.6}$$

Due to high value of  $K$  (equilibrium constant) CuS precipitated quickly.

46. (a) For titration between HCl and NaOH, pH at equivalence point is found to be 7.

47. (b)  $\text{HCl} + \text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COOH} + \text{NaCl}$

Initial  $100 \times 0.1$        $200 \times 0.1$

= 10 mmol      = 20 mmol

Final 0      10 mmol      10 mmol      10 mmol  
moles

$\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{OONa}$  both are present. Both form acidic buffer.

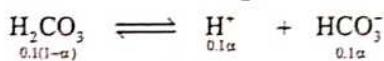
48. [37]

At 30 bar pressure mass of  $\text{CO}_2$  in 1 kg water

$$= 44 \text{ gm}$$

At 3 bar pressure mass of  $\text{CO}_2$  in 1 kg water

$$= 4.4 \text{ gm Moles of } \text{CO}_2 \text{ in 1 kg water} = 0.1$$



$$K_{a_1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

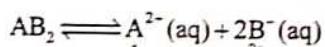
$$4 \times 10^{-7} = \frac{0.1\alpha^2}{1-\alpha} \approx 0.1\alpha^2$$

$$\alpha = 2 \times 10^{-3}$$

$$[\text{H}^+] = 0.1 \alpha = 2 \times 10^{-4}; \text{pH} = 3.7$$

$$= 37 \times 10^{-1}$$

49. [02.00]



$$K_{sp} = 4s^3 = 3.2 \times 10^{-11}$$

$$\Rightarrow s^3 = 8 \times 10^{-12}$$

$$s = 2 \times 10^{-4}$$

50. (b) (a) 0.01 M HCl

$$[\text{H}^+] = 10^{-2}, \text{pH} = -\log 10^{-2} = 2$$

$$\text{pOH} = 14 - 2 = 12$$

(b) 0.01 M NaOH

$$[\text{OH}^-] 10^{-2}, \text{pOH} = -\log [\text{OH}^-] = 2$$

(c) 0.01 M  $\text{CH}_3\text{COONa}$

$$\text{pH} = 7 + \frac{1}{2} [\text{pK}_a \log 0.01]$$

$$\text{pH} > 7 \Rightarrow \text{pOH} < 7$$

(d) 0.01 M NaCl, pH = 7, pOH = 7

Order of pOH value A > D > C > B

51. [1]  $K = K_1 \times K_2 \times K_3 \times K_4$   
 $= 10^4 \times 1.58 \times 10^3 \times 5 \times 10^2 \times 10^2$

$K = 7.9 \times 10^{11}$

Where  $K \rightarrow$  Equilibrium constant for formation of  $[Cu(NH_3)_4]^{2+}$  So equilibrium constant ( $K$ ) for dissociation of  $[CuCNH_3]^{2+}$  is  $\frac{1}{K}$

$K' = \frac{1}{K}$

$K' = \frac{1}{7.9 \times 10^{11}} = 1.26 \times 10^{-12}$

So, the value of  $x = 1.26$

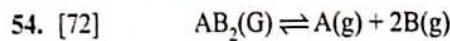
52. [5]

$\because$  No. of atoms of Cl = no. of molecules of  $Cl_2$  i.e  $n_{Cl} = n_{Cl_2}$   
According Dalton's law of partial pressure.

$P_{Cl} = 0.5 \text{ atm} = P_{Cl_2}$

$\therefore K_p = \frac{(0.5)^2}{0.5} = 0.5$

53. [1380]  $\Delta G^\circ = -RT \times \log K_{eq}$   
 $= -R \times 300 \times \log 10^2$   
 $= -1380 R$



$$\begin{array}{cccc} t=0 & 1 & - & - \\ t=eq^m & 1-\alpha & \alpha & 2\alpha \end{array}$$

$\therefore$  No. of moles at equilibrium

$= 1 + 2\alpha = \frac{PV}{RT} = 1.93$

$\therefore \alpha = 0.465$

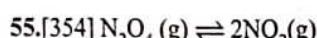
$\therefore P_{AB_2} = \frac{1-\alpha}{1+2\alpha} \times P_T \approx 0.46 \text{ atm}$

$P_A = \frac{\alpha}{1+2\alpha} \times P_T \approx 0.46 \text{ atm}$

$P_B = \frac{2\alpha}{1+2\alpha} \times P_T \approx 0.91 \text{ atm}$

$K_B = \frac{P_A \cdot (P_B)^2}{P_{AB_2}}$

$= \frac{0.46 \times (0.91)^2}{0.53} = 72 \times 10^{-2}$



$\Delta n_g = 2 - 1 = 1$

$K_p = K_c (RT)^{\Delta n_g}$

$6000.1 = 20.4 (0.0831 \times T) 1$

$t = \frac{600.1}{20.4 \times 0.0831}$

56. [1.66]  $\Delta G^\circ = -RT \ln K_p$

$25200 = -2.3 \times 8.3 \times 400 \log (KP)$

$K_p = 10^{-33} = 10^{-3} \times 0.501$

$K_p = 5.01 \times 10^{-4} \text{ bar}^{-1}$

$= 5.01 \times 10^{-5} \times 10^{-4} \text{ Pa}^{-1}$

Relation of  $K_p$  and  $K_c$ ,

$K_p = K_c (RT)^{\Delta n_g}$

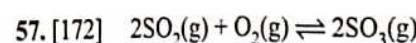
$\Delta n_g = -1$

$K_p = \frac{K_c}{RT}$

$K_p = \frac{K_c}{8.3 \times 400}$

$K_c = 1.66 \times 10^{-5} \text{ m}^3/\text{mole}$

$= 1.66 \times 10^{-2} \text{ L/mol}$



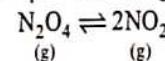
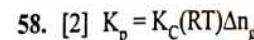
$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}}$

$= \frac{(43)^2}{(0.53)(45)^2}$

$= 1.7228 \text{ kPa}^{-1}$

$= 172.28 \times 10^{-2} \text{ kPa}^{-1}$

$= 172 \times 10^{-2} \text{ kPa}^{-1}$

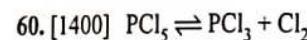


$\Delta n_g = 1$

$K_c = \frac{K_p}{(RT)} = \frac{47.9}{(0.083 \times 288)}$

$= 2$

59. (a) Fact based.

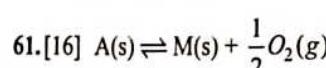


$$\begin{array}{cccc} t=0 & 3 & - & - \\ t=t_{eq} & 3-x & x & x \end{array}$$

$\frac{x^2}{3-x} = 1.844$

$x = 1.60$

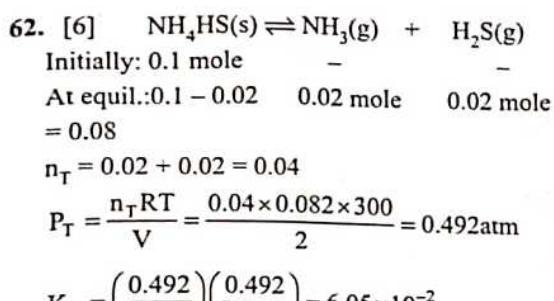
Moles of  $PCl_5$  at equilibrium =  $3 - x = 3 - 1.6 = 1.4$   
or  $1400 \times 10^{-3} \text{ mol}$



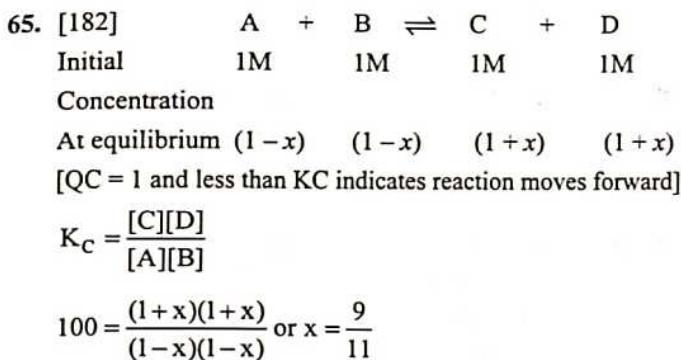
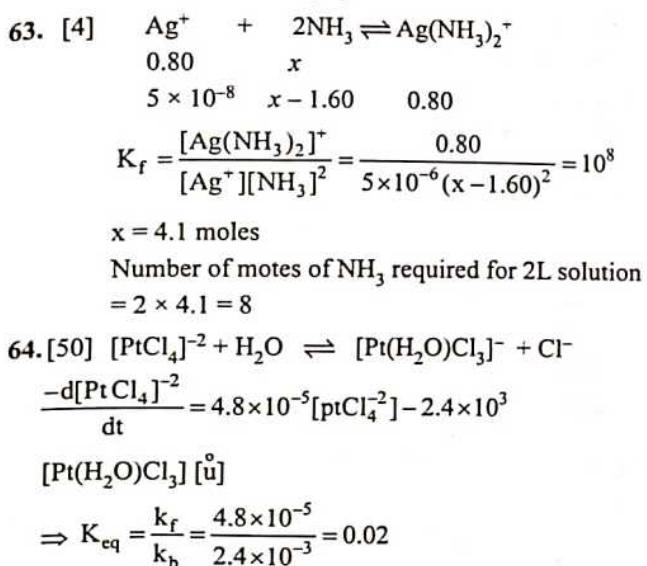
$K_p = (P_{O_2})^{1/2} = 4$

$P_{O_2} = 16$



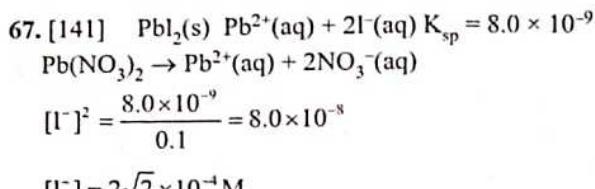
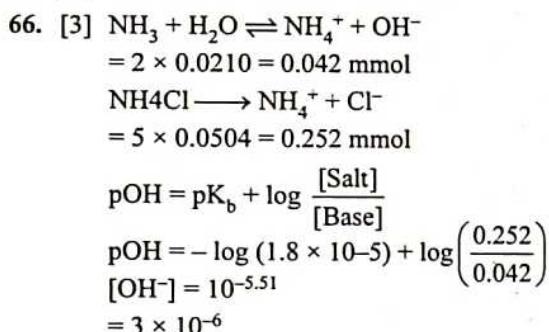


$$\therefore x = 6 \text{ (nearest integer)}$$



$$[D] = 1+x = \frac{20}{11}$$

$$[D] = 182 \times 10^{-2} \text{ M}$$

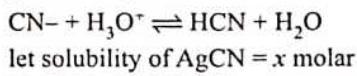
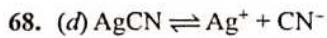


$$[\text{I}^-]^2 = \frac{8.0 \times 10^{-9}}{0.1} = 8.0 \times 10^{-8}$$

$$[\text{I}^-] = 2\sqrt{2} \times 10^{-4} \text{ M}$$

Solubility of  $\text{PbI}_2$  in 0.1 M  $\text{Pb}(\text{NO}_3)_2$  solution

$$= \frac{[\text{I}^-]}{2} = 141 \times 10^{-6} \text{ M}$$



$$\frac{[\text{HCN}]}{[\text{CN}^-]} = 1.6 \times 10^6$$

As each  $\text{CN}^-$  ion hydrolyses to give one HCN

$$x = [\text{Ag}^+] = [\text{CN}^-] + [\text{HCN}]$$

$$\therefore [\text{CN}^-] \ll [\text{HCN}]$$

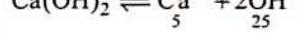
$$\therefore x = [\text{Ag}^+] = [\text{HCN}]$$

$$[\text{CN}^-] = \frac{x}{1.6 \times 10^6}$$

$$K_{sp} = [\text{Ag}^+][\text{CN}^-] = \frac{x^2}{1.6 \times 10^6}$$

$$2.2 \times 10^{-16} = \frac{x^2}{1.6 \times 10^6}$$

$$x = 1.9 \times 10^{-5} \text{ M}$$



$$K_{sp} = [\text{Ca}^{+2}][\text{OH}^-]^2 = s \times (2s)^2$$

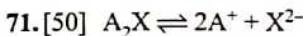
$$5.5 \times 10^{-6} = 4s^3$$

$$s = 1.11 \times 10^{-2}$$

70. [7.00]  $(\text{NH}_4)_3$  is a salt of weak base and weak acid.

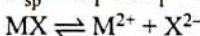
$$\begin{aligned} \text{pH} &= \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b \\ &= 7 + \frac{1}{2}(5.23) - \frac{1}{2}(4.75) \end{aligned}$$

$$= 7.00 \text{ (nearest integer)}$$



$$2s_1 \quad s_1$$

$$K_{sp} = 4s_1^3 \text{ or } s_1 = 10^{-4}$$



$$K_{sp} = s_2^2 \text{ or } s_2 = 2 \times 10^{-6}$$

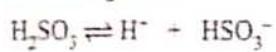
$$s_1 = s(\text{A}_2\text{X})$$

$$s_2 = s(\text{MX})$$

$$\frac{s_1}{s_2} = \frac{10^{-4}}{2 \times 10^{-6}} = 50$$

72. [01]  $K_a$  of  $H_2SO_3 \gg K_a$  of  $H_2SO_4$

i. The contribution of  $H^+$  from 2<sup>nd</sup> dissociation of  $H_2SO_3$  can be neglected.



$$c(1-\alpha) \quad c\alpha \quad c\alpha$$

$$K_a = \frac{c\alpha^2}{1-\alpha} = 1.7 \times 10^{-2}$$

$$\alpha = 0.156$$

$$[H^+] = c\alpha = 0.092$$

$$pH = -\log[H^+]$$

$$= 1.036$$

$$= 1$$

73. [2]  $HCl \rightarrow H^+ + Cl^-$

$$0.1M \quad 0.1M$$



$$0.01(1-\alpha) \quad 0.1 + 0.01\alpha \quad 0.01\alpha = 0.1$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$2 \times 10^{-6} = \frac{0.1 \times 0.01\alpha}{0.01(1-\alpha)}$$

$$\alpha = 2.0 \times 10^{-5}$$

74. [10]  $pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$

$$\text{or } 5.74 = 4.74 + \log \frac{x}{1}$$

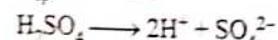
$$x = 10 M$$

75. [64]  $CdSO_4 \rightleftharpoons Cd^{2+} + SO_4^{2-}$

$$K_{sp} = S^2$$

$$= (8 \times 10^{-4})^2$$

$$K_{sp} = 64 \times 10^{-8}$$



$$64 \times 10^{-8} = S^2 \times 0.01$$

$$S^2 = \frac{64 \times 10^{-8}}{0.01} = 64 \times 10^{-6} \text{ mol/L}$$

76. (d) Cons. of  $Cl^- = 0.1 M = 10^{-1} M$

Conc. of  $CrO_4^{2-} = 0.001 M = 10^{-3} M$

$$K_{sp}(AgCl) = [Ag^+][Cl^-]$$

$$[Ag^+]_{AgCl} = \frac{1.7 \times 10^{-10}}{10^{-1}} = 1.7 \times 10^{-9}$$

$$K_{sp}(Ag_2CrO_4) = [Ag^+]^2 [CrO_4^{2-}]$$

$$[Ag^+] = \sqrt{19} \times 10^{-4}$$

$\therefore AgCl$  will be precipitated first

77. [1]  $Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

$$[OH^-] = 2 \times 0.005 = 0.01 M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.01} = 0.001 M$$

78. [2]  $Zn(OH)_2(s) \rightleftharpoons Zn^{2+} + 2OH^-$

$$K_{sp} = [Zn^{2+}][OH^-]^2$$

$$2 \times 10^{-20} = (s)(2s+0.1)^2$$

Neglecting 2s w.r.t. 0.1 gives  $s = 2 \times 10^{-18} M$

So value of  $x$  is 2

79. [6021]  $HCl + NaOH \rightarrow NaCl + H_2O$

$$\text{Initial (m mol)} \quad 50 \times 1 \quad 30 \times 1 \quad -$$

$$\text{Final (m mol)} \quad 20 \quad - \quad 30$$

$$pH = -\log [H^+]$$

$$= -\log \left( \frac{20}{80} \right)$$

$$= -\log(0.25)$$

$$= -\log(2.5 \times 10^{-1})$$

$$= -\log(2.5) - \log(10^{-1})$$

$$= -0.3979 + 1$$

$$= 6.021 \times 10^{-4}$$

80. [108]  $A_3B_3 \rightleftharpoons 3A^{2+} + 2B^{3-}$

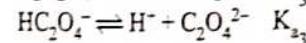
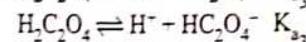
$$K_{sp} = \left( \frac{3x}{M} \right)^3 \times \left( \frac{2x}{M} \right)^2 = 108 \left( \frac{x}{M} \right)^5$$

$$x = 108$$

81. (b) Titration of strong acid and weak base uses methyl orange as indicator.

For titration of weak acid and strong base, phenolphthalein is a suitable indicator.

82. (d)  $H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-} \quad K_{a_3}$



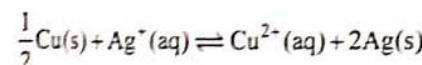
$$K_{a_2} = \frac{[H^+]^2 [C_2O_4^{2-}]}{[H_2C_2O_4]}$$

$$K_{a_1} = \frac{[H^+] [HC_2O_4^-]}{[H_2C_2O_4]}, K_{a_2} = \frac{[H^+] [C_2O_4^{2-}]}{[HC_2O_4^-]}$$

$$K_{a_1} = K_{a_1} \times K_{a_2}$$

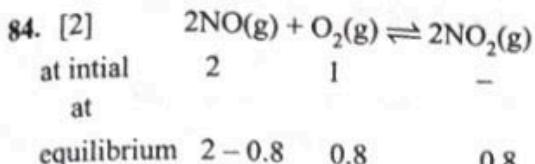
83. [2]  $Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$

$$k = 2 \times 10^{15}$$



$$K' = \frac{1}{(K)^{\frac{1}{2}}} = \frac{1}{(2 \times 10^{15})^{\frac{1}{2}}}$$

$$x = 2$$



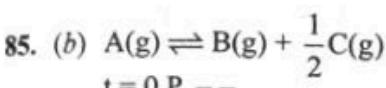
$$\text{Partial pressure of NO(g)} = \frac{1.2}{2.6} \times 1$$

$$\text{Partial pressure of O}_2(\text{g}) = \frac{0.6}{2.6}$$

$$\text{Partial pressure of NO}_2(\text{g}) = \frac{0.8}{2.6}$$

$$K_p = \frac{(\text{P}_{\text{NO}_2})^2}{(\text{P}_{\text{NO}})^2 (\text{P}_{\text{O}_2})} = \frac{0.8 \times 0.8 \times 2.6}{1.2 \times 1.2 \times 0.6}$$

$$= 2$$



$$t = 0 \quad P_i --$$

$$(e.g.mconditions) \quad P_i - p_i\alpha \quad p_i\alpha \quad \frac{p_i\alpha}{2}$$

$$\therefore P(\text{equilibrium pressure}) = p_i - p_i\alpha + p_i\alpha + \frac{p_i\alpha}{2}$$

$$= p_i \left(1 + \frac{\alpha}{2}\right)$$

$$= p_i \frac{p}{\left(1 + \frac{\alpha}{2}\right)}$$

$$K_p = \frac{\left(p_i \frac{\alpha}{2}\right)^{\frac{1}{2}} \times p_i\alpha}{p_i(1-\alpha)}$$

$$= \frac{p^{\frac{1}{2}}\alpha^{\frac{1}{2}}}{(2+\alpha)^{\frac{1}{2}}(1-\alpha)}$$



$$\text{Initial} \quad 5$$

$$\text{moles}$$

$$\text{Equilibrium} \quad 5-x \quad x \quad x$$

$$\text{moles}$$

$$\text{Number of moles of N}_2 = 2$$

$$\text{Equilibrium pressure} = 2.46 \text{ atm}$$

$$P_{\text{eq}} = \frac{(7+x) \times 0.082 \times 600}{200} = 2.46$$

$$x = 3$$

$$K_p = \frac{\left(\frac{3P}{10}\right)\left(\frac{3P}{10}\right)}{\left(\frac{2P}{10}\right)} = 1107 \times 10^{-3} \text{ atm}$$



$$t = 0 \quad 1\text{mol}$$

$$t = t \quad (1-0.5)\text{ mol} \quad 0.5 \times 2 \text{ mol}$$

$$= 0.5\text{mol} \quad 1\text{mol}$$

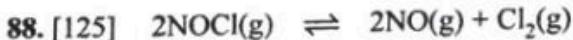
$$K_p = \frac{\left(\frac{1}{1.5} \times 1\right)^2}{\left(\frac{0.5}{1.5} \times 1\right)}$$

$$= 1.33$$

$$\Delta G^\circ = -RT \ln K_p$$

$$= -8.31 \times 300 \times \ln(1.33) = -710.45 \text{ J/mol}$$

$$= -710 \text{ J/mol.}$$



$$t = 0 \quad 2$$

$$t = t_{\text{eq}} \quad 2 - 0.4 \quad 0.4 \quad 0.2$$

$$K_C = \frac{(0.2) \times (0.4)^2}{(1.6)^2}$$

$$= 125 \times 10^{-4}$$



$$t = 0 \quad 5 \quad - \quad -$$

$$t = t \quad 5-n \quad n \quad n$$

$$\text{Total moles} = 5 - n + n + n$$

$$= 5 + n.$$

For Argon

$$\text{Total moles} = n_{\text{Ar}} + n\text{PCl}_5 + n\text{PCl}_3 + n\text{PCl}_2$$

$$= 4 + 5 + n$$

$$= 9 + n$$

$$K_p = \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}} PV = nRT$$

$$6 \times 100 = (9+n) \times 0.082 \times 610$$

$$n = 3$$

$$= \frac{\left(\frac{3}{12} \times 6\right) \times \left(\frac{3}{12} \times 6\right)}{\frac{2}{12} \times 6}$$

$$= \frac{27}{12} = \frac{9}{4} = 2.25 \text{ amt}$$



$$\frac{0.90}{18} - x$$

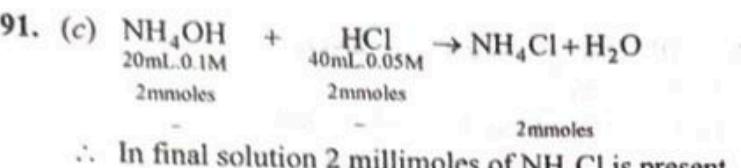
$$PV = nRT$$

$$\frac{32}{760} \times V = 0.082 \times (x) \times 300$$

$$x = \frac{0.90}{18}$$

$$V = 0.082 \times \frac{0.90}{18} \times \frac{300 \times 760}{32}$$

$$= 29.21 \text{ L} = 29 \text{ L}$$



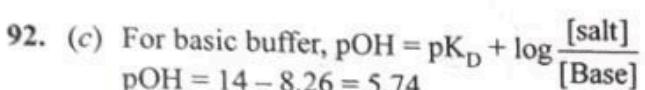
$\therefore$  In final solution 2 millimoles of  $\text{NH}_4\text{Cl}$  is present.

$$\therefore [\text{NH}_4\text{Cl}] = \frac{1}{30} \text{ molar}$$

$$\text{pH} = \frac{1}{2} [\text{pk}_w - \text{pk}_b - \log C]$$

$$= \frac{1}{2} [14 - 5 - (-1.48)]$$

$$= 5.24$$



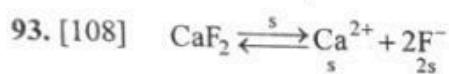
$$\text{pOH} = 14 - 8.26 = 5.74$$

$$5.74 = 4.74 + \log \frac{[\text{NH}_4\text{Cl}]}{0.2}$$

$$[\text{NH}_4\text{Cl}] = 2 \text{ M}$$

$$\text{Moles of NH}_4\text{Cl} = 2 \times 1 = 2 \text{ moles}$$

$$\text{Weight of NH}_4\text{Cl} = 2 \times 53.5 = 107 \text{ g}$$



$$K_{sp} = s(2s)^2$$

$$= 4s^3$$

$$\text{Solubility}(s) = 2.34 \times 10^{-3} \text{ g}/100 \text{ mL}$$

$$= \frac{2.34 \times 10^{-3} \times 10}{78} (\text{mole/L})^3$$

$$= 3 \times 10^{-4} \text{ mole/L}$$

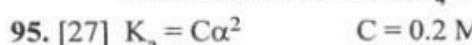
$$\therefore K_{sp} = 4 \times (3 \times 10^{-4})^3$$

$$= 108 \times 10^{-12}$$

$$= 0.0108 \times 10^{-8} (\text{mole/L})^3$$

$$\therefore x = 0$$

94. (a)  $\text{NH}_4\text{OH}$  is a weak base and  $\text{HCl}$  is a strong acid. On additional  $\text{HCl}$  to  $\text{NH}_4\text{OH}$ , pH.



$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$K_a = 2 \times 10^{-5}$$

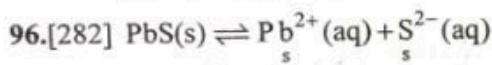
$$= \sqrt{\frac{2 \times 10^{-5}}{2 \times 10^{-1}}}$$

$$= 10^{-2}$$

$$[\text{H}^+] = C\alpha$$

$$= 0.2 \times 10^{-2} = 2 \times 10^{-3}$$

$$\text{pH} = 3 - \log 2 = 2.7$$



$$K_{sp} = \text{S}^2$$

$$8 \times 10^{-28} = \text{S}^2$$

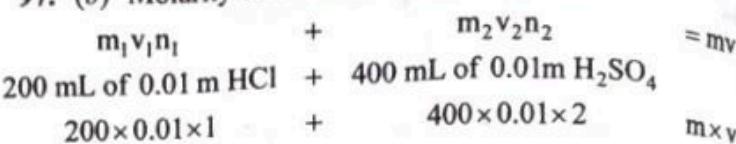
$$\text{S} = 2\sqrt{2} \times 10^{-14} \text{ mol/L}$$

$$\text{or } 2.82 \times 10^{-14} \text{ mol/L} = 282 \times 10^{-16} \text{ mol/L}$$

$$\text{Hence,}$$

$$x = 282$$

97. (b) Molarity of resultant solution is given by

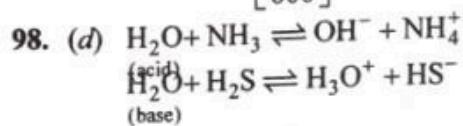


$$\text{Molarity} = \frac{10}{600} \text{ of equivalents.}$$

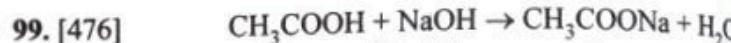
$$[\text{H}^+] = \frac{10}{600}$$

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

$$\text{pH} = -\log \left[ \frac{10}{600} \right] = 1.778$$



Hence, A is false but R is true

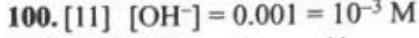


at initially	$50 \times 0.1$ mmoles	$25 \times 0.1$ mmoles	
at time t	2.5mmoles	0	2.5mmol

$$\text{pH} = \text{pKa} + \log \frac{(\text{salt})}{(\text{acid})}$$

$$\text{pH} = 4.76 + \log \frac{2.5}{2.5}$$

$$\text{pH} = 4.76$$



$$[\text{H}^+] [\text{OH}^-] = 10^{-14}$$

$$[\text{H}^+] = 10^{-11}$$

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

$$\text{pH} = 11$$



$$\text{pH} = \text{pKa} + \log \frac{[\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

$$4 = -\log 1.3 \times 10^{-5} + \log \frac{[\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

$$\frac{[\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]} = 0.13$$

102. (d) Solubility decreases with increasing the concentration of common ion. Therefore, the maximum solubility of  $\text{AgCl}$  will be in deionized water.

## JEE ADVANCED

103. (a,b,d)

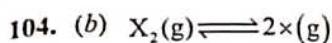
(a)  $\Delta H_2 - \Delta H_1 = C_p \text{ (rxn)} (T_2 - T_1)$  and  $C_p$  depends on temperature. Hence enthalpy also depends on temperature.

(b)  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$   $K_p = (P_{\text{CO}_2})_{\text{at equilibrium}}$   
For a give reation

$K_{eq}$  depends only on temperature.

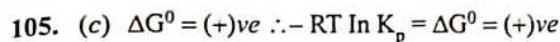
(c)  $K_{eq}$  depends only on temperature.

(d) Enthalpy of reaction is independent of the catalyst. Catalyst generally changes activation energy.



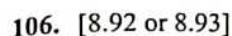
$$K_p = \frac{\left(\frac{\beta}{\left(1 + \frac{\beta}{2}\right)}\right)^2 \times 2^2}{\frac{1 - \frac{\beta}{2} \times 2}{1 + \frac{\beta}{2}}} = \frac{\beta^2}{1 - \frac{\beta^2}{4}} \times 2$$

$$K_p = \frac{8\beta^2}{4 - \beta^2}$$



$$K_p < 1$$

Also  $\beta$  can't be 0.7 otherwise  $K_p$  will have to be (+) ve

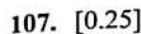


$$\begin{array}{rcl} Fe^{+2}_{(aq)} + S^{-2}_{(aq)} & \rightleftharpoons & FeS(s) \\ 0.03 \text{ M} & & 0.1 \text{ M} \\ (0.03-x) & & (0.1-x) \\ =y & & =0.07 \\ K_c \gg 10^3 \Rightarrow 0.03-x \approx 0=y \\ \Rightarrow x=0.03 \end{array}$$

$$K_c = 1.6 \times 10^{17} = \frac{1}{y \times 0.07}$$

$$y = \frac{10^{-17}}{1.6 \times 0.07} = 8.928 \times 10^{-17} = Y \times 10^{-17}$$

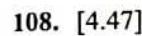
$$y = 8.93$$



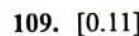
$$K_{eq} = \frac{[B]}{[A]}$$

$$K_{1000} = \frac{10}{1} = 10 \text{ and } K_{2000} = \frac{100}{1} = 100$$

$$\text{Now, } \frac{\Delta G_{1000}^0}{\Delta G_{2000}^0} = \frac{(-RT \ln K_{eq})_{1000}}{(-RT \ln K_{eq})_{2000}} = \frac{1000 \times \ln 10}{2000 \times \ln 100} = 0.25$$



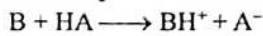
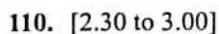
$$S = \sqrt{K_{sp} \left( \frac{[H^+]}{K_a} + 1 \right)} = \sqrt{2 \times 10^{-10} \left( \frac{10^{-3}}{10^{-8}} + 1 \right)} = \sqrt{2 \times 10^{-5}} = 4.47 \times 10^{-3}$$



No. of eq. of oxalic acid = No. of eq. of NaOH

$$\text{or } \frac{5.00 \times 0.10}{1000} \times 2 = \frac{9.0 \times M}{1000} \times 1$$

$$\therefore \text{Molarity of NaOH solution} = \frac{1}{9} = 0.11 \text{ M}$$



$$0.1 \text{ M, V ml}$$

$$0.1V \text{ mol} \quad 0.1 \text{ V m mol} \quad 0.1 \text{ V 0.1V}$$

$$[BH^+] = \frac{0.1V}{2V} = 0.5 \text{ M}$$

pH at eq. pt = 6 to 6.28

$$\text{pH} = 7 - \frac{1}{2} [\text{p}K_b + \log 0.05]$$

So  $\text{p}K_b = 2.30 - 2.80$ , Possible

**Solution 2**

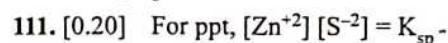
at V = ml rx is complete

So V = 3 ml is half of eq. pt

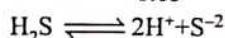
at which pH = 11

$\text{pOH} = (14 - 11) = \text{p}K_b + \log 1$

$\text{p}K_b = 3$

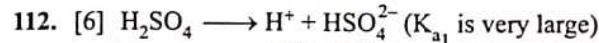


$$[S^{-2}] = \frac{1.25 \times 10^{-22}}{0.05} = 2.5 \times 10^{-21} \text{ M}$$



$$K_{Net} = 10^{-21} = \frac{[H^+]^2 \times 2.5 \times 10^{-21}}{0.1}$$

$$[H^+]^2 = \frac{1}{25} \quad [H^+]^2 = \frac{1}{5} \text{ M} = 0.2 \text{ M}$$



$$1 \text{ M} \quad 1 \text{ M}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \quad K_{a2} = 1.2 \times 10^{-2}$$

$[SO_4^{2-}]$  coming from  $Na_2SO_4 = 1.8 \times 10^{-2}$

$$\frac{[SO_4^{2-}][H^+]}{[HSO_4^-]} = \frac{1.8 \times 10^{-2} \times 1}{1} > K_{a2}$$

$\therefore$  Rather than dissociation of  $HSO_4^-$  into H and  $SO_4^{2-}$  ions, association between already present  $H^+$  and  $SO_4^{2-}$  will take place.

Assuming 'x' mol/L of  $SO_4^{2-}$  and  $H^+$  combines to form  $HSO_4^-$

$$[SO_4^{2-}] = 1.8 \times 10^{-2} - x$$

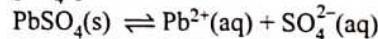
$$[H^+] = 1 - x \approx 1$$

$$[HSO_4^-] = 1 + x \approx 1 \quad (\text{assuming } x \ll 1)$$

$$\frac{(1.8 \times 10^{-2} - x)}{1} = 1.2 \times 10^{-2}$$

$$\Rightarrow x = 0.6 \times 10^{-2}$$

$$[SO_4^{2-}] = 1.2 \times 10^{-2} \text{ M}$$



If solubility of  $PbSO_4 = s \text{ M}$

$$\therefore [Pb^{2+}] = s$$

$$[SO_4^{2-}] = s + 1.2 \times 10^{-2} \approx 1.2 \times 10^{-2}$$

(assuming  $s \ll 1.2 \times 10^{-2}$ )

$$\therefore s \times 1.2 \times 10^{-2} = 1.6 \times 10^{-8}$$

$$s = \frac{1.6}{1.2} \times 10^{-6} = 1.33 \times 10^{-6}$$

On comparing with  $X \times 10^{-Y}$

$$Y = 6ss$$

# CHAPTER

# 6

# Redox Reaction

O

## Exercise-1 (Topicwise)

1. (b) CO is a neutral molecule So, O.S. of Ni is zero.

2. (c)  $\text{NH}_2\text{OH}$

suppose O.S. of N is x.

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

$$x = -1$$

3. (c)  $\text{CH}_4 \Rightarrow x + 4(+1) = 0$

$$x = -4$$

$\text{CH}_3\text{Cl} \Rightarrow x + 3(+1) + 1(-1) = 0$

$$x = -2$$

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

$$x = 0$$

$\text{CHCl}_3 \Rightarrow x + 1(+1) + 3(-1) = 0$

$$x = +2$$

$\text{CCl}_4 \Rightarrow x + 4(-1) = 0$

$$x = +4$$

4. (b)  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^{-1}$

suppose O.S. of Pt is x

$$x + 0 + 3(-1) = -1$$

$$x = -1 + 3$$

$$x = +2$$

5. (a) HNC

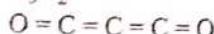
suppose O.S. of C is x.

$$(+1) + 1(-3) + x = 0$$

$$-2 + x = 0$$

$$x = +2$$

6. (b)  $\text{C}_3\text{O}_2$



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

$$3x = +4$$

$$x = +4/3$$

7. (a)  $\text{Na}_2\text{S}_2\text{O}_3$

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

$$2x = +4$$

$$x = +2$$

8. (b)  $\text{N}_3\text{H}$

$$3(x) + 1 = 0$$

$$3x = -1$$

$$x = -1/3$$

9. (a)  $\begin{array}{c} \xrightarrow{\text{Oxidation}} \\ \text{O} \quad \text{O} \quad +1 \quad -1 \\ \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \\ \xrightarrow{\text{Reduction}} \end{array}$

10. (c)  $\begin{array}{c} \xrightarrow{\text{Reduction}} \\ \text{O} \quad -1 \quad +7 \\ \text{Cl}_2 + \text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}_4^- \quad \text{H}_2\text{O} \\ \xrightarrow{\text{Oxidation}} \end{array}$

Oxidised as well as reduced.

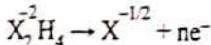
11. (d)  $\begin{array}{c} \xrightarrow{\text{Reduction}} \\ \text{O} \quad +1 \quad -1 \\ \text{Cl}_2 + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O} \\ \xrightarrow{\text{Oxidation}} \end{array}$

$\begin{array}{c} \xrightarrow{\text{Oxidation}} \\ +1 \quad \text{O} \quad +2 \\ \text{Cu}_2\text{O} + 2\text{H}^- \rightarrow \text{Cu} + \text{Cu}^{2+} + \text{H}_2\text{O} \\ \xrightarrow{\text{Reduction}} \end{array}$

$\begin{array}{c} \xrightarrow{\text{Oxidation}} \\ +1 \quad \text{O} \quad +2 \\ 2\text{HCuCl}_2 \xrightarrow{\text{Reduction}} \text{Cu} + \text{Cu}^{2+} + 4\text{Cl}^- + 2\text{H}^- \\ \xrightarrow{\text{Reduction}} \end{array}$

12. (c)  $\text{X}_2\text{H}_4$

or



$$\text{No. of electrons} = 2 \times \{-1/2 - (-2)\}$$

$$= 3/2 \times 2$$

$$= 3$$

13. (a)  $\begin{array}{c} \xrightarrow{\text{Reduction}} \\ -2 \quad -1 \quad \text{O} \quad -2 \\ \text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} + 2\text{H}_2\text{O} \\ \xrightarrow{\text{Oxidation}} \end{array}$

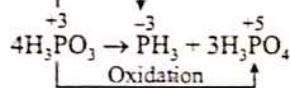
$\text{H}_2\text{S} \Rightarrow$  Reducing agent

$\text{H}_2\text{O}_2 \Rightarrow$  Oxidising agent

14. (b)  $\text{H}_2\text{O}_2$

In  $\text{H}_2\text{O}_2$ , O.S. of oxygen is (-1) which can be increase and decrease.

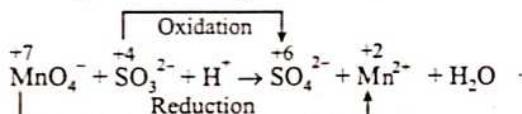
15. (c) Reduction



same element undergoes for oxidation as well as reduction.

16. (a)  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$  is a decomposition reaction.

17. (c)



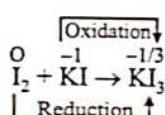
18. (d)  $\text{BaO}_2$

$$1(+2) + 2(x) = 0$$

$$2x = -2$$

$$x = -1$$

19. (c)



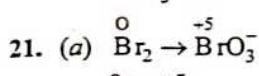
Both Oxidation as well as Reduction.

20. (a)  $\text{KNO}_3 \Rightarrow \text{N} = +5$

$$\text{HNO}_2 \Rightarrow \text{N} = +3$$

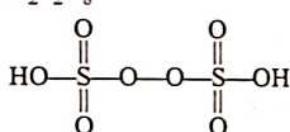
$$\text{NH}_4\text{Cl} \Rightarrow \text{N} = -3$$

$$\text{NaN}_3 \Rightarrow \text{N} = -1/3$$



$$0 \text{ to } +5$$

22. (d)  $\text{H}_2\text{S}_2\text{O}_8$



suppose O.S. of S = x

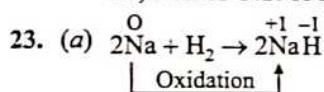
$$2x + 2(+1) + 6(+2) + 2(-1) = 0$$

$$2x + 12$$

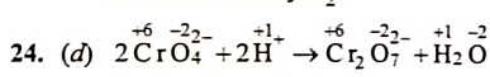
$$x = +6$$

One S has +6 O.S.

So, sum of O.S. of S = 6 + 6 = +12



Na is oxidised by  $\text{H}_2$ .



So there is no element that changes its O.S.

25. (d)  $\text{H}_3\text{AsO}_4$

suppose O.S. of As is x

$$3(+1) + x + 4(-2) = 0$$

$$x = +5$$

26. (c)  $\text{MgHxO}_3$

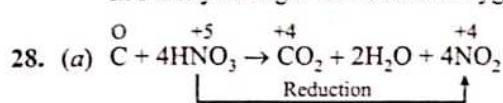
$$(+2) + 1(+1) + x + 3(-2) = 0$$

$$x = +3$$

27. (a)  $\text{O}-\text{O}\cdot$

Peroxy linkage

In Peroxy linkage, The O.S. of Oxygen is (-1).



$\text{HNO}_3 \Rightarrow$  Oxidising agent

29. (c)  $[\text{K}_3\text{Fe}(\text{CN})_6]$

$$3(+1) + x + 6(-1) = 0$$

$$x = +3$$

30. (d)  $\text{H}_2\text{SO}_3 \Rightarrow \text{S} = +4$

$$\text{H}_2\text{S} \Rightarrow \text{S} = -2$$

$$\text{H}_2\text{SO}_4 \Rightarrow \text{S} = +6$$

$$\text{H}_2\text{S}_2\text{O}_3 \Rightarrow \text{S} = +2$$

$\text{H}_2\text{S}, \text{H}_2\text{S}_2\text{O}_3, \text{H}_2\text{SO}_3, \text{H}_2\text{SO}_4$

31. (d)  $\text{KIO}_4$

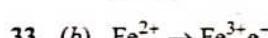
$$(+1) + x + 4(-2) = 0$$

$$x = +7$$

32. (d)  $\text{XeF}_5^-$

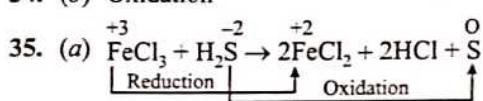
$$x + 5(-1) = -1$$

$$x = +4$$



loses one electron.

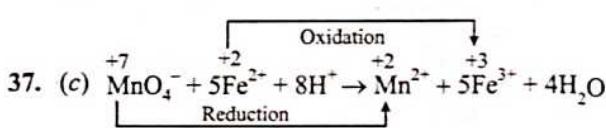
34. (b) Oxidation



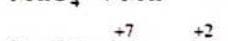
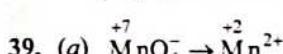
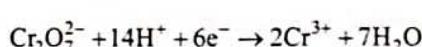
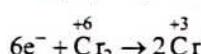
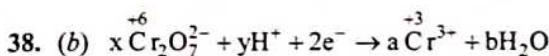
$\text{FeCl}_3 \Rightarrow$  O.A.

$\text{H}_2\text{S} \Rightarrow$  R.A.

36. (a) Reducing Potential



This is a spontaneous oxidation reduction reaction.



$$x = 5$$





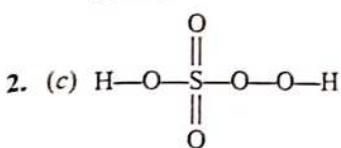


## Exercise-2 (Learning Plus)

1. (d)  $\text{H}_2\text{S}_2\text{O}_7$

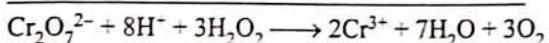
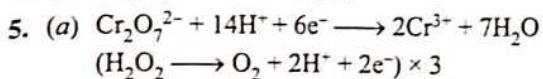
$$+2 + 2x + (-14) = 0$$

$$x = +6$$



3. (d)  $\text{F}_2\text{O}$

4. (c)  $\text{Fe}_3\text{O}_4 \Rightarrow \overset{+2}{\text{Fe}}\text{O}, \overset{+3}{\text{Fe}}_2\text{O}_3$



The reaction practically occurs with this stoichiometry.

6. (c) Let the O.N. of Co be x

O.N. of  $\text{NH}_3$  is zero

O.N. of Cl is -1

O.N. of Br is -1

$$\text{Hence, } x + 6(0) - 1 \times 2 - 1 = 0$$

$$\therefore x = +3$$

so, the oxidation number of cobalt in the given complex compound is +3.

7. (c) In the reaction  $\text{P}_2\text{O}_5 \rightarrow \text{H}_4\text{P}_2\text{O}_7$

The O.N. of P in  $\text{P}_2\text{O}_5$  is  $2x + 5(-2) = 0$  or  $x = +5$

The O.N. of P in  $\text{H}_4\text{P}_2\text{O}_7$  is  $4(+1) + 2(x) + 7(-2) = 0$   
 $2x = 10$  or  $x = +5$

Since there is no change in O.N. of P, hence the above reaction is neither oxidation nor reduction.

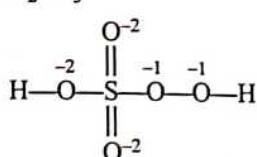
8. (b)  $\overset{+2}{\text{Fe}} \rightarrow \overset{+3}{\text{Fe}}, \quad \overset{-1}{2\text{I}^-} \rightarrow \overset{0}{\text{I}_2}$

9. (b) In Phosphorus acid  $\text{H}_3\text{PO}_3$

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

$$x = +3$$

10. (c)  $\text{H}_2\text{SO}_5$



$$x + 2(+1) + 3(-2) + 2(-1) = 0 \Rightarrow x = +6$$

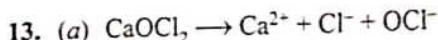
11. (c)  $(\text{N}_2\text{H}_5)_2\text{SO}_4$

$$4(x) + 10(+1) - 2 = 0$$

$$4x + 8 = 0$$

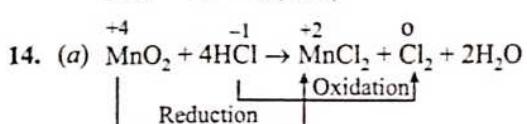
$$\therefore x = -2$$

12. (b)  $\overset{+6}{\text{Mo}} \rightarrow \overset{+3}{\text{Mo}}$  so, Oxidising agent

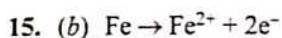


$$\text{Cl}^- \Rightarrow -1 \text{ (O.S.)}$$

$$\text{OCl}^- \Rightarrow +1 \text{ (O.S.)}$$

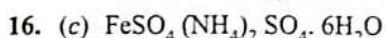


Two different elements undergo for Oxidation and Reduction



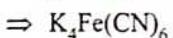
$$1 \text{ mole Fe} \rightarrow 2 \text{ mole e}^-$$

$$2 \text{ mole e}^- = 2N_A \text{ electrons}$$



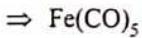
$$x + (-2) + 2(+1) + (-2) + 6(0) = 0$$

$$x = +2$$



$$4(+1) + x + 6(-1) = 0$$

$$x \Rightarrow +2$$



$$x + 5(\text{O}) = 0$$

$$x = 0$$



$$0.94(x) + (-2) = 0$$

$$x = 2/0.94$$

17. (c) Valency factor ratio is inversely related to molar ratio.

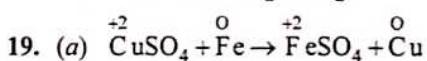
$$(\text{V.f.})\text{HI} : (\text{V.f.})\text{HNO}_3 = 1 : 3 = 2 : 6$$

$$\therefore \text{Molar ratio} = 6 : 2$$

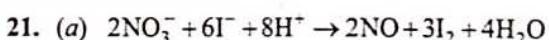


$$\text{V.f.} = 5 \qquad \qquad \qquad \text{V.f.} = 2$$

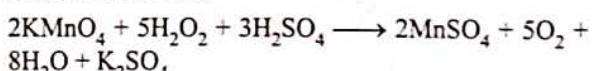
$\therefore$  Balanced equation:  $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$



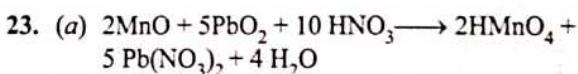
20. (a) Fact Based



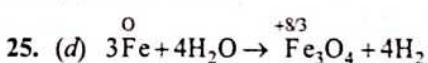
22. (a) Balance reaction is



$\therefore$  Sum of stoichiometric coefficients =  $2 + 5 + 3 + 2 + 5 + 8 + 1 = 26$

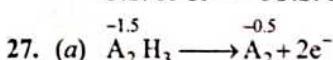


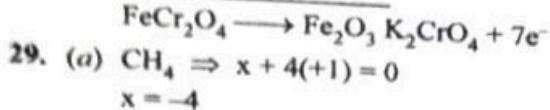
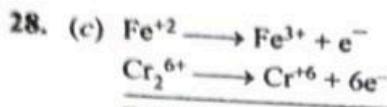
24. (d) Fact Based



$$\text{O.S. of N} = -3 \text{ O.S. of Cr} = +3$$

$$\text{O.S. of Cr} = +6 \text{ O.S. of N} = 0$$





30. (b) Weight of Metal =  $x$

Weight of Oxide =  $y$

Oxygen consumed =  $(y-x)$

$$(y-x) \rightarrow x$$

$$8 \rightarrow \frac{x \times 8}{y-x}$$

$$\text{Eq. wt.} = \frac{x \times 8}{y-x}$$

31. (c) n factor for  $\text{Mn}^{+3} = 1/2$

32. (a)  $\text{Eq.}_{\text{MO}} = \text{Eq.}_{\text{MCP}}$

$$\frac{3}{E_M + E_{O_2^-}} = \frac{5}{E_M + E_{Cl^-}}$$

$$\frac{3}{E_M + 8} = \frac{5}{E_M + 35.5}$$

$$EM = 33.25$$

33. (a) n.F. = 3

Equivalent wt. of  $\text{FeC}_2\text{O}_4 = M/3$

34. (a)  $\text{BrO}_3^- \rightarrow \text{Br}_2$

$$\begin{array}{ccc} +5 & & 0 \\ \text{BrO}_3^- & \rightarrow & \text{Br}_2 \end{array}$$

$$\therefore (\text{V.F.}) \text{BrO}_3^- = 5 \quad \therefore \text{Eq wt} = M/5$$

35. (a) In this reaction  $\text{H}_2\text{SO}_4$  is providing only 1  $\text{H}^+$  therefore, its n-factor = 1 and equivalent mass =  $\frac{98}{1}$ .

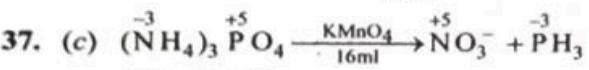
36. (a) Given  $E_{\text{metal}} = 2 \times 8 = 16$

$$\frac{\text{Weight}_{\text{oxide}}}{\text{Weight}_{\text{metal}}} = ?$$

$$\frac{\text{eq}_{\text{metal}}}{\text{eq}_{\text{oxide}}} = \frac{\text{Weight}_{\text{oxide}}}{\text{Weight}_{\text{metal}}}$$

$$\text{eq}_{\text{metal}} = \text{eq}_{\text{oxide}}$$

$$\frac{w_{\text{metal}}}{16} = \frac{w_{\text{oxide}}}{16+8} \quad \therefore \frac{w_{\text{oxide}}}{w_{\text{metal}}} = \frac{24}{16} = \frac{3}{2} = 1.5$$



$$+24 - 8 = 16$$

$$50 \times 0.2 \text{ M}$$

n-factor of  $\text{KMnO}_4$  in acidic medium = 5

n-factor of  $(\text{NH}_4)_3\text{PO}_4$  = 16

Eq. of  $(\text{NH}_4)_3\text{PO}_4$  = Eq. of  $\text{KMnO}_4$

$$\frac{0.2 \times 50}{1000} \times 16 = \frac{N \times 16}{1000}$$

$$N = 10$$

38. (d) Eq. of  $\text{NaH}_2\text{PO}_4$  + Eq. of  $\text{NaHCO}_3$  = Eq. of  $\text{NaOH}$

$$\frac{20 \times 0.1}{1000} \times 1 + \frac{40 \times 0.1}{1000} \times 1 = x$$

$$x = 6 \times 10^{-3}$$

## Exercise-3 (JEE Advanced Level)

1. (c,d) In (C) option, Cl goes from +5 to +7 and -1, while (D) option, Cl goes from 0 to +1 and -1.

2. (b,c) 'Cl' should be in intermediate oxidation state.

3. (a,b,c)

(a) Oxidation state of S = +6 in both.

(b) Oxidation state of Cr = +6 in both.

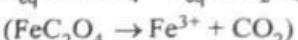
(c) Oxidation state of P = +5 in both.

4. (b,c,d)  $\text{PbO}_2$  is an oxide.

5. (b) As  $\text{KMnO}_4$  reduces, the compound must oxidize.  $\text{Fe}^{+3}$  cannot oxidize.

6. (b,c) S undergoes increase in oxidation number from +2 to +2.5, while I undergoes decrease in oxidation number from 0 to -1.

7. (a)  $n_{\text{eq}} \text{KMnO}_4 = n_{\text{eq}} \text{FeC}_2\text{O}_4$



$$\text{or } n \times 5 = 1 \times 3 \Rightarrow n = \frac{3}{5}$$

8. (a,b) m.eq. of  $\text{KMnO}_4$  = m.eq. of  $\text{KHC}_2\text{O}_4$

$$0.02 \times 100 \times 5 = \frac{x}{M} \times 2 \times 1000$$

m eq. of  $\text{Ca}(\text{OH})_2$  = m. eq of  $\text{KHC}_2\text{O}_4$

$$0.05 \times 100 \times 2 = \frac{y}{M} \times 1 \times 1000 \quad (M = \text{Mol. wt. of KHC}_2\text{O}_4)$$

Divide (i) and (ii)

$$\frac{0.02 \times 100 \times 5}{0.05 \times 100 \times 2} = \frac{2x}{y} \Rightarrow 1 = \frac{2x}{y} \Rightarrow 2x = y$$

9. (a,c)

(a)  $6 M_1 V_1 = M_2 V_2$  [ ∵ For  $\text{K}_2\text{Cr}_2\text{O}_7$ , Eq. wt. =  $\frac{\text{M.wt.}}{6}$ ]

(c)  $N_1 V_1 = N_2 V_2$

(b) and (d) are not possible.

10. (a,b,c,d)

Equivalent of oxidising agent = equivalents of reducing agent

$$\text{Eq.}_{\text{MnO}_4^-} = \text{Eq.}_{\text{Fe}^{2+}}$$

$$n_{\text{MnO}_4^-} \times 5 = n_{\text{Fe}^{2+}} \times 1$$

$$\text{Eq.}_{\text{Cr}_2\text{O}_7^{2-}} = \text{Eq.}_{\text{Fe}^{2+}}$$

$$n_{\text{Cr}_2\text{O}_7^{2-}} \times 6 = n_{\text{Fe}^{2+}} \times 1$$

$$\text{Eq.}_{\text{MnO}_4^-} = \text{Eq.}_{\text{Cu}_2\text{S}}$$

$$n_{\text{MnO}_4^-} \times 5 = n_{\text{Cu}_2\text{S}} \times 8$$

$$\text{Eq.}_{\text{Cr}_2\text{O}_7^{2-}} = \text{Eq.}_{\text{Cu}_2\text{S}}$$

$$n_{\text{Cr}_2\text{O}_7^{2-}} \times 6 = n_{\text{Cu}_2\text{S}} \times 8$$

11. (a,c)

$$\text{n}_{\text{eq}} \text{ metal nitrate} = \text{n}_{\text{eq}} \text{ metal sulphate}$$

$$\text{or } \frac{0.5}{E_M + 62} = \frac{0.43}{E_M + 48} \Rightarrow E_M = 38$$

12. (a,b,c,d) For HCl N = M

$$\text{Final molarity} = \frac{V_1 \times 1 + V_2 \times 0.25}{(V_1 + V_2)} = 0.75$$

$$0.75(V_1 + V_2) = V_1 + V_2 \times 0.25$$

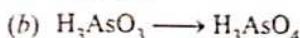
$$0.75 V_1 + 0.75 V_2 = V_1 + V_2 \times 0.25$$

$$0.5 V_2 = 0.25 V_1$$

$$\frac{V_1}{V_2} = 2 \text{ (All options are possible)}$$

13. (a,c,d) milli equivalent of  $\text{KMnO}_4 = 25 \times 0.2 = 5$  meq.

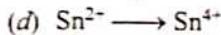
$$\text{milli equivalent of } \text{FeSO}_4 = 25 \times 0.2 \times 1 = 0.2 \times 25 = 5 \text{ (same)}$$



$$\text{milli equivalent of } \text{H}_3\text{AsO}_3 = 2 \times 50 \times 0.1 = 10 \text{ (not same)}$$

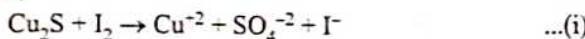


$$\text{milli equivalent of } \text{H}_2\text{O}_2 = 25 \times 0.1 \times 2 = 5 \text{ (same)}$$

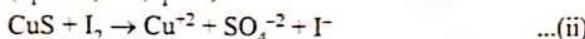


$$\text{milli equivalent of } \text{SnCl}_2 = 25 \times 0.1 \times 2 = 5 \text{ (same)}$$

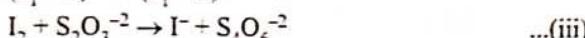
14. (a,b,d)



$$(n_f = 10) \quad (n_f = 2)$$



$$(n_f = 8) \quad (n_f = 2)$$



$$(n_f = 2) \quad (n_f = 1) \quad (n_f = 2)$$

In reaction (i):

$$\text{Meq of Cu}_2\text{S} = \text{Meq of I}_2$$

$$0.5 \times 10 \times V = 250 \times 1 \times 2$$

$$V = 100 \text{ ml (of Cu}_2\text{S)}$$

In reaction (ii):

$$\text{Meq of CuS} = \text{Meq of I}_2$$

$$0.5 \times 8 \times V_{\text{CuS}} = 250 \times 1 \times 2$$

$$V_{\text{CuS}} = 125 \text{ ml}$$

$$\text{Eq.wt. of I}_2 = \frac{\text{mol wt}}{n_f} = \frac{254}{2} = 127$$

15. (c)  $10 \text{ e}^- + 2\text{MnO}_4^- \longrightarrow 2\text{Mn}^{2+}$ ; v.f. = 10

$$\therefore \text{Eq. mass of Ba}(\text{MnO}_4)_2 = \frac{M}{10}$$

16. (b)  $\text{Fe}_{0.9}\text{O} + \text{K}_2\text{Cr}_2\text{O}_7 \longrightarrow \text{Fe}^{+3} + \text{Cr}^{+3}$ 

$$\text{n factor of Fe}_{0.9}\text{O} = 0.9 \left( 3 - \frac{2}{0.9} \right) = 0.7$$

$$\therefore \text{Eq mass} = \frac{M}{0.7} = \frac{10M}{7}$$

17. (c) n factor is 2 for  $\text{CaC}_2\text{O}_4$ 

$$\text{Eq. weight} = \frac{M}{2} = \frac{128}{2} = 64.$$

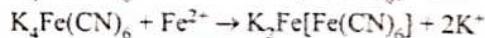
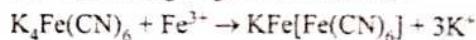
18. (d) Let x mole  $\text{FeCr}_2\text{O}_4$  and y mole  $\text{Fe}_{0.95}\text{O}$  present the sample.

Given eqn

So, Net n factor = 7 ( $\text{FeCr}_2\text{O}_4$ )

$$nf = .85 \quad .85e^- \text{ approx}$$

Now according to given information

milli moles of  $\text{K}_4\text{Fe}(\text{CN})_6$  reacted with  $\text{Fe}^{3+}$ 

$$= V_{\text{ml}} \times M - V_{\text{ml}} \times M$$

$$= 10 \times 1 - 7 \times .1 [N = M \times nf]$$

$$= \text{milli moles of } \text{Fe}^{3+}$$

Now,

$$x + 9.5y = 9.3 \times 10^{-3}$$

$$7x + .85y = .0482$$

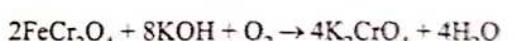
$$\text{So, solving } x = 6.5319 \times 10^{-3}$$

$$y = 2.9138 \times 10^{-3}$$

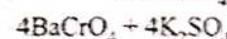
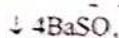
$$\text{wt of } x(\text{FeCr}_2\text{O}_4) = 6.5319 \times 10^{-3} \times 224$$

$$= 1.463$$

$$\text{mole of FeCr}_2\text{O}_4 = \frac{1.463}{224} = 6.5319 \times 10^{-3}$$



$$6.53 \times 10^{-3} \quad 2 \times 6.53 \times 10^{-3} + \text{Fe}_2\text{O}_3$$

∴ Wt of  $\text{BaCrO}_4$  PPt

$$= 2 \times 6.53 \times 10^{-3} \times 253$$

(mass of  $\text{BaCrO}_4$  = 253)

$$= 3.304\text{g}$$

19. (b) Mass  $\text{Fe}_{0.95}\text{O}$ 

$$= \text{mole of FeO} \times \text{mass of Fe}_{0.95}\text{O}$$

$$= 2.9138 \times 10^{-3} \times 69.20$$

(Calculated above)

$$=.2016\text{g}$$

$$\% = \frac{.2016}{2} \times 100$$

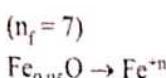
$$= 10.08\%$$

20. (b) Fact Based

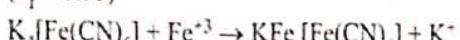
21. (c)  $\text{FeCr}_2\text{O}_4 \quad \text{Fe}_{0.95}\text{O}$ 

$$x \text{ mol} \quad y \text{ mol}$$

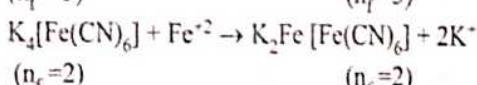




$$(n_f = 0.85)$$



$$(n_f = 3) \quad (n_f = 3)$$



$$(n_f = 2) \quad (n_f = 2)$$

m moles of  $\text{K}_4[\text{Fe}(\text{CN})_6]$

$$\text{reacted with Fe}^{+3} = 10 \times 1 - 0.7 = 9.3$$

= m moles of  $\text{Fe}^{+3}$

$$x + 0.95y = 9.3 \times 10^{-3}$$

$$7x + 0.85y = 0.0482$$

$$x = 6.5319 \times 10^{-3}$$

$$y = 2.9138 \times 10^{-3}$$

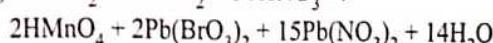
$$w_{\text{Fe}_{0.95}\text{O}} = 0.2016 \text{ gm}$$

$$w_{\text{FeCr}_2\text{O}_4} = 1.463$$

22. (c) Fact Based

23. (a) Fact Based

24. (b)  $2\text{MnBr}_2 + 17\text{PbO}_2 + 30\text{HNO}_3 \rightarrow$



The reaction is balanced by the loss or gain of 34 electrons.  
Hence,

$$E_{\text{HNO}_3} = \frac{30+63}{34} = 55.6$$

25. (a)-p, q; (b)-r, s; (c)-r, s; (d)-p, q

(a) n factor of  $\text{Cu}_2\text{S} = 8$

$$\begin{array}{ll} \text{KMnO}_4 & \text{K}_2\text{Cr}_2\text{O}_7 \\ 1 \times 5 = x & 1 \times 6 = x \times 8 \\ 1 = x & x = 1 \end{array}$$

$$x = \frac{5}{8} \quad x = \frac{6}{8} = \frac{3}{4}$$

(b) Container-I reacts with container-II

n factor of  $\text{KI} = 6$

$$\begin{array}{ll} \text{KMnO}_4 & \text{K}_2\text{Cr}_2\text{O}_7 \\ 1 \times 5 = x \times 6 & 1 \times 6 = x \times 6 \\ 1 = x & x = 1 \end{array}$$

(c) n factor of  $\text{NH}_4\text{SCN} = 6$

$$\begin{array}{ll} \text{KMnO}_4 & \text{K}_2\text{Cr}_2\text{O}_7 \\ x = \frac{5}{6} & x = 1 \end{array}$$

(d) n factor of  $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O} = 8$

$$\begin{array}{ll} \text{KMnO}_4 & \text{K}_2\text{Cr}_2\text{O}_7 \\ x = \frac{5}{8} & x = \frac{3}{4} \end{array}$$

26. [50%]  $\text{Mn}^{2+} + \text{KMn}^{+7}\text{O}_4 \rightarrow \text{Mn}^{3+}$

$$\text{mole of Mn}^{2+} = \text{mole of KMnO}_4 \times 4$$

$$= \text{vol. of KMnO}_4 \times \text{molarity} \times 4$$

$$= 3 \times 0.25 \times 4$$

$$= 3$$

(In acidic medium, n-factor for  $\text{KMnO}_4$  is 5 so molar  
= normality /5)

$$\begin{aligned} \text{Mole of Mn}_3\text{O}_4 &= \frac{1}{3} \text{ mole of Mn}^{2+} \\ &= 1 \text{ mole} \\ &= 229 \text{ gm} \\ \% \text{ of Mn}_3\text{O}_4 &= \frac{229}{458} \times 100 = 50\% \end{aligned}$$

27. [80%]  $\text{CuSO}_4 + \text{KI} \rightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$



$$\text{meq. of Na}_2\text{S}_2\text{O}_3 = \text{meq. of I}_2$$

$$\text{meq. of I}_2 = 40 \times 1 = 40$$

$$= \text{meq. of CuSO}_4 \text{ in } 25 \text{ ml}$$

$$\text{meq. of CuSO}_4 \text{ in } 250 \text{ ml} = 400 \text{ meq.}$$

$$\text{wt. of CuSO}_4 = 6.4 \times 160 = 64$$

$$\% \text{ Purity} = \frac{64}{80} \times 100 = 80\%$$

28. [5]  $\text{Fe}_2\text{O}_3 \xrightarrow{\text{Zn}} \text{Fe}^{2+} \rightarrow 30 \times \frac{100}{25} \text{ ml; } 0.01 \text{ M}$

$$100 \times N = 120 \times 0.01 \times n$$

$$N = 1.2 \times 10^{-2} n$$

$$\frac{0.48}{160} \times \frac{1000}{100} = 1.2 \times 10^{-2} n$$

$$n = 5$$

29. [2]  $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$  n-factor = 5

Equivalents of

$$\text{MnO}_4^- = 1.61 \times 10^{-3} \times 5 = 8.05 \times 10^{-3}$$

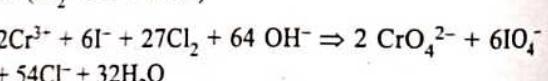
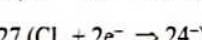
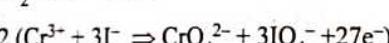
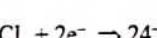
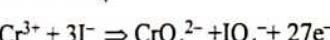
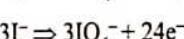
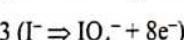
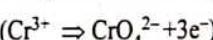
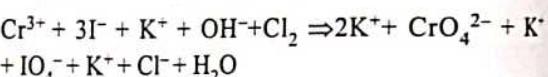
$$\text{Equivalents of A}^{n+} = 8.05 \times 10^{-3}$$

$$\text{N-factor of AO}_3^- = 5 - n$$

$$\therefore (5 - n) \times 2.68 \times 10^{-3} = 8.05 \times 10^{-3}$$

$$5 - n = 3 \quad n = 2$$

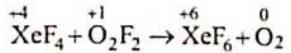
30. [27]  $\text{CrI}_3 + \text{KOH} + \text{Cl}_2 \Rightarrow \text{K}_2\text{CrO}_4 + \text{KIO}_4 + \text{KCl} + \text{H}_2\text{O}$



## Exercise-4 (Past Year Questions)

### JEE MAIN

1. (a) In the reaction



Xenon undergoes oxidation while oxygen undergoes reduction.

2. (a)  $\text{I}_2 + 10\text{HNO}_3 \rightarrow 2\text{HIO}_3 + 10\text{NO}_2 \uparrow + 4\text{H}_2\text{O}$   
Iodine in  $\text{HIO}_3$  has +5 oxidation state.

3. (d) Fact based.

4. (b)  $5\text{C}_2\text{O}_4^{2-} + 2\text{KMnO}_4 + \text{H}^+ \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + \text{H}_2\text{O}$   
After balancing 10 gain or loss of electron.

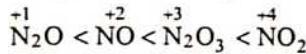
5. (c) H directly attached to P atom.

6. (b)  $n_{\text{eq.}} \text{KMnO}_4 = n_{\text{eq.}} [\text{FeC}_2\text{O}_4 + \text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{FeSO}_4]$   
or  $n \times 5 = 1 \times 3 + 1 \times 6 + 1 \times 1$

$$\therefore n = 2$$

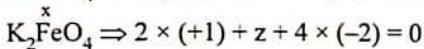
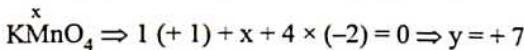
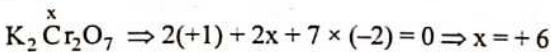
Correct option: (b)

7. (d) Correct order of oxidation state of nitrogen in oxides of nitrogen is following



8. (c)  $2\overset{+1}{\text{Cu}}\text{Br} \xrightarrow{\substack{\text{Oxidation} \\ \text{Reduction}}} \overset{+2}{\text{CuBr}_2} + \overset{0}{\text{Cu}}$

9. [19]

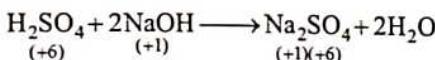


$$\Rightarrow z = +6$$

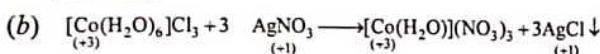
$$\text{So, } (x + y + z) = 6 + 7 + 6 = 19$$

10. (a)

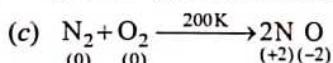
- (a) The given reaction are as follows :



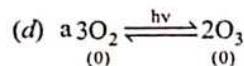
(No change in oxidation state, so not a redox reaction).



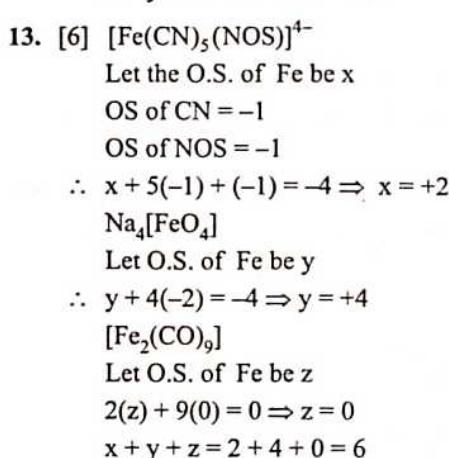
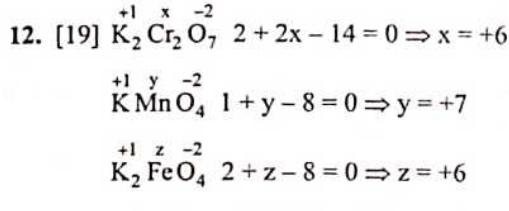
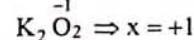
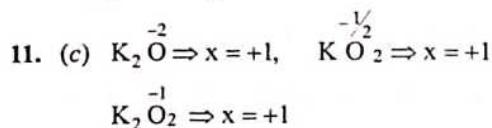
(No change in oxidation state, so not a redox reduction).



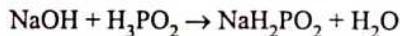
( $\text{N}_2$  oxidised from 0 to +2 oxidation state and  $\text{O}_2$  reduced from 0 to -2 oxidation state).



(No change in oxidation state, so not a redox reaction).



14. [10.00] Phosphinic acid is  $\text{H}_3\text{PO}_2$



Milliequivalents of NaOH = milliequivalents of  $\text{H}_3\text{PO}_2$

$$V \times 0.1 = 10 \times 0.1$$

$$V = 10 \text{ mL}$$

$$15. [10.00] \text{ Normality} = \frac{\text{No. of equivalents of solute}}{\text{Volume of Solution(in L)}}$$

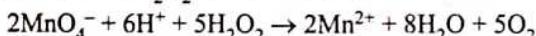
$$0.1 = \frac{1.43}{(106+18x)} \times 0.1$$

$$\Rightarrow \frac{106+18x}{2} = 143$$

$$\Rightarrow 18x = 286 - 106 = 180$$

$$x = 10$$

16. [19.00]  $2\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{3+} + 2\text{OH}^-$



$$\therefore x + y + x' + y' + z' = 19$$

17. [85]  $5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$

$$\text{Moles of KMnO}_4 = \frac{0.316}{158} = 2 \times 10^{-3}$$

$$\text{Equivalents of H}_2\text{O}_2 = \text{Equivalent of KMnO}_4 = 2 \times 10^{-3} \times 5 = 0.01$$

$$\text{Moles of H}_2\text{O}_2 = \frac{0.01}{2} = 0.005$$

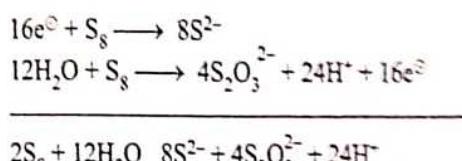
$$\text{Mass of pure H}_2\text{O}_2 = 0.005 \times 34 = 0.170 \text{ gm}$$

$$\text{Percentage purity} = \frac{0.17}{0.2} \times 100 = 85\%$$

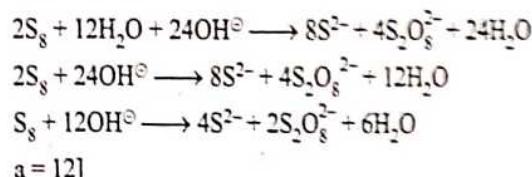
18. (d) Colour of  $\text{Fe}^{2+}$  is observed green and  $\text{Fe}^{3+}$  is yellow.  
 19. (c) No option contains all species that show disproportionation reaction. So question is bonus.

$\text{MnO}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$  – Cl, Mn, Cr in these anions are present in highest oxidation state. These will not undergo disproportionation.

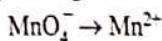
20. [12]



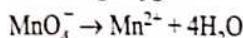
for balancing in basic medium add equal number of  $\text{OH}^-$  that of  $\text{H}^+$



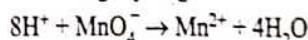
21. [16] Writing the half reaction oxidation half reaction



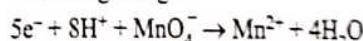
Balancing oxygen



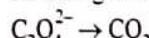
Balancing Hydrogen



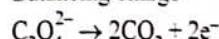
Balancing charge



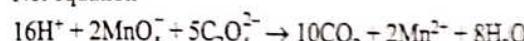
Reducing half



Balancing charge

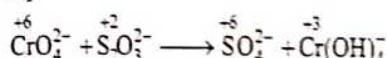


Net equation



$$\text{So, } c = 16$$

22. [173]



$$\text{gm equi. of CrO}_4^{2-} = \text{S}_2\text{O}_3^{2-}$$

$$0.154 \times 3 \times v = 0.25 \times 40 \times 8$$

$$v = 173.16 = 173 \text{ ml}$$

23. [24]

$$n_{\text{eq}} \text{Fe}^{2+} = n_{\text{eq}} \text{Cr}_2\text{O}_7^{2-}$$

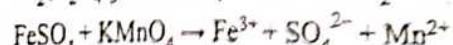
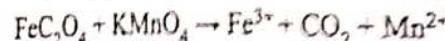
$$\text{or, } \left( \frac{15 \times M_{\text{Fe}^{2+}}}{1000} \right) \times 1 = \left( \frac{20 \times 0.03}{1000} \right) \times 6$$

$$\therefore = 0.24 \text{ M} = 24 \times 10^{-2} \text{ M}$$

24. (a) The oxidation of a dilute solution of each of



$\text{Fe}_2(\text{SO}_4)_3$  in acidic medium with  $\text{KMnO}_4$  is as follows



Change in oxidation number of Mn is 5. Change in oxidation number of Fe in (i), (ii) and (iii) are +3, +6, respectively

$$n_{\text{eq}} \text{KMnO}_4 = n_{\text{eq}} [\text{FeC}_2\text{O}_4 + \text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{FeSO}_4]$$

$$n \times 5 = 1 \times 3 + 1 \times 6 + 1 \times 1$$

$$n = 2$$

25. (d)

$$\text{Given, } W_{\text{Ca}(\text{HCO}_3)_2} = 0.81 \text{ g}$$

$$W_{\text{Mg}(\text{HCO}_3)_2} = 0.73 \text{ g}$$

$$W_{\text{Ca}(\text{HCO}_3)_2} = 162 \text{ g mol}^{-1}$$

$$W_{\text{Mg}(\text{HCO}_3)_2} = 146 \text{ g mol}^{-1}$$

$$W_{\text{H}_2\text{O}} = 100 \text{ ml}$$

$$\text{Now, } n_{\text{eq}} [\text{CaCO}_3] = n_{\text{eq}} [\text{Ca}(\text{HCO}_3)_2] + n_{\text{eq}} [\text{Mg}(\text{HCO}_3)_2]$$

$$\frac{W}{100} \times 2 = \frac{0.81}{162} \times 2 + \frac{0.73}{146} \times 2$$

$$\therefore \frac{W}{100} = 0.005 + 0.005$$

$$W = 0.01 \times 100 = 1$$

$$\text{Thus, hardness of water sample} = \frac{1}{100} \times 10^6$$

$$= 10,000 \text{ ppm}$$

26. (a) Upto first end point

$$\text{gm equi. of (NaOH + Na}_2\text{CO}_3) = \text{HCl}$$

$$x + y \times 1 = \frac{1}{10} \times 17.5$$

$$x + y = 1.75$$

Upto second end point

$$\text{NaOH} + \text{Na}_2\text{CO}_3 \equiv \text{HCl}$$

$$x + y \times 2 = \frac{1}{10} \times 19$$

$$x + 2y = 1.9$$

$$y = 0.15$$

$$\% \text{Na}_2\text{CO}_3 = \frac{0.15 \times 10^{-3}}{0.4} \times 100$$

$$= 3.975\%$$

$$= 4\%$$

27. [6]  $V_{\text{NaOH}} = 4.4 \text{ ml}$

$$\text{eq. of NaOH} = \text{eq. of H}_2\text{C}_2\text{O}_4$$

$$\text{or, } M \times 4.4 \times 1 = 1.25 \times 10 \times 2$$

$$\text{or, } M = 5.68 \text{ M}$$

$\therefore$  Nearest integer answer is 6



28. [50] Most precise volume of HCl = 5 ml at equivalence point

Meq. of  $\text{Na}_2\text{CO}_3$  = meq. of HCl.

Let molarity of  $\text{Na}_2\text{CO}_3$

Solution = M, then

$$M \times 10 \times 2 = 0.2 \times 5 \times 1$$

$$M = 0.05 \text{ mol/L}$$

$$= 0.05 \times 1000 = 50 \text{ mM}$$

29. [3] Acid + Base  $\rightarrow$  Salt +  $\text{H}_2\text{O}$

$$0.1 \text{ M} \quad \text{M(OH)}_2$$

$$10 \text{ mL} \quad 0.05 \text{ M}$$

$$30 \text{ mL}$$

At equivalence point

Equivalent of acid = equivalent of base

$$0.1 \times 10 \times n = 30 \times 0.05 \times 2$$

$$n = 3$$

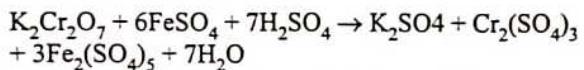
30. (a)  $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$   
+6                    +7                    +4

So, it is disproportionation reaction.

## JEE ADVANCED

1. (d) The formula of Mohr's salt is  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ . It is a mixture of ferrous sulfate and ammonium sulfate. Ferrous sulfate is oxidized by potassium dichromate.

The reaction is as follows:



1 mole of potassium dichromate reacts with 6 moles of ferrous sulphate. Thus, the number of moles of Mohr's salt required per mole of dichromate is 6.

2. (c) Milli mole of Hypo =  $0.25 \times 48$

$$= 2 \times \text{milli mole of Cl}_2$$

$$\text{milli mole of Cl}_2$$

$$= \frac{0.25 \times 48}{2} = 6 \text{ milli mole}$$

$$= \text{milli mole of Cl}_2 = \text{milli mole of CaOCl}_2$$

$$\text{So, molarity} = \frac{6}{25} \text{ M} = 0.24 \text{ M}$$

3. (a,b,d)



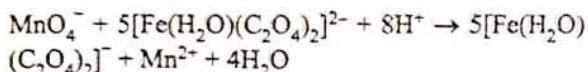
Hence,  $\text{I}^-$  is oxidised to  $\text{I}_2$

Coefficient of  $\text{HSO}_4^-$  = 6

and  $\text{H}_2\text{O}$  is one of the product.

Hence (a), (b), (d)

4. [8] The balanced chemical equation for the oxidation of the complex is as given below.

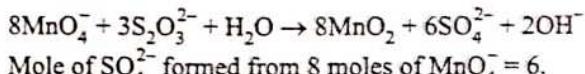


$$\text{Hence, } -\frac{d}{dt}[\text{MnO}_4^-] = \frac{1}{8} \frac{d}{dt}[\text{H}^+]$$

$$\frac{\frac{d}{dt}[\text{H}^+]}{\frac{d}{dt}[\text{MnO}_4^-]} = 8$$

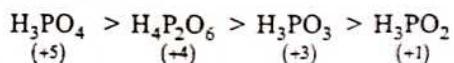
Hence, the ratio of the rate of change of  $[\text{H}^+]$  to the rate of change of  $[\text{MnO}_4^-]$  is 8.

5. [6]

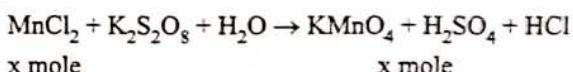


Mole of  $\text{SO}_4^{2-}$  formed from 8 moles of  $\text{MnO}_4^-$  = 6.

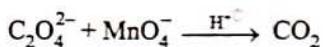
6. (b) Correct order:



7. [126]



$$x \text{ mole} \quad \quad \quad x \text{ mole}$$



milli equivalents of  $\text{C}_2\text{O}_4^{2-}$  = milli equivalents of  $\text{MnO}_4^-$

$$2 \times \frac{0.225}{90} = x \times 5$$

$$x = 1 \times [55 + 71]$$

$$= 126 \text{ mg}$$

# CHAPTER

# 7

# Classification of Elements and Periodicity in Properties



## Exercise-1 (Topicwise)

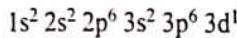
1. (c) According to Doberiner's Traid rule, in a traid atomic mass of middle element was approximately equal to average atomic mass of other two element

$$x - y = \frac{x + z}{2}$$

y

$$z - 26 = \frac{10 + z}{2}, 10 + Z = 52, Z = 42$$

2. (c) For k, electronic configuration would be:

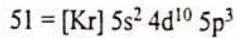
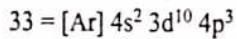


↑

So it will belong to d block.

3. (b) If n = 7 then it will be 5f or actinide series.

4. (b)  $15 = [\text{Ne}] 3s^2 3p^3$



So all belongs to nitrogen family as outermost configuration is  $ns^2 np^3$  or belongs to 15<sup>th</sup> group.

5. (a) Fluorine only shows negative oxidation state whereas other halogen shows negative as well as positive oxidation state.

6. (c)  $Z_{\text{eff}} = z - \sigma$

$Z$  = atomic no

S = shielding constant

If  $(Z_{\text{eff}})_{4s} = z - \sigma$

$$\sigma = 0.85 + 8 + 10 \times 1 + 0.35 \times 0 = 16.8$$

$$Z_{\text{eff}} = 19 - 16.8 = 2.20$$

If  $(Z_{\text{eff}})_{3d} = z - \sigma$

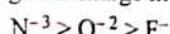
$$\sigma = 0.85 \times 8 + 0.35 \times 8 + 1 \times 2 = 11.8$$

$$(Z_{\text{eff}})_{3d} = 19 - 11.8 = 7.40$$

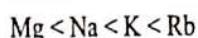
7. (a)  $Z_{\text{eff}}$  increases on moving left to right in a period.

8. (a) The atomic radius is lower due to the high effective nuclear charge.

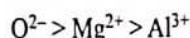
9. (c) As negative charge increases ionic radius increases



10. (c) On moving top to down no. of increases. Hence atomic radius increases.

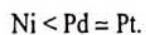


11. (b) For isoelectronic species more the negative charge more the size.



12. (c) The compound in which Mn has least +ve oxidation state will have maximum radius. In  $MnO$ , Mn have +2 oxidation state which is least among all other compound.

13. (a) Down the group atomic size increases due to increase in no. of shell. but in Pd and Pt this increase is very less due to the poor shielding of d and f orbital electrons. Thus  $Pd = Pt$ .



14. (c) The atomic radius always decreases from left to right. Hence incorrect option is  $Y = La$

15. (c) Cationic radius < atomic radius < anionic radius



16. (d) On moving down the group, no. of shell increases. Hence  $N < P$

17. (a) On moving left to right  $Z_{\text{eff}}$  increases hence atomic radius decreases.

18. (d) On moving top to bottom in a group, the ionic radius increases. Hence  $I^- > Br^- > F^-$

The ionic radius for  $O^{2-} > F^-$  due to low effective nuclear charge. Hence



19. (b) After removing 1 e<sup>-</sup> from 3p orbital, it will achieve fully filled electronic configuration.

$$20. (a) r<sub>cl<sup>-</sup></sub> =  $\frac{d}{2} = \frac{10}{2} = 5\text{\AA}$$$

$$r_{H^+} = \frac{d}{2} = \frac{2}{2} = 1\text{\AA}$$

$$r_{HCl} = r^+ + r^- - 0.9 (\Delta E.N)$$

$$= 1 + 5 - 0.9(3 - 2.1)$$

$$= 5.919\text{\AA}$$

21. (c)  $\text{Al} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^1$   
 $\text{Mg} \rightarrow 1s^2 2s^2 2p^6 3s^2$   
 $\text{O} \rightarrow 1s^2 2s^2 2p^4$   
 $\text{N} \rightarrow 1s^2 2s^2 2p^3 \rightarrow$  Max no. of unpaired  $e^-$   
Hence  $\text{Mg} < \text{Al} < \text{O} < \text{N}$
22. (d) Lanthanide Contraction is the steady decrease of size of the atom with increase in atomic no. in the lanthanide series.
23. (d) He has small size and stable configuration.
24. (d)  $\text{Al} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^1$   
After removing  $3e^-$  Al will have stable configuration hence +3 is most stable and  $\text{Al}^+$  contain completely filled 3s orbital hence  $\text{Al}^{+3} > \text{Al}^+ > \text{Al}^{+2}$ .
25. (b)  $\text{Mg} \rightarrow \text{Mg}^+ + e^- \quad \text{IP}_1 = 178 \text{ K cal mol}^{-1}$   
 $\text{Mg}^+ \rightarrow \text{Mg}^{+2} + e^- \quad \text{IP}_1 = 348 \text{ K cal mol}^{-1}$   
 $\text{Mg} \rightarrow \text{Mg}^{+2} + 2e^- \quad \text{IP} = \text{IP}_1 + \text{IP}_2$   
 $= 348 + 178 = 526 \text{ K cal}$
26. (b) Ionisation energy increases from left to right ( $\text{Li} \rightarrow \text{B}$ ) and decrease from top to bottom in periodic table But Be ( $1s^2 2s^2$ ) has higher ionisation energy than B ( $1s^2 2s^2 2p^1$ ) due to fully filled s-orbital.  
 $\text{Be} > \text{B} > \text{Li} > \text{Na}$
27. (d)  $1s^2 2s^2 2p^6 3s^2$  as there is drastic change in I.P from I.P<sub>2</sub> to I.P<sub>3</sub>.
28. (c) Alkali metals have general electronic configuration of  $ns^1$  hence it would be easy to remove only  $1e^-$  for removal of second  $e^-$  large amount of energy would be given.
29. (a) Element can be Be as there is large IP difference between I.P<sub>2</sub> and I.P<sub>3</sub>.
30. (c) The order of I.P is Si > S > P > Cl.  
The chlorine has highest I.P value because it has smallest atomic size than others.  
P has half filled  $e^-$  configuration which leads to stability of the atom so it has higher I.P.
31. (a)  $\text{IE}_1 < \text{IE}_2 < \text{IE}_3 \dots < \text{IE}_4$
32. (b) On addition of an electron to Li, energy is released.
33. (a) 3<sup>rd</sup> period elements of p block has more electron affinity than 2<sup>nd</sup> period elements as the incoming  $e^-$  will suffer less repulsion.
34. (d) The most positive  $\Delta H_{eg}$  will be for  $\text{O}^{2-}$  and most negative  $\Delta H_{eg}$  will be for  $\text{O}^{2+}$
35. (c) S has highest electron affinity.
36. (c) A is N element  
B is O element  
C is P element  
D is S element  
electron affinity of 3<sup>rd</sup> period element in p block is greater than 2<sup>nd</sup> period element and group 16 has more  $e^-$  affinity than 15 group.  
So order is D > C > B > A.
37. (d) Electron affinity order for 16<sup>th</sup> group is  
 $\text{Te} < \text{Se} < \text{O} < \text{S}$   
S has more electron affinity than oxygen as the incoming  $e^-$  will suffer less repulsion than O due to large size of S.
38. (c) Addition of  $e^-$  to isolated atom results in release of energy but as nitrogen has half filled configuration hence energy will be given to add an electron in it.
39. (c) As  $ns^2 np^3$  half filled configuration hence it will have least electron affinity.
40. (d) 2<sup>nd</sup> electron affinity of an element is always endothermic.
41. (a) 3<sup>rd</sup> period elements of P block have more electron gain enthalpy than 2<sup>nd</sup> period as incoming  $e^-$  will suffer less repulsion and in a period E.A. increases from left to right due to increase in  $Z_{\text{eff}}$  Hence  
 $\text{N} < \text{O} < \text{F} < \text{Cl}$
42. (b)  $\text{P} < \text{S} < \text{N} < \text{O}$   
In a period, electronegativity increases from left to right and in a group, the electronegativity decreases down the group.
43. (a) Electron affinity of F is less than Cl.
44. (a) F atom can't hold additional  $e^-$  more tightly than Cl atom as additional  $e^-$  will experience repulsion in F-atom due to smaller size.
45. (c) Hydrogen has more ability to attract shared pair of  $e^-$ .
46. (b) Electronegativity decrease down the group  
 $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$
47. (a)  $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3 > \text{SiO}_2$   
More the metallic character higher the  $e^-$  donating tendency. Therefore lower the I.E. more the basic nature of oxide.
48. (c) Greater the oxidation state, greater will be the nature of acidic oxide. In  $\text{Mn}_2\text{O}_7$ , Mn have +7 oxidation state hence it is most acidic.
49. (d) All are amphoteric oxide. It reacts with both acid and base to produce respective salts.

## Exercise-2 (Learning Plus)

- (d) Terbium (z = 65)  
Actinoids are in 2n d f-block element series starting from (z = 90 to z = 103)
- (c) Period number is the maximum (n) value
- (b) d-subshell can have maximum 10 electrons, so it has 10 groups (d block)
- (c) → 1st inner-transition elemental series are lanthanoids in which electrons are filled in 4f-orbitals.
- (d) → as it resembles properties of alkali metals; so it can be placed in group.
- (c) Cu has atomic No. (47–18) = 29 above Ag (47).  
Below Ag has Au with Atomic No. (47 + 32) = 79.



7. (b) In Modern periodic table and long form of periodic table, physical and chemical properties are periodic function of atomic Number.

8. (a) for Lanthanoids, this term is used.

$$9. (a) \frac{z}{e}$$

$$N^{+} \Rightarrow \frac{7}{10} \Rightarrow 0.7$$

$$O^{-} \Rightarrow \frac{8}{10} \Rightarrow 0.8$$

$$F^{-} \Rightarrow \frac{9}{10} \Rightarrow 0.9$$

$$10. (a) \sigma_{Cu} = x$$

$$\sigma_{Zn} = x + 0.35$$

(as last electron comes in outer 4s) {so electron of 4s is taken}

$$11. (c) \sigma \text{ for } d \text{ and } f = 0.85$$

12. (a) as diffuseness of s-orbitals increases, their shielding effect decrease.

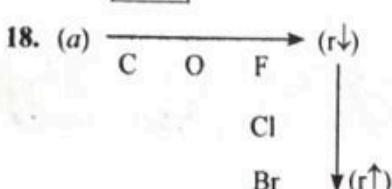
$$13. (c) r \propto \frac{1}{z} \text{ for isoelectronic species}$$

$$14. (d) r \propto \frac{1}{z} \text{ for isoelectronic species}$$

$$15. (d) r \propto \frac{1}{\text{amount of +ve charge}}$$

$$16. (b) r \propto \frac{1}{z}$$

$$17. (c) r \propto \frac{1}{z}$$



$$\therefore Br > Cl > C > O > F$$

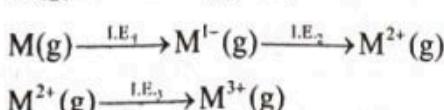
19. (c) It is because ( $z_{\text{eff}} = \sigma$ ) (in 3d series)

$$20. (d) M(g) \xrightarrow{IE_1} M^+(g) \xrightarrow{IE_2} M^{2+}(g) \xrightarrow{IE_3} M^{3+}(g)$$

$$IE_3 > IE_2 > IE_1$$

(successive I.E. always increases)

$$21. (b) M(g) \rightarrow M^{3+}(g) + 3e; \Delta H = x \text{ kJ}$$



$$IE_1 + (IE_2)_M + (IE_3) = x \quad [(IE_3)]_M = [(IE_1)]_M$$

$$y + (IE_2)_M + z = x$$

$$(IE_2)_M = x - y - z \text{ (kJ/mol)}$$

$$22. (c) \text{ order of } (IE_1) \text{ of N, O, Be, B} \Rightarrow B < Be < O < N$$

23. (c) (down the group  $IE \downarrow$ )

24. (c) → Assertion is correct because Be has stable electronic configuration.

→ Reason is false because  $n + \ell$  value of  $2p > 2s$

25. (b) Down the group I.E. decreases.

$$26. (d) K < Ca (IE_1)$$

$K > Ca (IE_2)$  {due to stable electronic configuration of K}

27. (c) I.E.  $\alpha$  positive charge; (greater than Neutral one)  
along the period from  $(Be^+ > Be)$  L to R  $\Rightarrow IE \uparrow (C > B)$

$$28. (b) Ne > Cl > P > S > Mg > Al$$

→ Along the period from left to right I.E. increases exceptionally due to stable electronic configuration of Mg and P, they have more I.E. than that of element which is next after to them.

$$29. (d) A \xrightarrow{IE_1} A^+ \xrightarrow{IE_2} A^{2+}$$

If diff  $> 16$  ev  $\Rightarrow$  then lower O.S. is stable

If diff  $< 11$  ev  $\Rightarrow$  then higher O.S. is stable

$$30. (d) C \quad N \quad O \quad F$$

$$2s^2 2p^2 \quad 2s^2 2p^3 \quad 2s^2 2p^4 \quad 2s^2 2p^5$$

$$\left[ \begin{array}{cccc} C^+ & N^+ & O^+ & F^+ \\ 2s^2 2p^1 & 2s^2 2p^2 & 2s^2 2p^3 & 2s^2 2p^4 \end{array} \right] \Rightarrow$$

$(IE \uparrow)$  (but exceptionally  $O^+ > F^+$ )

So 2<sup>nd</sup> I.E. order  $\Rightarrow O > F > N > C$

31. (a) Tendency to gain electron  $\uparrow \Rightarrow$  from left to right (exceptionally half filled and full filled has low tendency to gain electron)  
iv > ii > iii > i

32. (c)  $O^-$  ion will tend to resist the addition of another electron due to electron-electron repulsion.

$$33. (c) Be + e^- \rightarrow Be^-$$

Due to stable electronic configuration in Be. We have to give energy, so it is unstable.

34. (b) Adding second electron energy is absorbed due to repulsion.

35. (b)  $S^- + e^- \rightarrow S^{2-}$  (polyanionic species are endothermic in nature)

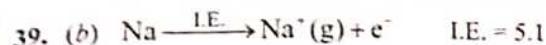
$$36. (a) N + e^- \rightarrow N^- \text{ (endothermic step)}$$

And reverse is exothermic due to stable nitrogen electronic configuration.

37. (b) as size of Cl is bigger than F, so it will accommodate electron with least repulsion if we compare it with F.

38. (b) Cl > F > S > O

E.G.E of 3<sup>rd</sup> period element is greater than 2<sup>nd</sup> period elements and group 17 has more E.G.E. than 2<sup>nd</sup> period.



40. (d) All statements are correct as per the theory of Electron gain enthalpy.

41. (b) As Nitrogen has half filled p subshell, so electron removal is tough. Hence Ionisation energy is high.

42. (c) Electron gain enthalpy and ionisation energy are affected by stable electronic configuration.

43. (c) Down the group electronegativity decreases.

44. (c) Down the group metallic character increases; hence basic strength of metal oxide increases.

45. (d) From left to right, Metallic character decreases.



46. (a) SnO, ZnO, PbO → are amphoteric oxides

47. (a)  $\text{Cl}_2\text{O}_7 \rightarrow$  There is maximum oxidation number on Cl; i.e. = 7

Hence it is more acidic

→ as O.N. ↑ ⇒ acidic strength increases.

48. (b) The correct order is



↑

due to stable electronic configuration.

49. (d)  $\text{CO}_2 > \text{SiO}_2$

Acidic strength decreases down the group.

### Exercise-3 (JEE Advanced Level)

1. (c,d) 1<sup>st</sup> group elements show + 1 oxidation state and 2<sup>nd</sup> group elements show + 2 oxidation state.

Group 18 elements are all noble gases, [He, Ne, Ar, Kr] does not show any oxidation state while Xe shows oxidation states namely II, IV, VI.

2. (b,d) Cu shows + 1 and + 2 oxidation state so  $\text{Cu}_2\text{Cl}_2$  exist. Similarly potassium shows + 1 O.S. so general formula with 'O' is  $\text{K}_2\text{O}$ .

3. (a,b,d)

Zn have only + 2 or zero oxidation state.

4. (a,b,c,d)

Due to inert pair effect, Pb, Tl, Bi has their lower oxidation state more stable than higher ones. O has (-2) O.S. more stable than other oxidation states.

5. (a,b,c,d)

As positive charge increases by which  $Z_{\text{eff}}$  increases, so  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  has greater  $Z_{\text{eff}}$  than Zn.

6. (a,b,d)

(a) Size of aluminium and gallium is nearly same due to poor shielding of 3d orbital in Ga.

(b)  $\text{Te}^{2-}$ ,  $\text{I}^-$ ,  $\text{Cs}^+$ ,  $\text{Ba}^{2+}$  are isoelectronic to Xe so elements with more electrons have higher size.

(d) Pd and Pt have similar size because of poor shielding of 4f orbital in Pt.

7. (a,b,c,d)

$\text{H}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  has greater radius than F and  $\text{H}^-$  is very much larger due to very less  $Z_{\text{eff}}$  in  $\text{H}^-$ , its outer electron are free to maximize the radii.

8. (a,b,d)

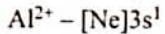
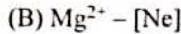
(a) As removal of second electron takes place from half filled valence shell, electron configuration of  $\text{O}^+$  i.e.  $2s^22p^3$ .

(b) Due to higher nuclear charge in phosphorus, I.E.<sub>3</sub> of P is greater than aluminium.

(d) I.E.<sub>2</sub> of Cu is greater than Zn because in  $\text{Cu}^+$  electron is removed from fully filled configuration  $[\text{Ar}]3d^{10}$ .

9. (a,b,c)

(A) Mg has  $[\text{Ne}]3s^2$  configuration so difficult to remove electron from it than Na.



Low I.E. required to remove electron from  $\text{Al}^{2+}$ .

So I.E.<sub>3</sub>(Mg) > I.E.<sub>3</sub>(Al)

(C) I.E.<sub>1</sub>(Al) < I.E.<sub>1</sub>(Mg)

Mg has  $[\text{Ne}]3s^2$  electronic configuration so difficult to remove electron from it.

10. (a,d)  $\text{I.E.} \propto |\text{magnitude of + ve charge}| \propto \frac{1}{\text{Magnitude of - ve charge}}$

As it is easy to remove electron from a anion (loosely bound electron).

11. (a,c) Elements of group 1 and 2 have low I.E. values so they import colour to flame.

12. (a,c,d)

(A) More the ionisation energy, then more will be its electronegativity because that atom has high affinity towards electrons.

(C) If ionisation energy is low than we can say it is easier to remove outer electron.

(D) On moving along period electron affinity increases.

13. (a,b,c,d)

Electron affinity increases on moving along a period and exact order of electron affinity for group 16 is  $\text{S} > \text{Se} > \text{Te} > \text{O}$

14. (a,b,d)

Due to smaller size of 2nd period elements it resists the incoming electron making electron affinity of 3rd period elements greater than 2nd.

15. (b,c)

(B) First ionisation enthalpy of nitrogen is higher than its neighbour's due to half filled electronic configuration.

(C) Cl has higher electron gain enthalpy than F due to compact size of F.

16. (a,b,d)

(A) Ionisation enthalpy increases along a period so C has highest first ionisation enthalpy.

(B) Atomic size increases down the group and decreases along a period. So Al has largest atomic size.

(D) Metallic character increases down the group so Al has most metallic character.

17. (a,b,c,d)

Hydroxides of metals which shows both acidic as well as basic behaviour are amphoteric.

e.g.  $Zn(OH)_2$ ,  $Be(OH)_2$ ,  $Al(OH)_3$ ,  $Pb(OH)_2$ .

18. (b) I.E.<sub>3</sub> > I.E.<sub>2</sub> of an atom because  $Z_{eff}$  of an atom in its dipositive ion is more than in mono-positive ion.

19. (d) Alkali metals have lowest ionisation energy in period as by loosing only one electron stable noble gas configuration is achieved.

20. (c) I.E.<sub>2</sub> is highest for IIIrd element as after removing 1st electron stable noble gas configuration is achieved so it is difficult to remove the 2nd e<sup>-</sup>.

21. (a) (A) has highest I.E.<sub>1</sub> by which, this elements is likely to be the noble gas.

22. (b) Fully filled and half filled configuration have higher ionisation energy order than its neighbour elements.

So, B < Be < C < O < N

23. (a) In Na I.E.<sub>1</sub> << I.E.<sub>2</sub> because  $Na^+$  has stable noble gas electronic configuration.

So difference is maximum in case of sodium.

24. (c) As phosphorus has stable half filled electronic configuration so I.E.<sub>1</sub> is highest for it.

Now on moving along a period I.E. increases so sulphur has more I.E. than Mg and Al.

25. (c) Group 14 is the carbon family consisting of non-metals (carbon and silicon), metalloid (germanium) and metal (lead and tin).

26. (b) Non-metals belong to the p-block of the modern periodic table.

27. (c) Metallic character is inversely proportional to electronegativity and Non-metallic character is directly proportional to electronegativity of elements.

28. (c) Electronegativity increases along a period and decreases down the group.

29. (d) Metallic character decreases on moving along a period so potassium has more metallic character than Mg, Al and B.

30. (b) Non-metals have larger size than metals so size of  $I^-$  and  $Br^-$  is greater than  $Li^+$  and  $Na^+$  and ionic radius increases along a group and decreases along a period.

31. (c) On moving left to right in a period, atomic radii decreases due to increase in  $Z_{eff}$  and addition of electron to the same outer most shell.

32. (a) La - 57, Cl - 17, K - 19, Cu - 29.

(A) La - 57 is a d-block elements and violet Aufbau's principle.

(B) Cl - 17 is a p-block element and is a non-metal.

(C) K - 19 is a s-block element and belongs to 4th period.

(D) Cu - 29 is a d-block and violet Aufbau's principle ( $[Ar]_{1s}^{10}3d^{10}4s^1$ ).

33. (c) Electronic configuration's

$O \rightarrow 1s^2 2s^2 2p^4$

$O^- \rightarrow 1s^2 2s^2 2p^5$

$O^{2-} \rightarrow 1s^2 2s^2 2p^6$

(A) In 'O' electron is gained, So energy is released so making negative electron gain enthalpy.

(B) (E.G.E.)<sub>2</sub> is generally positive because the incoming electron faces the repulsion and energy is taken by it to accept an e<sup>-</sup>.

(C)  $Na^-$  has stable configuration and so energy is needed to remove e<sup>-</sup> from it.

(D)  $Mg^+$  gains e<sup>-</sup> easily due to higher  $Z_{eff}$ , making the process exothermic with negative electron gain enthalpy.

34. (b) (A) Iodide ion is the strongest reductant.

(B) Chromium has half filled d-orbital  $[Ar]_{1s}^{10}3d^54s^1$

(C) Aurum/Gold is a coinage metal.

(D) Cerium is a lanthanide element.

35. (d) (A) Gallium -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

(B) Vanadium -  $2s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

(C) Zinc -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

(D) Scandium -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

36. [0015]

$Ni^+ = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

Max. no. of electron having same spin = 15

$1s$							
1	1	1	1	1	1	1	1
2s							
2	2	2	2	2	2	2	2

37. [350]

Lattice enthalpy = 772 kJ/mol

$$\frac{[\Delta H.E.]_{Na^+}}{[\Delta H.E.]_{Cl^-}} = \frac{30}{25} = \frac{6}{5}$$

$$(x) \quad (y)$$



$$x = \frac{6}{5}y$$

$(\Delta H)_{soln}$  = Lattice enthalpy + H.E. of  $\text{Na}^+$  + H.E. of  $\text{Cl}^-$

$$2 = 272 + y + \frac{6}{5}y$$

$$y = -350 \text{ kJ}$$

38. [8]  $r_A + r_A = 10 \text{ Å}^\circ$  ... (1)

$$r_B + r_B = 6 \text{ Å}^\circ$$
 ... (2)
 

Add (1) and (2),

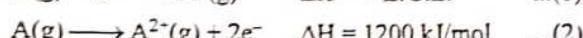
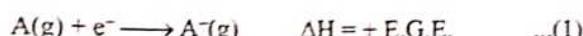
$$2(r_A + r_B) = 16 \text{ Å}^\circ$$

$$r_A + r_B = 8 \text{ Å}^\circ$$

39. [30]

Zn has largest size among Ni, Cu and Zn  
Because of repulsion of d-electron in zinc.

40. [1]



$$\text{eq}^n (3) = (2) - (1)$$

$$1100 = 1200 - \text{E.G.E.}$$

$$\text{E.G.E.} = 100 \text{ kJ/mol}$$

$$\text{E.G.E.} = 1 \times 10^2 \text{ kJ/mol.}$$

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

41. [23]



$$\text{Number of mole of A} = \frac{10}{30}$$

As 1 mole of A released the amount energy =  $-3 \times 23$  kcal/mol.

Energy released for conversion of  $\frac{10}{30}$  mole of gaseous

$$\text{A into A}^- \text{ ions} = \frac{3 \times 23}{30} \times 10 = -23 \text{ kcal/mol.}$$

42. [3]

$$(i) \text{N}^{3-} > \text{P}^{3-}$$

$$(ii) \text{Ca}^{2+} > \text{Sr}^{2+}$$

$$(iii) \text{Cl}^- > \text{S}^{2-}$$

43. [6]

$$\text{Zn}^{2+} = 1s^2 2s^2 2p^6 3s^2 2p^6 3d^{10} 4s^0$$

All s-electrons i.e.  $1s^2, 2s^2, 3s^2$  have  $\ell = 0$ .

44. [3]

Li – Mg, Be – Al, B – Si shows diagonal relationship.

45. [7]

The element is nitrogen which belongs to second period and group 15.

46. [4]

$\text{SnO}, \text{PbO}, \text{Al}_2\text{O}_3, \text{ZnO}$  are amphoteric in nature.

47. [5]

$(\text{Na}^+, \text{Li}^+), (\text{Se}, \text{S}), (\text{I}^-, \text{Br}^-), (\text{Ca}, \text{Mg}), (\text{S}^{2-}, \text{Cl}^-)$  are the pair's in which size of first species is greater than second one.

48. [4]

He, Be, N, Ne possess a positive value of electron gain enthalpy.

49. [4]

$(\text{N}, \text{O}), (\text{Be}, \text{B}), (\text{Me}, \text{Ne}), (\text{Mg}, \text{Na})$  are the pair(s) in which I.E. of first element is greater than second element.

50. [4.35]

$$\text{Zn} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$$

$Z_{\text{eff}} = \text{Atomic no.} - \text{shielding constant } (\sigma)$

$$\sigma = 10 + 0.85 \times 18 + 0.35 \times 1 = 25.65$$

$$Z_{\text{eff.}} = 30 - 25.65 = 4.35.$$

51. [5]

Na, Mg, P, S, Al have ionisation energy less than chlorine atom.

52. [2]

Sudden jump in I.E.<sub>2</sub> and I.E.<sub>3</sub> is observed showing valence shell's electron = 2

So group number of element X is 2.

## Exercise-4

### (Past Year Questions)

#### JEE MAIN

1. (d) Sc has highest first ionization energy because:

- Sc: [Ar] 4s<sup>2</sup> 3d<sup>1</sup>

- Poor screening of d-orbitals.

- I.E. increases left to right in a period.

2. (a)  $\text{O}^{2-}, \text{F}^-, \text{Na}^+, \text{Mg}^{2+}$  are isoelectronic species as all of these has same no. of  $e^- = 10$ .

3. (b)  $[\text{Og}_{118}] 8s^2$  is the electronic configuration for  $Z = 120$ , (Og is Oganesson).

So, as per the configuration, it will be in II<sup>nd</sup> Group.

4. (c) due to lanthanide contraction, atomic and ionic radii decreases.

5. (b) E.N. of Al is same as that of Be due to presence of Diagonal Relationship.

6. (d) Correct order of radii : Eu > Ce > Ho > N.

It is because in case of lanthanide, 2 peaks appear at (<sub>63</sub>Eu and <sub>70</sub>Yb) as Eu and Yb both provide only  $2e^-$  for bonding while other members provide  $3e^-$  for bonding purpose.

7. (b) Electronegativity increases from left to right in a period and decreases down the group.

8. (a) Inert pair effect gradually increases down the group. Hence stability of lower O.S. increases down the group.
9. (c) On moving down a group, Electronegativity decreases and atomic radius increases for representative elements.
10. (a) The outer most electronic configuration of Tl is  $6s^2 6p^1$ . The  $6s$  electrons are strongly attracted towards the nucleus due to its more penetrating power and deshielding of d and f-electrons. Hence  $6s$ -electrons do not participate in bonding.
11. (d) 2<sup>nd</sup> electron gain enthalpy of oxygen is positive.
12. (a) On moving down, size increases:  
order : C < S < Al < Cs.
13. (d) 119 symbol is : Ununennium (uue)
14. (a) In case of "Be" electron remove from "2s" orbital while in case of "B" electron remove from "2p" orbital. '2s' orbital have greater penetration effect than '2p' orbitals. So, 'Be' have more I.E. than 'B'.
15. (c) Atomic number (Z) 15  $\Rightarrow$  P  $\rightarrow$  [Ne]  $3s^2 3p^3$   
Phosphorus belongs to 15<sup>th</sup> group.  
no. of valence e<sup>-</sup> = 5  
and valency = 3 in (G.S.)
16. (a) As we move down the group, Bond strength decreases thereby decreasing the catenation tendency.  
Hence; the order expected is  
 $C > Si > Ge \approx Sn$
17. (b) Ti  $\rightarrow$  [Ar]  $3d^2 4s^2$   
Mn  $\rightarrow$  [Ar]  $3d^5 4s^2$   
Ni  $\rightarrow$  [Ar]  $3d^8 4s^2$   
Zn  $\rightarrow$  [Ar]  $3d^{10} 4s^2$
18. (a) The element which release more energy upon an e<sup>-</sup> gain are [Cl, S and Li]
19. (d) Correct order of Ionization energy will be:  
 $Na < Al < Mg < Si$
20. (d)  $_{26}Fe = [Ar] 3d^6 4s^2$
21. (b)
- |   |   |   |    |                            |
|---|---|---|----|----------------------------|
| C | N | O | F  |                            |
|   |   |   |    | Size decreases             |
|   |   |   | Cl |                            |
|   |   |   | Br | Order: F < O < C < Cl < Br |
|   |   |   |    | Size increases             |
22. (d) The electronic configuration of B and Be are:  
B  $\Rightarrow$   $1s^2 2s^2 2p^1$   
Be  $\Rightarrow$   $1s^2 2s^2$
- (I) 2s - orbital experienced more  $Z_{eff}$  than 2p therefore 2p electron could be easily removed than 2s.
- (II) In case of B there are total 4 inner core electrons but in Be only 2e<sup>-</sup> (in 1s<sup>2</sup>) therefore 2p more shielded in B than 2s of Be.

- (III) s-orbital has spherical shape through that  $Z_{eff}$  is 10% but p-orbital is dumbbell shape therefore  $Z_{eff}$  less and penetrating power less than 2s.
- (IV) Atomic radius of B less than Be due to more Z  
According to the above explanation only (I), (II) and (III) are correct,
23. (a) According to the given data of I.E., this element must belong to group I and thus is monovalent and form hydroxide of the type M(OH).  
 $MOH + HCl \rightarrow MCl + H_2O$   
 1 mol 1 mol  
 $2 MOH + H_2SO_4 \rightarrow M_2SO_4 + H_2O$   
 1 mol 1/2 mol
24. (d) In periodic table, in a period on moving left to right atomic number increases the nature of oxide follows the order basic then amphoteric and then acidic i.e., oxide of X is basic, oxide of Y is amphoteric, oxide of Z is acidic.  
– Hence, atomic number follows the order:  
 $Z > Y > X$
25. (d) Atomic radius decreases on moving left to right in periodic table, while other properties given increases (in magnitude) on moving left to right across a period.
26. (a) For Unnilennium: Atomic no : 109  
Symbol : Une
27. (b)  $Ar(g) + e^- \rightarrow Ar^-(g)$  (Endo.)  
 $H(g) + e^- \rightarrow H^-(g)$  (Exo.)  
 $Na(g) \rightarrow Na^+ + e^-$  (Endo.)  
 $O^-(g) + e^- \rightarrow O^{2-}(g)$  (Endo.)  
– E. G. E. of H(g) is negative while that of Ar(g) is positive due to ns<sup>2</sup> np<sup>6</sup> configuration.  
– 2<sup>nd</sup> E. G. E. is always positive for an atom.  
– Ionisation potential of an atom is positive
28. (d) Among Isoelectronic species greater the  $Z_{eff}$  smaller will be the radius.  
Order of  $Z_{eff}$ :  $O^{2-} < F^- < Na^+ < Mg^{2+}$   
Order of Ionic Radii :  $O^{2-} > F^- > Na^+ > Mg^{2+}$
29. (b) Actinoids contains 14 elements with atomic number 90 to 103. Hence, element with atomic number 101 is actinoids.  
Element with atomic number 104 is a d-block element of group 4.
30. (a) For isoelectronic species, as the no. of protons increases, size of ions decreases.  
∴ Correct order of ionic Radii :  
 $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$
31. [101]  
Unnilunium  
IUPAC Symbol : Unu  
At. no. (Z) = 101



32. (d)  $Mn(25) = [Ar] 3d^5 4s^2$

$$Mn^{3+} = [Ar] 3d^4 4s^0$$

- Ru-belong to 4-d Transition series
- $Co(27) = [Ar] 3d^7 4s^2$
- $Co^{3+} = [Ar] 3d^6 4s^0$
- $Fe(26) = [Ar] 3d^6 4s^2$
- $Fe^{3+} = [Ar] 3d^5$

33. (a) Elements with atomic number 21, 25, 42 and 72 belongs to transition metals.

34. (b) From left to right in periodic table:

- Metallic character decreases.
- Non-metallic character increases.
- This is due to increase in ionization enthalphy and increase in electron gain enthalphy.

35. (b)  $Mg(Z = 12) = 1s^2 2s^2 2p^6 3s^2 \Rightarrow$  (Fully-filled)

$$Al(Z = 13) = 1s^2 2s^2 2p^6 3s^2 3p^1$$

$$Si(Z = 14) = 1s^2 2s^2 2p^6 3s^2 3p^2$$

$$P(Z = 15) = 1s^2 2s^2 2p^6 3s^2 3p^3 \Rightarrow$$
 (Half-filled)

$$S(Z = 16) = 1s^2 2s^2 2p^6 3s^2 3p^4$$

In general from left to right in a period. I.E. increases due to increase in effective nuclear charge but due to extra stability of half-filled and fully-filled electronic configuration. I.E. of P > S and Mg > Al.

Hence, the order for first I.E. is as follows:

$$Al < Mg < Si < S < P$$

36. (b) The major components in "Gun metal" which is an alloy are as follows:

$$Cu : 87\%$$

$$Zn : 3\%$$

$$Sn : 10\%$$

37. (a) The given electronic configuration belong to the following elements:

(a)  $1s^2 2s^2 \Rightarrow Be \Rightarrow$  Fully filled  $\Rightarrow$  stable

(b)  $1s^2 2s^2 2p^4 \Rightarrow O$

(c)  $1s^2 2s^2 2p^3 \Rightarrow N \Rightarrow$  Half filled  $\Rightarrow$  stable

(d)  $1s^2 2s^2 p^1 \Rightarrow B$

Order for Ionization enthalpy is

$$B < Be < O < N$$

Ionization enthalpy depends upon many factors but in given question it can be explained on the basis of half filled and fully filled stable configuration of elements.

Be has more I.E. compared to B due to extra stability (fully filled), whereas N has more I.E. compared to oxygen due to extra stability as it is half-filled.

Point to be noted: "Fully-filled" orbitals are more compared to half-filled orbitals.

Hence,

$$N \Rightarrow 1402 \text{ kJ/mol}$$

$$O \Rightarrow 1314 \text{ kJ/mol}$$

$$B \Rightarrow 801 \text{ kJ/mol}$$

$$Be \Rightarrow 899 \text{ kJ/mol}$$

38. (a) The correct order of electron gain enthalpy is as follows:

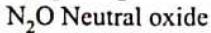
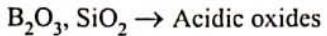
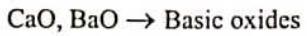
$$S > Se > Te > O$$

Due to small size of oxygen atom, it exerts electron-electron repulsion as a result of which incoming electron will not be able to add into the shell and gets repelled by the electron, so more amount of energy is required. Therefore, electron gain enthalpy of oxygen becomes less negative compared to the rest of the elements.

$$O < S > Se > Te$$

$$S > Sc > Te > O$$

39. (b) The nature of the oxide depends upon the nature of the elements whether it is a metal, non-metal or a metalloid.



The nature of oxide also depends upon the oxidation state of the element. Higher the O.S. of elements more acidic is the oxide where as lower O.S. of element, more basic is the compound.

40. (a) I.E.<sub>1</sub> of alkali metals is lowest and I.E.<sub>2</sub> of alkali metals is highest because after losing one electron they acquire noble gas configuration so 'X' is Na.

41. (b)  $X_{33} - 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$

Similar configuration to 15<sup>th</sup> group so its a metalloid.

$$Y_{53} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$$

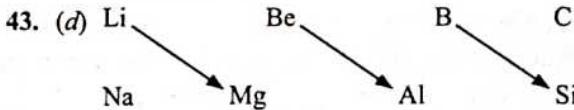
Similar configuration to halogen period so it is a non-metal.

$$Z_{83} - 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^3$$

It's belong to 15<sup>th</sup> group p-block. As metallic character increases down the group.

It is only metal in group 15.

42. (c) Due to small size of F there are inter electronic repulsions on accepting electron so  $\Delta H_{e.g}$  of Cl is more negative than F.



[These three pairs diagonally show similar properties]

44. (b) Radius  $\propto \frac{1}{Z}$

$$Al^{3+} < Mg^{2+} < Na^+ (\text{radius})$$

$$0.54\text{\AA} \quad 0.72\text{\AA} \quad 1.02\text{\AA}$$



45. (c) Let's first arrange elements asked in choices in periodic table.

Li Ne

Na Mg Cl Ar

Na < Mg < Cl < Ar

X is Ar, Y is Cl, Z is Na

46. (d)

	gp 13		gp 14	
Periodic-2	B	C		
Periodic-3	Al	Si		
Periodic-4	Ga	Gc		
Periodic-5	In	Sn	Tl	Pb

In 5th period:

Orbital filled are 5s, 4d, 5p

E.C. of Sn is [Kr]4d<sup>10</sup> 5s<sup>2</sup> 5p<sup>2</sup>

47. (d) At the time of Mendeleev structure of atom was not known as his basis of classification was atomic mass.

48. (b) Na<sup>+</sup> Mg<sup>2+</sup> Al<sup>3+</sup> (isoelectric species)

No. of e <sup>-</sup>	10	10	10
Z	11	12	13
$\frac{Z}{e}$	11	12	13
	10	10	10

More the  $\frac{Z}{e}$ , then smaller is the radii

Al<sup>3+</sup> < Mg<sup>2+</sup> < Na<sup>+</sup>

K<sup>+</sup> is in lower period, higher value of 'n' so large radius.

Al<sup>3+</sup> < Mg<sup>2+</sup> < Na<sup>+</sup> < K<sup>+</sup>

49. (b)

N<sup>3-</sup>, O<sup>2-</sup>, F<sup>-</sup> isoelectronic species

more Z then small size.

So size N<sup>3-</sup> > O<sup>2-</sup> > F<sup>-</sup>

But size of anion is more than its neutral counter part.

N<sup>3-</sup> > N

50. (c)

I.E. increases from left to right with exception.

Mg > Al (More penetration effect in Mg)

P > S (Half filled p-subshell in P)

51. (a) Group-16 are chalcogens

52. (b) Among isoelectronic species more Z then smaller radius as they have same no. of e<sup>-</sup>s.

Ca<sup>2+</sup> < K<sup>+</sup> < Cl<sup>-</sup> < S<sup>2-</sup> < P<sup>3-</sup>

53. (b) Acidic  $\rightarrow$  Cl<sub>2</sub>O<sub>7</sub>

Basic  $\rightarrow$  Na<sub>2</sub>O

Amphoteric  $\rightarrow$  As<sub>2</sub>O<sub>3</sub>

Neutral  $\rightarrow$  NO, N<sub>2</sub>O

54. (d)

Species	Al <sup>3+</sup>	Mg <sup>2+</sup>	Be <sup>2+</sup>	O <sup>2-</sup>	Br <sup>-</sup>	Cl <sup>-</sup>	Li <sup>+</sup>	S <sup>2-</sup>	K <sup>+</sup>
No. of e <sup>-</sup>	10	10	2	10	36	18	2	18	18

So, Mg<sup>2+</sup> and O<sup>2-</sup> are isoelectronic with Al<sup>3+</sup>

55. (b) Chlorine has the highest e<sup>-</sup> gain enthalpy, even greater than F, due to small size and repulsion in fluorine atom down the group, e<sup>-</sup> gain enthalpy decreases and along the period it increases

So the correct order is

Po < Te < F < Cl.

56. (d)

16<sup>th</sup> group: O S Se Te Po  
non metal metalloid metal

15<sup>th</sup> group: N P As Sb Bi  
metal

14<sup>th</sup> group: C Si Ge Sn Pb  
metal

Sc is d-block metal.

57. (a) Ion O<sup>2-</sup> Mg<sup>2+</sup>

No. of e<sup>-</sup> 10 10 (isoelectronic)

Z 8 12

$\frac{Z}{e}$  8 12  
10 10

$\frac{Z}{e} \propto$  force of attraction  $\propto \frac{1}{\text{size}}$

Thus size of Mg<sup>2+</sup> < O<sup>2-</sup>.

58. (a)

Species	N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>
No. of e <sup>-</sup>	10	10	10	10	10
Z	7	8	9	11	12

size  $\propto \frac{1}{z/e}$  thus the order is

Mg<sup>2+</sup> < Na<sup>+</sup> < F<sup>-</sup> < O<sup>2-</sup> < N<sup>3-</sup>

59. (a)

16 <sup>th</sup> group	EC	Period
O	2s <sup>2</sup> 2p <sup>4</sup>	2
S	3s <sup>2</sup> 3p <sup>4</sup>	3
Se	4s <sup>2</sup> 4p <sup>4</sup>	4
Te	5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>4</sup>	5

Above it

60. (b)

Cl<sub>2</sub>O<sub>7</sub> - Acidic

Na<sub>2</sub>O - Basic

Al<sub>2</sub>O<sub>3</sub> - Amphoteric

N<sub>2</sub>O - Neutral

61. (c)

Acidic  $\Rightarrow$  SiO<sub>2</sub>, SO<sub>3</sub>

Amphoteric  $\Rightarrow$  Al<sub>2</sub>O<sub>3</sub>

Basic  $\Rightarrow$  CaO



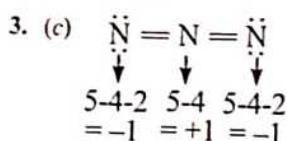
# Chemical Bonding and Molecular Structure



## Exercise-1 (Topicwise)

1. (d) In  $\text{BCl}_3$ , Boron forms 3 bond having  $6e^-$  & in  $\text{PCl}_5$ , phosphorous forms 5 bond i.e. having  $10e^-$  so both violates octet rule.

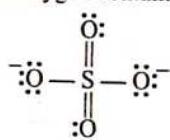
2. (d) Hydrogen bond is weakest bond.



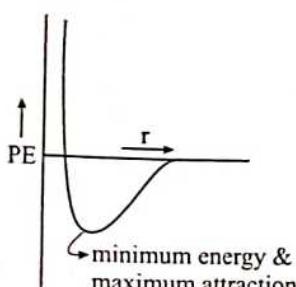
4. (b)  $\text{SO}_4^{2-}$

$$\text{Total bond pair} = \frac{8 \times 5 - 32}{2} = 4$$

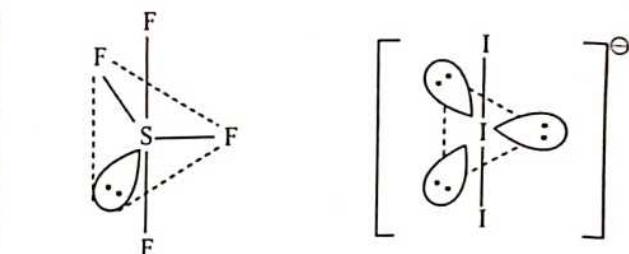
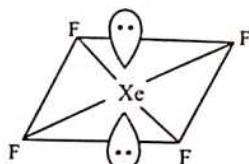
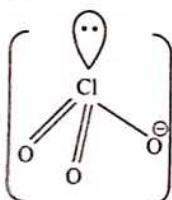
3 lone pair each oxygen contain



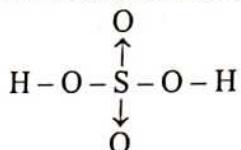
5. (c)



6. (d)



7. (b)  $\text{H}_2\text{SO}_4$  has co-ordinate covalent bond.



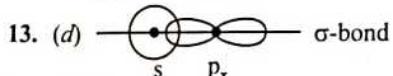
8. (d)  $\text{HNO}_2$  does not have co-ordinate bond. Structure is  $\text{H}-\text{O}-\text{N}=\text{O}$ .

9. (a)  $\text{CH}_3\text{N} \equiv \text{C}$  contain dative bond.

10. (d)  $(\text{C}_2\text{H}_5)_3\text{B} \leftarrow :\text{N}(\text{CH}_3)_3$   
 $\text{BF}_3 \leftarrow :\text{NH}_3$

11. (d) In  $\text{BF}_3$ , hybridisation changes from  $\text{sp}^2$  to  $\text{sp}^3$  when  $\text{NH}_3$  donates lone pair acting as Lewis base.

12. (b)  $\pi$ -bond is formed by lateral overlapping of unhybridised p-p orbitals.

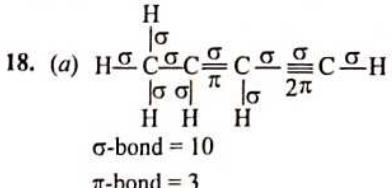


13. (c) Overlap order is  $p-p > s-p > s-s$ .

14. (b)  $\text{NH}_3$  has  $\text{sp}^3$  hybridised central atom so it is non planar.

15. (c)  $\text{C} \equiv \text{C}$  is a multiple bond so it is strongest.

16. (b)  $\pi$ -bond are formed by lateral overlap of orbitals.



17. (d)  $\text{H}_2\text{O}$  is not linear because oxygen is  $\text{sp}^3$  hybridised in  $\text{H}_2\text{O}$

20. (a)  $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}$  Linear

21. (b) In T.B.P.  $d_{z^2}$

22. (c)  $\text{NH}_4^+ \rightarrow \text{sp}^3 \rightarrow$  Tetrahedral

$\text{H}_3\text{O}^+ \rightarrow \text{sp}^3 \rightarrow$  Pyramidal

$\text{OF}_2^- \rightarrow \text{sp}^3 \rightarrow$  Bent

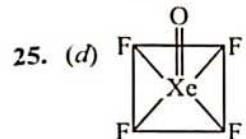
23. (b)  $d_{x^2-y^2}, d_{z^2}$  involved in  $d^2\text{sp}^3$ .

24. (d) Molecule Hybridisation Shape

$\text{SF}_4$   $\text{sp}^3\text{d}$  with one l.p. See-Saw

$\text{CF}_4$   $\text{sp}^3$  zero l.p. Tetrahedral

$\text{XeF}_4^-$   $\text{sp}^3\text{d}^2$  two l.p. Square-planar



26. (d)  $\text{Sp}^3\text{d}^3$

27. (c) Fluorine does not form any polyhalide as other Halogens because of the absence of d-orbitals in the valence shell of fluorine

28. (a) If bond order is high then stronger bond is formed & bond length decreases and bond energy is high.

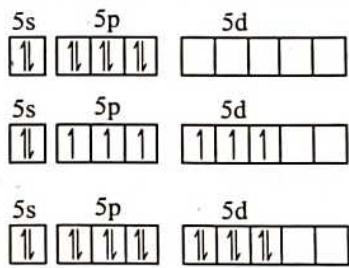
29. (d) Choice (a), (b), (c) are the resonance structures of  $\text{CO}_2$

30. (a) Bond angle :  $\text{sp} > \text{sp}^2 > \text{sp}^3 > \text{sp}^3\text{d}^2$

31. (b) Bond order     $\text{F}_2 = 1$   
                         $\text{O}_2 = 2$   
                         $\text{Cl}_2 = 1$   
                         $\text{N}_2 = 3$

In  $\text{Cl}_2$  bond length is more than  $\text{F}_2$  due to size.

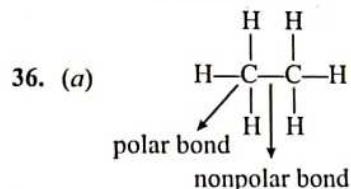
32. (b)  $\text{XeF}_6^-$  is distorted Octahedral. It has  $\text{sp}^3\text{d}^3$  hybridisation with lone pair of electron on Xe, so its shape is distorted.



33. (c) NBEPR THEORY: Larger the size of side atoms larger will be bond angle.

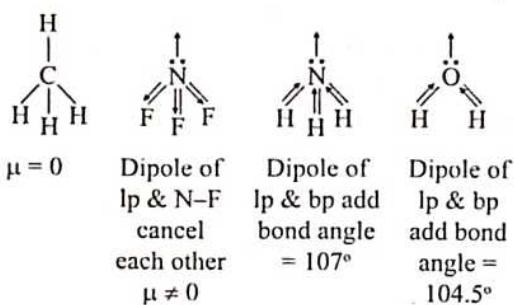
34. (c) Xe double excitation  $\text{XeF}_4^-$   $\text{sp}^3\text{d}^2$  - hybridization  
2 lone pairs + 4 bond pairs = Square planar

35. (c)  $\text{SO}_4^{2-}$  has 32 electrons  $\text{CO}_3^{2-}$  has 32 electrons;  $\text{NO}_3^-$  has 32 electrons.

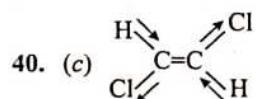
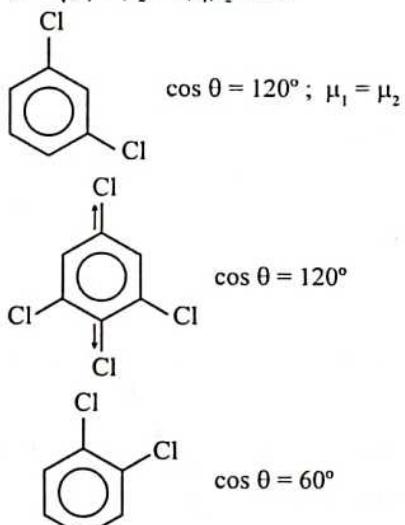


37. (a) Dipole moment  $\propto \cos \theta \propto \frac{1}{\theta}$

38. (a)

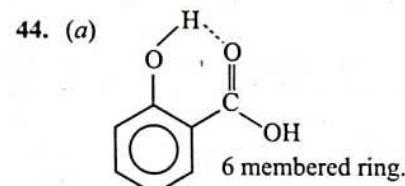
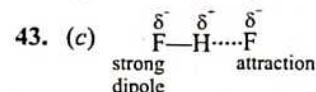


39. (a)  $\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$



41. (c)  $\text{H}-\text{F} \cdots \text{H}-\text{H}-\text{F} \cdots \text{H}-\text{H}-\text{F} \cdots \text{H}$  is correct as it will have least repulsion between F.

42. (c) In HF hydrogen bonding is present.



45. (c) Due to intermolecular H-bonding boiling point increases.

46. (b)  $\text{PH}_3$  has the lowest boiling point because it does not form Hydrogen bond.

47. (b) Hydrogen bonding increases heat of vaporisation.
48. (b) Benzene is non-polar.
49. (d) A discrete molecule is a covalent molecule in which the intermolecular forces are really weak, hence the low melting and boiling points of these molecular.  
In dry ice intermolecular forces are weak.
50. (d) Glycerol has a three OH group hence it is viscous in nature.
51. (a) In  $\text{BF}_3$  molecule back bonding is present hence slightly double bond character is generated.
52. (c) Nitrogen does not contain d-orbital so can not expand octet.
53. (d) Boron does not have d-orbital.
54. (a) Down the group both the lattic energy & hydration energy decreases.
55. (c) Valencies of L, Q, P and R is  $-2, -1, +1$  and  $+2$  respectively so they will form  $\text{P}_2\text{L}$ ,  $\text{RL}$ ,  $\text{PQ}$  and  $\text{RQ}_2$ .
56. (b) Due to its small size (fajan's rule)
57. (d) Valency of metal is  $+2$  by formula  $\text{MO}$  so its phosphate would be  $\text{M}_3(\text{PO}_4)_2$  because valency of  $[\text{PO}_4]$  is  $-3$ .
58. (b) Cation will be formed easily when IE is low.  
Anion will be formed easily when EA is high.
59. (c) More is charge/size ratio of cation, more is polarisation & more is covalent character.

So  $\text{Be}^{2+} \longrightarrow \text{Sr}^{2+}$   $\frac{\text{charge}}{\text{size}}$  ratio decrease.

60. (a) Cs is more electropositive.
61. (d)  $\text{AgI}$  is most covalent and Least soluble.
62. (d) Hexane has symmetrical structure so does not have polarity.
63. (a) According to Fajan's rule, polarisation of anion is influenced by charge and size of cation more is the charge on cation, more is polarisation of anion.

64. (b) Bond orders  $\text{O}_2^+ = \frac{15-10}{2} = 2.5$

$$\text{O}_2 = \frac{16-10}{2} = 2$$

$$\text{O}_2^- = \frac{17-10}{2} = 1.5$$

$$\text{O}_2^{2-} = \frac{18-10}{2} = 1$$

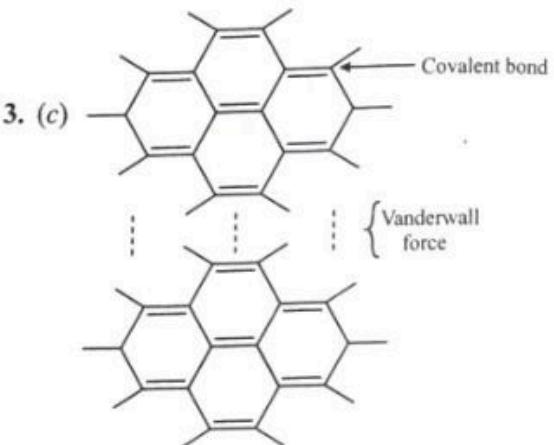
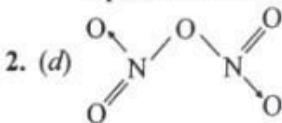
65. (c)  $\text{O}_2^- (2 \times 8 + 1 = 17)$  has odd number of electrons and hence it is paramagnetic. All the remaining molecules/ions, i.e.,  
 $\text{CN}^- (6 + 7 + 1 = 14)$  diamagnetic  
 $\text{NO} (7 + 8 = 15)$  has odd number of electrons and hence it is paramagnetic.

66. (a) Due to s-p mixing.

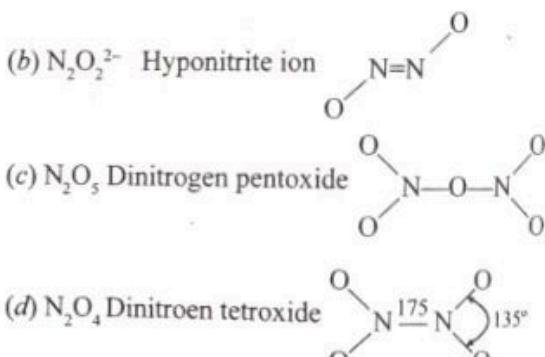
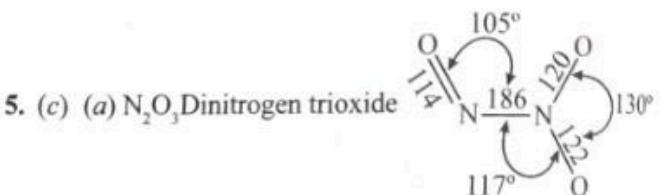
$$\pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi_{2p_y}^* = \pi_{2p_x}^* < \sigma_{2p_z}^*$$

## Exercise-2 (Learning Plus)

1. (d) The maximum covalency of representative element is equal to the number of s & p electrons in valence shell.

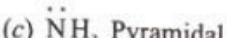
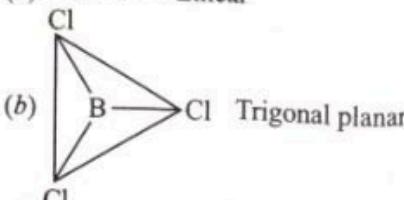


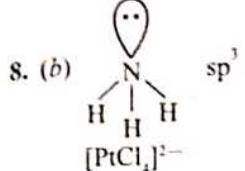
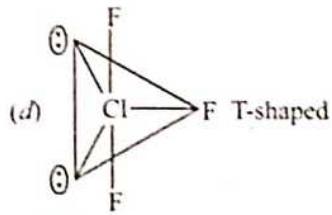
4. (d) In  $\text{SF}_6$ ,  $\text{PCl}_5$  and  $\text{IF}_7$ , the valence shell has 12, 10 and 14 electrons. As all contain more than 8 electrons in their valence shell they are example of super octet molecules.



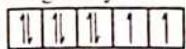
6. (d) The strength of metallic bonds depends upon the number of mobile electrons per atom. Sodium has only one mobile electron per atom whereas iron has 8 mobile electrons per atom.

7. (d) (a)  $\text{F}-\text{Be}-\text{F} \rightarrow$  Linear

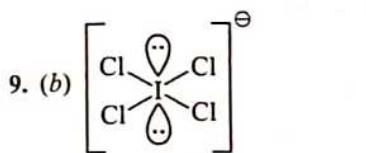
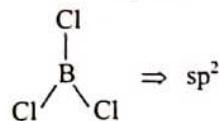
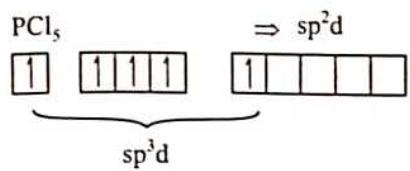
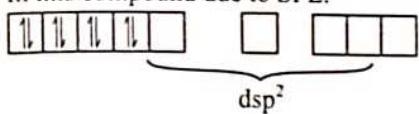




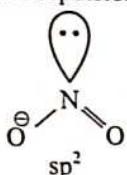
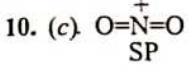
$\Rightarrow$  Pt is of 3<sup>rd</sup> transition series  
 $\Rightarrow$  all ligand will be strong field ligand  
 $\Rightarrow$  Hybridization  $\Rightarrow$   $dsp^2$   
 Originally



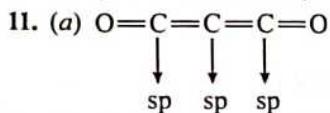
In this compound due to SFL.



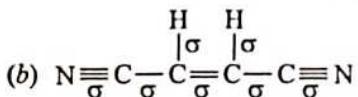
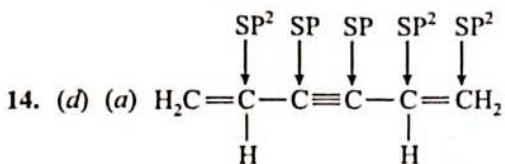
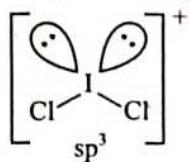
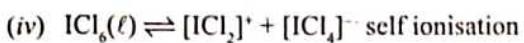
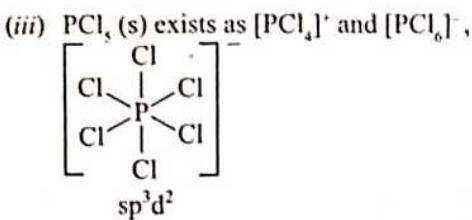
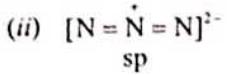
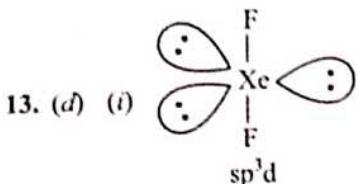
$\Rightarrow$  No of bond pair-lone pair repulsion = 8



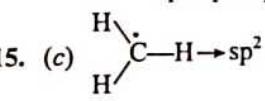
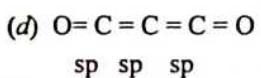
$(\text{NO}_2^- > \text{NO}_3^- > \text{NO}_2^-)$   
 $(\text{As L.P. } \uparrow, \text{B.A. } \downarrow)$



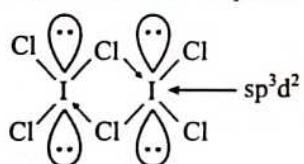
12. (a) As the p-character in hybrid orbital increases the size of hybrid orbital increases.



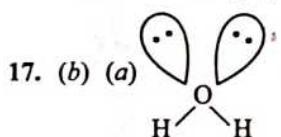
(c) In diamond each carbon atom is in  $\text{sp}^3$  hybridisation.

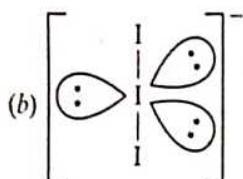


16. (d)  $\text{ICl}_3$  does not exist, but the dimer  $\text{I}_2\text{Cl}_6$  is a bright yellow solid. Its structure is planar.

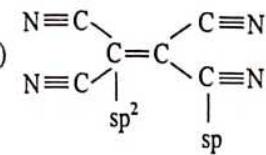
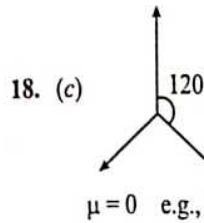
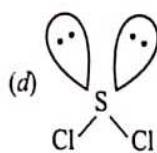
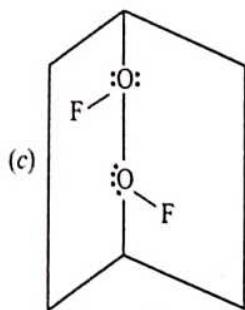


Note:  $\text{I}_2\text{Cl}_4\text{Br}_2$  will have the same hybridisation as that of iodine in  $\text{I}_2\text{Cl}_6$ . But it exists in 3 different forms.

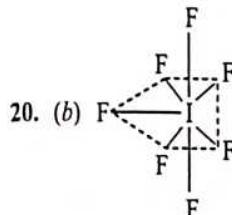




Number of bond pairs around I = 2.  
Number of lone pairs around I = 2.



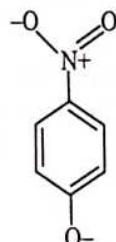
$\Rightarrow$  sp and sp<sup>2</sup> hybridized



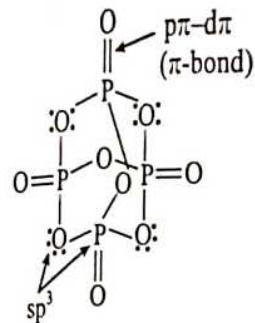
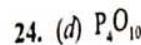
no. of B.P. = 7



22. (b) As E.N. of central atom  $\uparrow$  B.A.  $\uparrow$



23. (a) most stable.

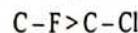


The P–O bond lengths show that the bridging bonds on the edges are 1.60 Å but the P = O bonds on the corners are 1.43 Å and this P = O is formed by p $\pi$  – d $\pi$  back bonding. A full p-orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P=P bonds.

25. (a) Atomic size arguments can be used for these species. Larger outer atoms result in larger angles due to steric repulsion.

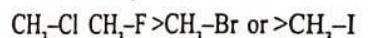
26. (a)  $\Rightarrow$  more s, more EN

27. (a) Polarity order



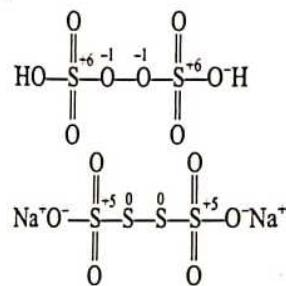
Distance (Bond) C–Cl > C–F

\*Here as exception, distance factor is dominant

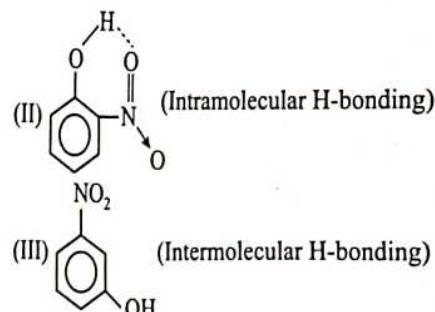
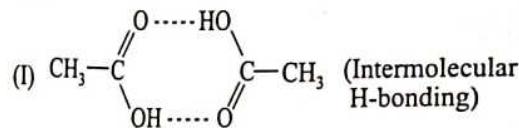


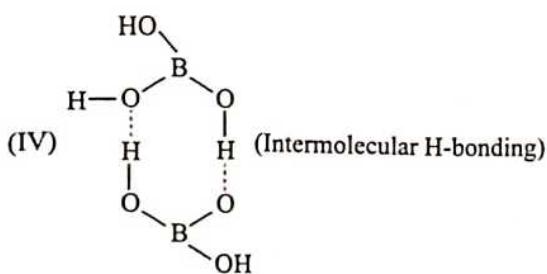
distance factor polarity factor dominant

28. (a)

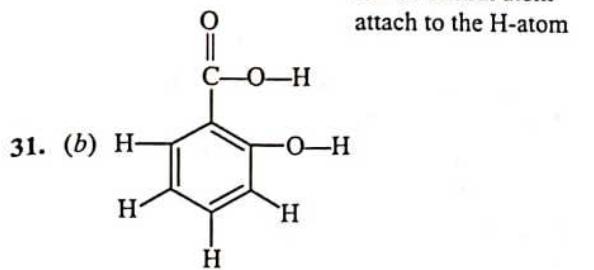


29. (c)





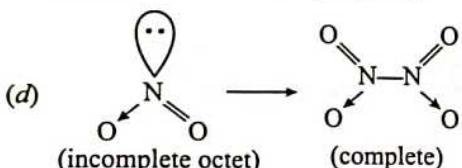
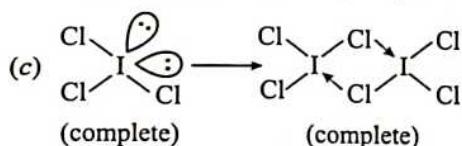
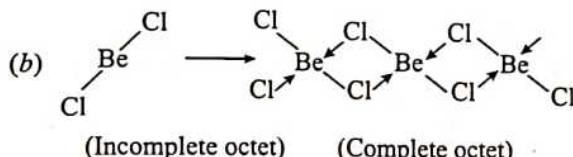
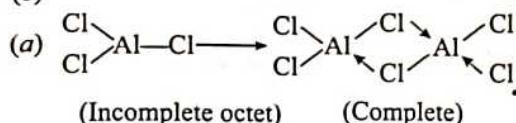
30. (b) Strength of H-bond  $\propto$  Polarity of H-atom  
EN of central atom attach to the H-atom



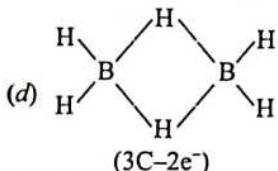
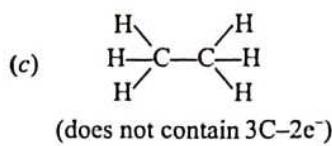
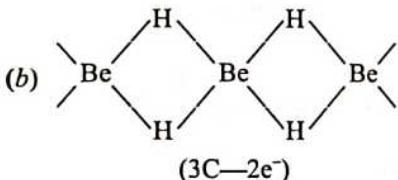
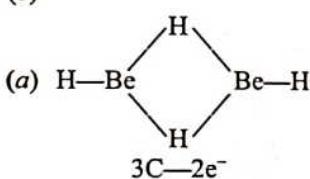
$$\sigma \text{ bond} = 16$$

$$\pi \text{ bond} = 4$$

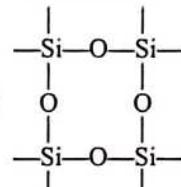
32. (c)



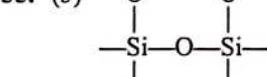
33. (c)



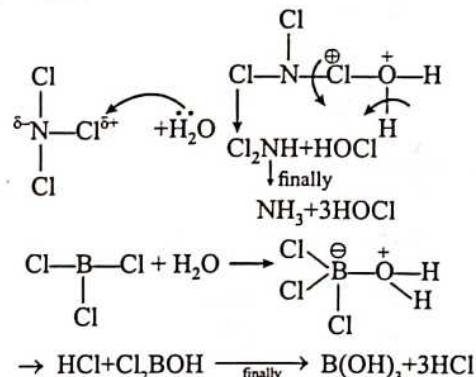
34. (a) The central atom of  $\text{PCl}_5$  have vacant d orbital therefore represent extended covalent bonding while in  $\text{NCl}_5$  N have no vacant d orbital



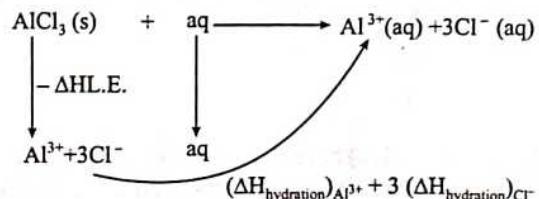
35. (b)



36. (c)



37. (c)

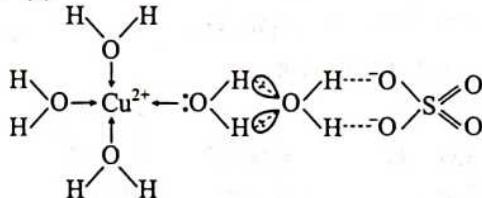


$$\Rightarrow \Delta H_{\text{solution}} = -4665 - 3 \times 381 + 5137 < 0$$

Hence  $\text{AlCl}_3$  will dissolve and solution consists of hydrated  $\text{Al}^{3+}$  and  $\text{Cl}^-$  ions.

38. (b)  $\text{Sn}^{4+}$  has highest polarising power amongst  $\text{Na}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{4+}$  and  $\text{Al}^{3+}$  because of smaller size and higher charge. So  $\text{SnCl}_4$  is most covalent and thus have least melting point.

39. (d)



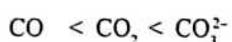
40. (a)  $C_3^{+} \Rightarrow {}^3C - C \equiv C^-$

$= \sigma$ - bond = 2

$\pi$ - bond = 2

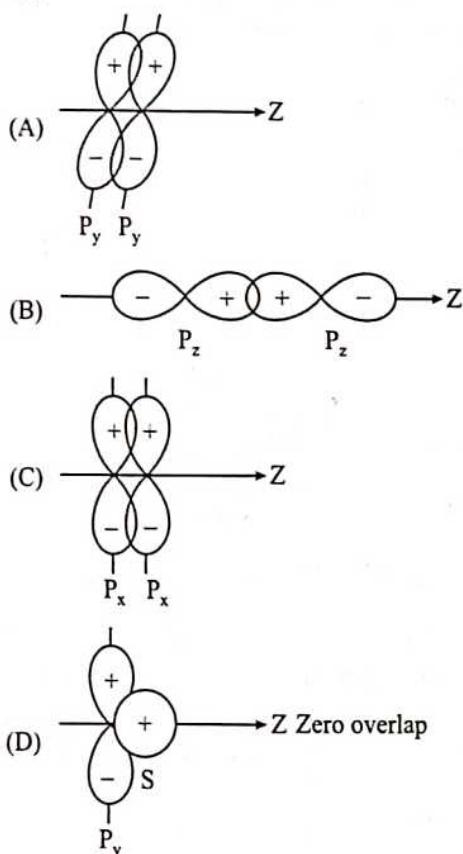
41. (b) According to Fajan's rule

42. (d) Bond length  $\propto \frac{1}{\text{bond order}}$



43. (a)  $\ddot{\text{N}} \equiv \ddot{\text{O}}$      $\ddot{\text{C}} \equiv \ddot{\text{O}}$      $\ddot{\text{C}} \equiv \ddot{\text{N}}^\Theta$

44. (d)



45. (c) (a) and (b) have negative overlap while (c) has positive overlap. Thus (c) will show effective overlapping.

46. (b) (OF)

$$\text{B.O.} = \frac{N_b - N_a}{2}$$

$$\text{B.O.} = \frac{10 - 7}{2} = 1.5$$

47. (a) (a)  $\bar{NO}$  ( $16\bar{e}$ ) = paramagnetic

(b)  $O_2^+$  ( $18\bar{e}$ ) = diamagnetic

(c)  $(\bar{CN})$  ( $14\bar{e}$ ) = diamagnetic

(d) ( $14\bar{e}$ )  $CO$  = diamagnetic

48. (d) (a)  $NO \rightarrow \dot{NO}$

$$\text{B.O.} = 2.5 \quad \text{B.O.} = 2$$

(b)  $O_2^+ \rightarrow O_2$

unpaired e = 1

B.O. = 2.5

(Para)

B.O. = 2

(Para)

(c)  $N_2 \rightarrow \overset{\ominus}{N}_2$

B.O. = 3

(dia)

B.O. = 2.5

(para)

49. (d) M.O for  $C_2 = \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 <$

$$\underbrace{\pi 2p_x^2}_{\text{HOMO}} = \pi 2p_y^2 < \underbrace{\sigma 2p_z^2}_{\text{LUMO}}$$

I is important to note that double bond in  $C_2$  consists of both pi bonds because of the presence of four electrons in  $2\pi$  molecular orbitals  $C_2^{2-}$   $[C = C]^{2-}$ .

50. (d)  $O_2^+$

B.O. = 3

$F_2^+$

B.O. = 0

$O_2^+$

B.O. = 1

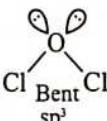
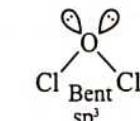
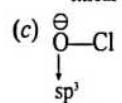
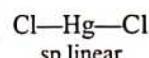
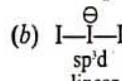
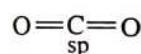
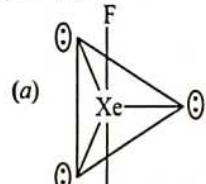
$H_2^-$

B.O. = 0.5

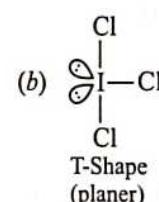
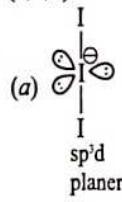
### Exercise-3

(JEE Advanced Level)

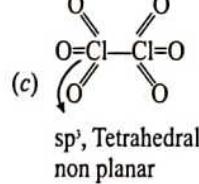
1. (a,b,c,d)



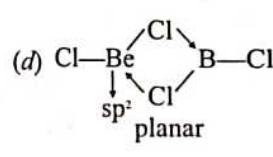
2. (a,b,d)



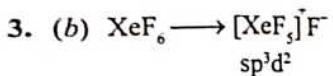
T-Shape  
(planer)



sp<sup>2</sup>, Tetrahedral  
non planar



sp<sup>2</sup>, planar

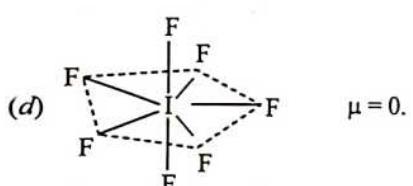
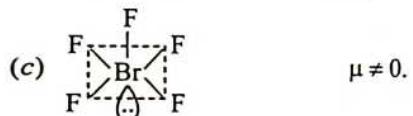
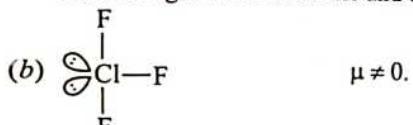


4. (a,c)

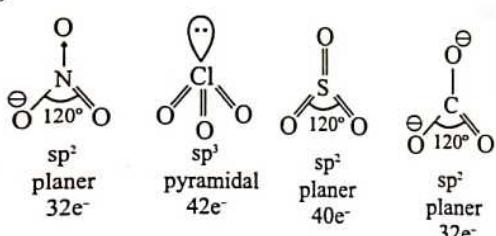
It is the orbital that undergo hybridisation and not the electrons. For example, for orbitals of nitrogen atom ( $2s^2$   $2p_1$ ,  $2p_2$ ,  $2p_3$ ) belonging to valence shell when hybridise to form four hybrid orbitals, one of which has two electrons (as before) and other three have one electron each. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

5. (a,b,c,d)

(a)  $\text{I}-\text{Cl}$ , linear and polar because of the difference in the electronegativities of iodine and chlorine.



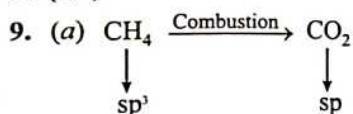
6. (a)



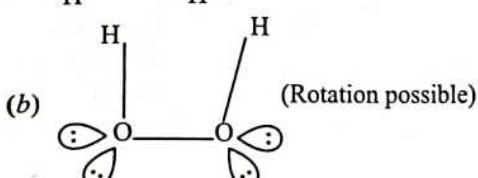
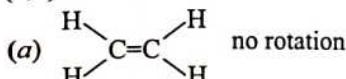
7. (a,b,d)

(According to VBT theory)

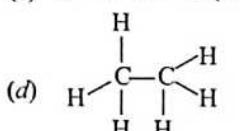
8. (a,b)



10. (a,c)



(c)  $\text{H}-\text{C}\equiv\text{C}-\text{H}$  (no rotation)



11. (a,b,d)

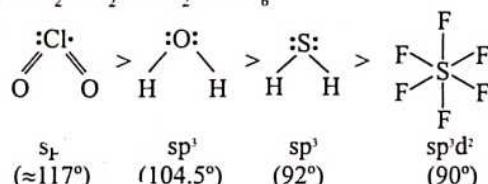
(a) According to VSEPR theory as electronegativity of central atom decreases, bond angle decreases. So bond angle of  $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

(b)  $\text{C}_2\text{H}_2 > \text{C}_2\text{H}_4 > \text{CH}_4 > \text{NH}_3$ . In  $\text{NH}_3$ , there is bp-lp repulsion so bond angle decreases to  $107^\circ$  from  $109.5^\circ$ .

$\text{sp}$	$\text{sp}^2$
$180^\circ$	$120^\circ$
$\text{sp}^3$	$\text{sp}^3$
$109.5^\circ$	$107^\circ$

(c)  $\text{SF}_6 < \text{NH}_3 < \text{H}_2\text{O} < \text{OF}_2$  in this case bond angle of  $\text{NH}_3$  is highest because lp - lp repulsion is absent in it.

(d)  $\text{ClO}_2 > \text{H}_2\text{O} > \text{H}_2\text{S} > \text{SF}_6$

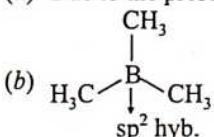


Note: It is supposed that in  $\text{H}_2\text{S}$  the hybrid orbitals do not participate in bonding but pure p-atomic orbitals participate in bonding.



13. (a,b)

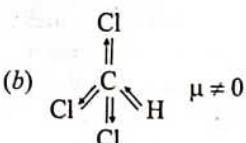
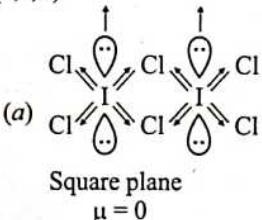
(a) Due to the presence of lone pair bond angle decreases.

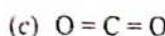


(c)  $\text{NH}_4\text{Cl}$  is an ionic compound and 'N' is in  $\text{sp}^3$  hybridisation.

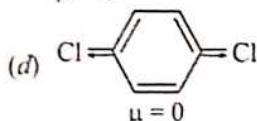
(d)  $\text{S}_8$  molecule has 16 electron pairs left behind after the bonding.

14. (a,c,d)





$$\mu = O$$



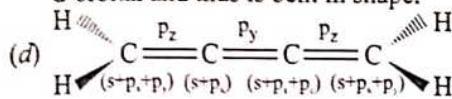
$\Rightarrow$  Ans. : (a,c,d)

15. (a,c,d)

(a) Ethyne being non-polar is more soluble in acetone.

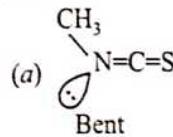
(b)  $CD_3F$  is more polar than  $CH_3F$ . In  $CD_3F$ , C-D bond is more polar as deuterium is more electropositive than hydrogen.

(c) Silyl isocyanate ( $SiH_3NCO$ ) is linear in shape because of  $p\pi-d\pi$  delocalisation of lone pair of electrons on nitrogen. While in methyl isocyanate ( $CH_3NO$ ) there is no  $p\pi-d\pi$  delocalisation of electron as carbon does not have empty d-orbital and thus is bent in shape.

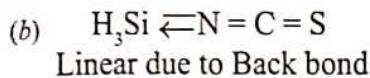


In  $CH_3=C=C=C=CH_3$ , the 2H-atoms on one C-atom lie in a plane perpendicular to the plane in which 2H-atoms on other C-atom lie.

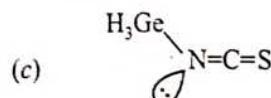
16. (b,c,d)



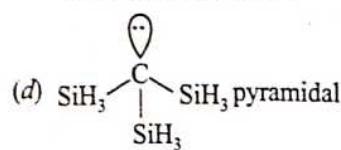
Bent



Linear due to Back bond



Bent as no effective Back Bonding due to large size of Ge



17. (c) The Fluoride ion, by process of hydrogen bonding forms the ion  $HF_2^-$ .

The compound is written as  $K^+[HF_2]^-$ .

18. (a) Lattice energy is directly proportional to the charge of the ions and inversely proportional to the size of the ions. Thus lattice energy increases as the size of ion decreases.

Lattice energy order:  $KF > KCl > KBr > KI$

19. (a,b,c)

(a) With hydrogen sulphur does not undergo  $sp^3d^2$  hybridisation because of larger difference in energies between s, p and d-orbitals. Sulphur shows +6 oxidation state with highly electronegative elements like O and F.

(b) As fluorine is smaller and more electronegative than oxygen.

(c) I<sup>-</sup> being stronger reducing agent reduces  $Fe^{3+}$  to  $Fe^{2+}$ .

20. (a,d)

$Ba^{2+}$  is larger than  $Mg^{2+}$ . According to Fajan's rule, smaller cation has higher polarising power, therefore,  $MgO$  is more covalent than  $BaO$  (i.e.  $BaO$  is more ionic).

Melting Points :  $BeO = 2500^\circ C$ ;  $MgO = 2800^\circ C$ ;  $CaO = 2572^\circ C$ ;  $BaO = 1923^\circ C$

21. (b,c,d)

(a) is incorrect, as ionic compounds have higher melting points as well as higher boiling points due to strong electrostatic force of attraction between the ions.

(c) and (d) are properties of ionic compounds.

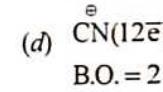
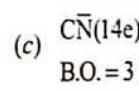
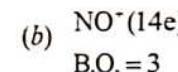
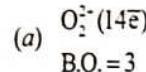
22. (b,c,d)

$\because$  A does not conduct electricity in aq. molten or solid  
 $\Rightarrow$  it must be non polar covalent comp.

$\Rightarrow$  B only conduct electricity in fused form or in solution hence it must be ionic.

$\Rightarrow$  C only conduct electricity in aq. solution hence

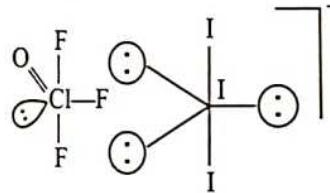
23. (a,b,c)



24. (b,d)

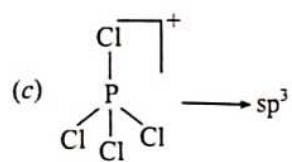
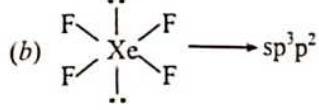
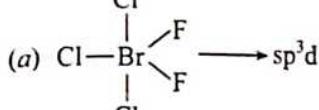
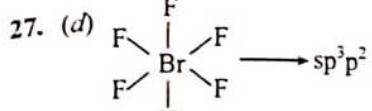
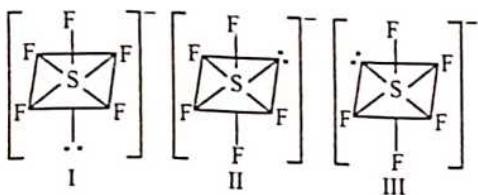
$N_2$ (14)	$CO$ (14e)	$C\bar{N}$ (14e)	$NO^-$ (14e)
$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$
Diamagnetic	Diamagnetic	Diamagnetic	Diamagnetic
$N \equiv N$ ( $\mu = O$ )	$\bar{C} \equiv O^+$ ( $\mu \neq O$ )	$\bar{C} \equiv N$ ( $\mu \neq O$ )	$N \equiv O^-$ ( $\mu \neq O$ )
Linear	Linear	Linear	Linear

25. (c)

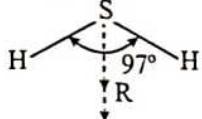


Cl-atom is in  $sp^3d$  hybridisation state. Hence geometry is trigonal bi-pyramidal which is similar to  $I^-$ .

26. (d) Number of electron pairs = 6; number of bond pairs = 5; number of lone pairs = 1. According to VSEPR theory, geometry of the molecule is trigonal bipyramidal. As all positions are equivalent the lone pair of electrons can occupy any position in octahedral geometry as given below.



28. (b)  $\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$   
 $(\therefore \mu_1 = \mu_2)$



$$\mu_R = \sqrt{2\mu_{S-H}^2 + 2\mu_{S-H}^2 \times \cos 97^\circ}$$

$$\mu_R = \sqrt{2} \times \mu_{S-H} \times \sqrt{1 - 0.12}$$

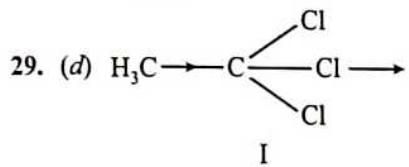
$$\mu_R = \sqrt{2} \times \mu_{S-H} \times \sqrt{0.88}$$

$$\mu_{S-H} = \frac{1.5}{\sqrt{2} \times 0.94} D$$

$$(\mu_{S-H})_{cal} = \frac{0.15 \times 10^{-9} \times 1.6 \times 10^{-19}}{\frac{10}{3} \times 10^{-30}}$$

$$(\mu_{S-H})_{cal} = 3 \times 0.15 \times 1.6 \times 10 D$$

$$\text{So \% Ionic character} = \frac{1.5}{\sqrt{2} \times 0.94} \times \left[ \frac{1}{0.15 \times 16 \times 3} \right] \times 100 = 16 \%$$

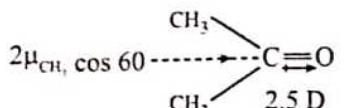


$$\mu_I = 3 \mu_{C-Cl} \times \cos 70.5 + \mu_{CH_3} = 1.5 + 0.4 = 1.9 D$$

$$\mu_{II} = 3 \mu_{C-Cl} \times \cos 70.5 - \mu_{C-H} = 1.5 - 0.4 = 1.1 D$$

$$\mu_{III} = 3 \mu_{C-H} \times \cos 70.5 + \mu_{C-Cl} = 1.9 D$$

30. (a)



$$\mu_{net} = 2.5 + \mu_{CH_3} = 2.5 + 0.4 = 2.9 D.$$

31. (b)

sp <sup>3</sup> d	Hybridisation	Geometry	T.B.P.
When	0 l.p.	5 b.p.	Shape
When	1 l.p.	4 b.p.	See-Saw
When	2 l.p.	3 b.p.	T-Shape
When	3 l.p.	2 b.p.	Linear

32. (b) sp<sup>3</sup>d<sup>2</sup> (s, p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>, d<sub>x<sup>2</sup>-y<sup>2</sup></sub>, d<sub>z<sup>2</sup></sub>)

33. (c) sp<sup>3</sup>d<sup>2</sup> (d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and d<sub>z<sup>2</sup></sub>)

34. (b) A → p; B → q; C → p; D → s

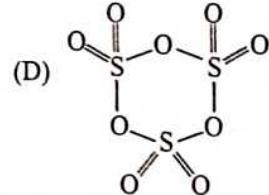
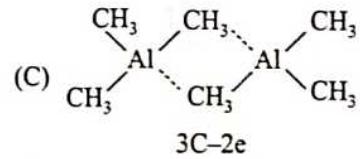
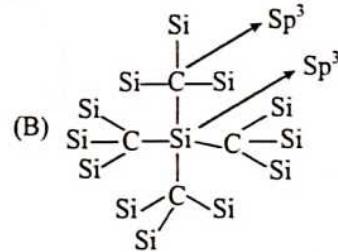
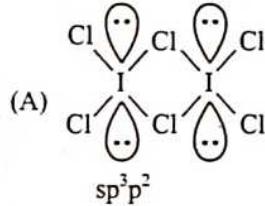
Steric no. of IO<sub>2</sub>F<sub>2</sub><sup>-</sup> = 4 + 1 = 5, sp<sup>3</sup>d;

Steric no. of F<sub>2</sub>SeO = 3 + 1 = 4, sp<sup>3</sup>;

Steric no. of ClOF<sub>3</sub> = 4 + 1 = 5, sp<sup>3</sup>d;

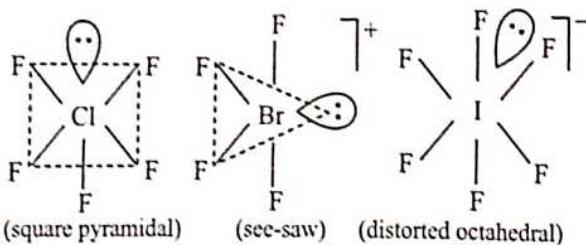
Steric no. of XeF<sub>5</sub><sup>-</sup> = 5 + 1 = 6, sp<sup>3</sup>d<sup>2</sup>

35. (a) A → r; B → p; C → s; D → q



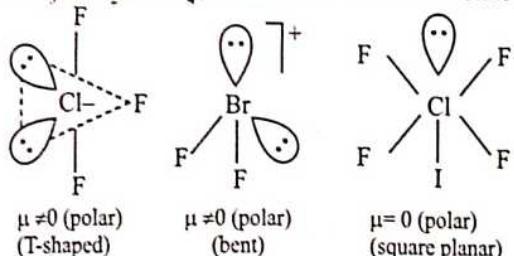
36. (c) A → p,r; B → r; C → q,s; D → p,q,r,s

(A) ClF<sub>5</sub>, BrF<sub>4</sub><sup>+</sup>, IF<sub>6</sub><sup>-</sup>; all have same oxidation state (+ 5)

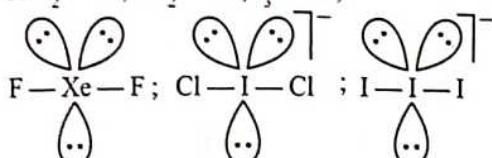


All have one lone pair of electrons each; but different shapes;  $\mu \neq 0$  so polar.

(B)  $\text{ClF}_3^+$ ,  $\text{BrF}_2^-$ ,  $\text{IClF}_4^-$ ; all have same oxidation state (+3);

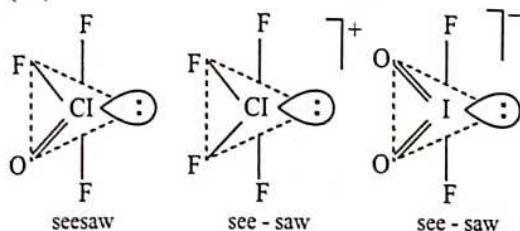


(C)  $\text{XeF}_2^+ = +2$ ;  $\text{ICl}_3^- = +1$ ;  $\text{I}_3^- = +1$ ;



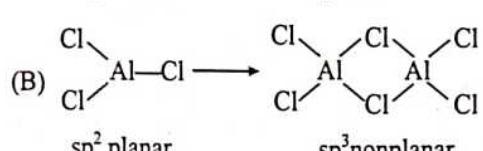
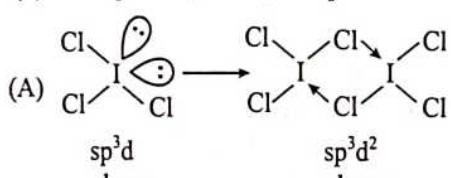
All have three lone pairs each and same shape but different oxidation state. In all  $\mu = 0$ ; so non-polar

(D)  $\text{ClOF}_3^+$ ,  $\text{ClF}_4^+$ ,  $\text{IO}_2\text{F}_2^-$ ; All have same oxidation number (+5)

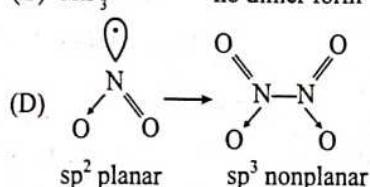


In all  $\mu \neq 0$ , so all polar.

37. (d) A  $\rightarrow$  q, B  $\rightarrow$  r, C  $\rightarrow$  s, D  $\rightarrow$  p

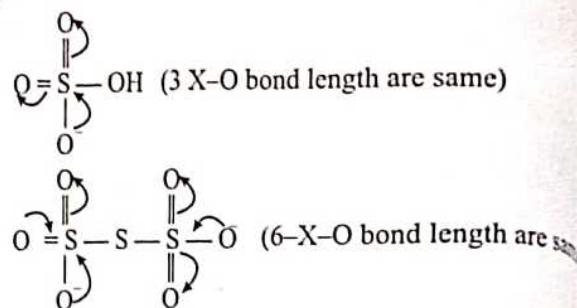


(C)  $\text{AlF}_3$       no dimer form

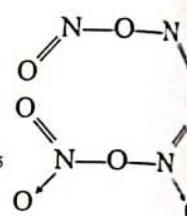
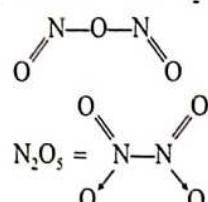


38. [4.5] Bond orders:  $\text{O}_2 = 2$ ,  $\text{O}_2^- = 1.5$ ,  $\text{O}_2^{2-} = 1 \Rightarrow 4.5$

39. [36]



40. [2] The structure of  $\text{N}_2\text{O}_3 =$



While that of  $\text{N}_2\text{O}_4$

Hence  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_5$  contain  $\text{N}-\text{O}-\text{N}$  bond while in  $\text{N}_2\text{O}_4$  does not.

Hence ans. = 2

## Exercise-4 (Past Year Questions)

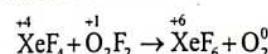
### JEE MAIN

1. (b) There is extensive intermolecular hydrogen bonding in the condensed phase.

2. (a) For  $\text{NO}_2^+$

$$\begin{aligned} x &= \frac{1}{2}[\text{V} + \text{G} - \text{C} + \text{A}] \\ &= \frac{1}{2}[5 + 0 - 1 + 0] \\ &= 2 \text{ sp} \end{aligned}$$

3. (a) In the reaction



Xenon undergoes oxidation while oxygen undergoes reduction.

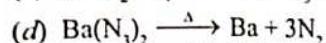
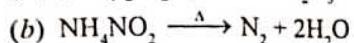
4. (b)  $\text{NO} \Rightarrow$  One unpaired electron is present in  $\pi^*$  molecular orbital

$\text{CO} \Rightarrow$  No unpaired electron is present.

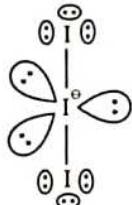
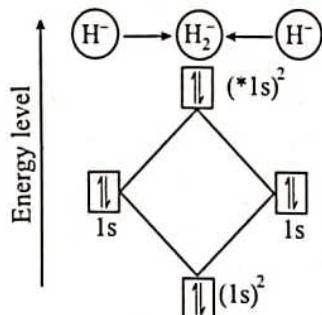
$\text{O}_2 \Rightarrow$  Two unpaired electrons are present in  $\pi^*$  molecular orbitals.

$\text{B}_2 \Rightarrow$  Two unpaired electrons are present in  $\pi$  bonding molecular orbitals.

5. (c)

In reaction (3)  $\text{NH}_3$  is evolved whereas in reaction 1, 2 and 4  $\text{N}_2$  is evolved.

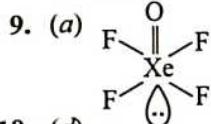
6. (b)

Total number of lone pairs in  $\text{I}^-$  is 9.7. (c) The electronic configuration of  $\text{H}_2^{2-}$  is  $(\sigma 1s^2), (\sigma^* 1s^2)$ 

Bond order of  $\text{H}_2^{2-} = \frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0$

Hence  $\text{H}_2^{2-}$  does not exist, due to zero bond order.8. (b)  $\text{PH}_3$ ,  $\text{P}_2$ ,  $\text{B}_2\text{H}_6$ ,  $\text{H}_2\text{SO}_4$  all are covalent compounds

KCl is ionic compound.



10. (d)

$\text{N}_2^\oplus \Rightarrow \text{BO} = 2.5 \Rightarrow [\pi\text{-Bond} = 2 \& \sigma\text{-Bond} = \frac{1}{2}]$

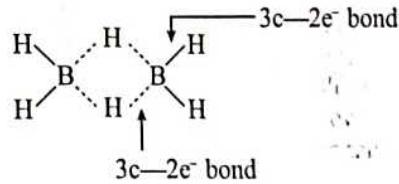
$\text{N}_2 \Rightarrow \text{BO} = 3.0 \Rightarrow [\pi\text{-Bond} = 2 \& \sigma\text{-Bond} = 1]$

$\text{O}_2^\oplus \Rightarrow \text{BO} = 2.5 \Rightarrow [\pi\text{-Bond} = 1.5 \& \sigma\text{-Bond} = 1]$

$\text{O}_2 \Rightarrow \text{BO} = 2.5 \Rightarrow [\pi\text{-Bond} = 1 \& \sigma\text{-Bond} = 1]$

11. (b) It is due to the smallest atomic size of carbon in the given options. Small size greater  $\pi\text{-p}\pi$  multiple bonds

12. (b)



13. (a)	$\text{NO} \rightarrow \text{NO}^+$	$\text{N}_2 \rightarrow \text{N}_2^+$
B.O.	2.5	3
Para	Dia	Dia Para
$\text{O}_2 \rightarrow \text{O}_2^+$		$\text{O}_2 \rightarrow \text{O}_2^{2-}$
B.O.	2	2.5
Para	Para	Dia

14. (b) Both  $\text{Li}_2^+$  and  $\text{Li}_2^-$  have same bond order. But the number of antibonding electrons is less in  $\text{Li}_2^+$  than in  $\text{Li}_2^-$ .15. (b) In case of only  $\text{C}_2$ , incoming electron will enter in the bonding molecular orbital which increases the bond order and stability too. Whereas rest of all takes electron in their antibonding molecular orbital which decreases bond order and stability.

16. (c) Chemical species Hybridisation of central atom

$\text{ICl}_2^-$	$\text{sp}^3\text{d}$
$\text{IF}_6^-$	$\text{sp}^3\text{d}^3$
$\text{ICl}_4^-$	$\text{sp}^3\text{d}^2$
$\text{BrF}_2^-$	$\text{sp}^3\text{d}$

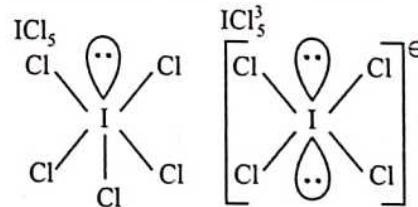
17. (a)

Chemical species	Bond order	Magnetic behaviour
$\text{C}_2^{2-}$	3	diamagnetic
$\text{N}_2^{2-}$	2	paramagnetic
$\text{O}_2$	2	paramagnetic
$\text{O}_2^{2-}$	1	diamagnetic

$$\text{B.O.} \propto \frac{1}{\text{bond length}}$$

18. (c)

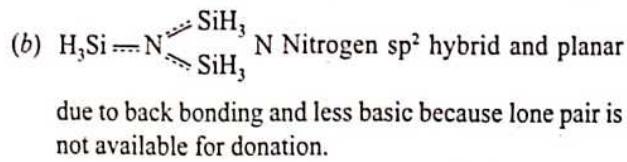
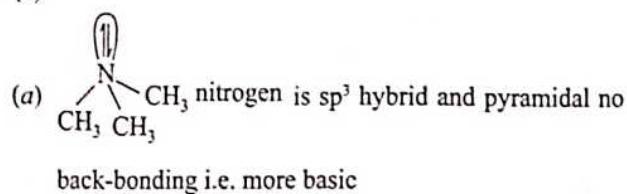
Chemical species	Hybridisation	Shape
$\text{ICl}_5$	$\text{sp}^3\text{d}^2$	Square pyramidal
$\text{ICl}_4^-$	$\text{sp}^3\text{d}^2$	Square planar

19. (c) In diamond C-C bond have only bond character while in case of graphite and fullerene ( $\text{C}_{60}$  and  $\text{C}_{70}$ ) C-C bond contain double bond character. That's why diamond having maximum C-C bond length.20. (d)  $\text{O}_2, \text{NO}, \text{B}_2$  are paramagnetic according to M.O.T whereas  $\text{CO}$  is diamagnetic.21. (a)  $\text{BeCl}_2$  exist as  $(\text{BeCl}_2)_n$  polymeric chain in solid form, while  $\text{BeCl}_2$  exist as dimer  $(\text{BeCl}_2)_2$  in vapour phase.

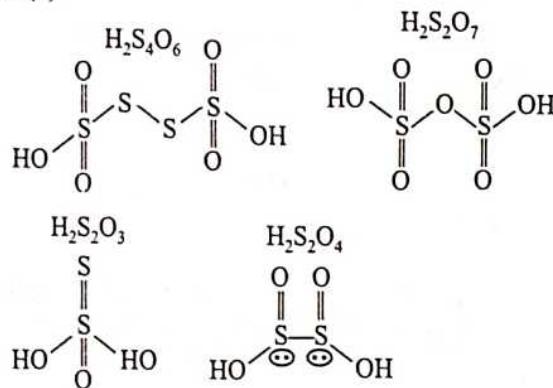
22. (c) HF has highest boiling point among hydrogen halides because it has strongest hydrogen bonding

23. (c) Based on NCERT, statement of limitations of VBT, I & III are correct

24. (d)

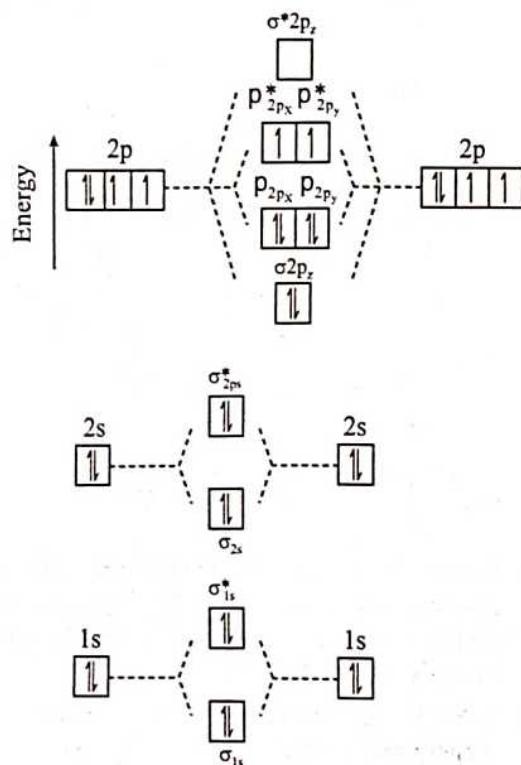


25. (b)



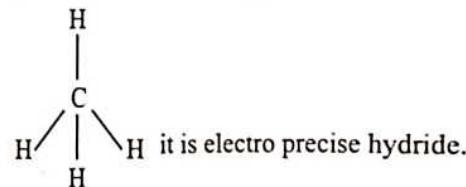
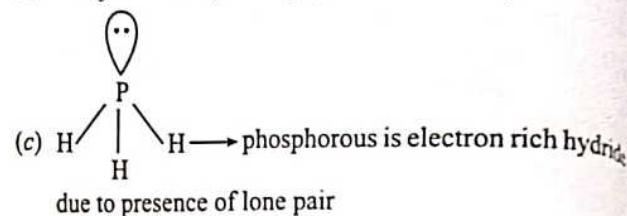
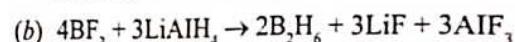
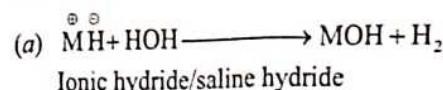
$\text{H}_2\text{S}_2\text{O}_7$  does not contain bond between sulphur atoms.

26. (c) Molecular orbital diagram of  $\text{O}_2$  is



An incoming electron will go in  $\pi^*2\text{Px}$  orbital.

27. (c)



(d)  $\text{HF}$  &  $\text{CH}_4$  are molecular hydride due to they are covalent molecules.

28. (b) Relative strength:

Ion-ion > ion-dipole > dipole-dipole

29. (d)  $\mu_{\text{CCl}_4} = \mu_{\text{CH}_4} = 0$  but  $\mu_{\text{CHCl}_3} \neq 0$

30. (c)  $\text{CN}^-$  is a 14 electron system.

31. (c) Ethyl acetate is polar molecular so dipole-dipole interaction will be present in it.

32. (b) Bond energy  $\propto \frac{1}{\text{Bond length}}$

33. (a)

$$\text{O}_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$$

$$\text{O}_2^- = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^0$$

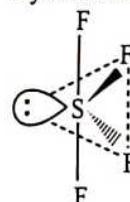
$$\text{O}_2^+ = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^1 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^0$$

34. (b)  $\text{SF}_4$  Bond pair = 4

Lone pair = 1

Steric number = 5

Hybridisation -  $\text{sp}^3\text{d}$



Geometry  $\rightarrow$  Trigonal bipyramidal

Shape  $\rightarrow$  See saw

35. (d) Ion-ion interaction energy  $\propto \frac{1}{r}$

Dipole-dipole interaction energy  $\propto \frac{1}{r^3}$

London dispersion  $\propto \frac{1}{r^6}$



36. (c)

Compound	Shape	Hybridization	Ip	Polarity
AB <sub>4</sub>	Tetrahedral	sp <sup>3</sup>	0	Nonpolar
AB <sub>4</sub>	Rectangular planar	sp <sup>3</sup> d <sup>2</sup>	2	Nonpolar
AB <sub>4</sub>	Square pyramidal	sp <sup>3</sup> d	1	polar
AB <sub>4</sub>	Square planar	sp <sup>3</sup> d <sup>2</sup>	2	Nonpolar

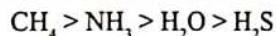
37. (a) Species with minimum bond order will have minimum bond strength.

NO<sup>-</sup> has maximum e<sup>-</sup> in anti-bonding orbitals hence will have minimum bond strength.

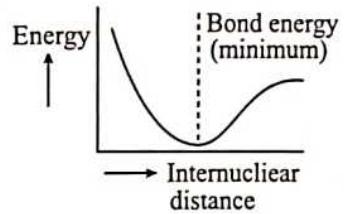
38. (a) The bond which has greater potential energy (more negative) is considered more stable as it requires more energy to dissociate.

∴ A-B bond has most negative potential energy hence it is strongest bond and has maximum bond enthalpy. A-D is longest bond.

39. (b) Order of bond angle is



40. (c)



41. [173]

$$\text{B}_2^+ \Rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_z}^1 = \pi_{2p_z}^0$$

It has one unpaired electron.

$$\text{Spin - only magnetic moment} = \mu = \sqrt{n(n+1)}$$

$$n = \text{Number of unpaired electrons}$$

$$= \sqrt{1(1+2)} = \sqrt{3}\text{BM}$$

$$= 1.73\text{BM}$$

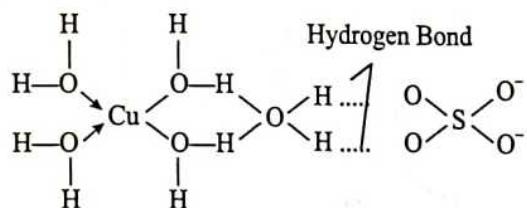
$$= 173 \times 10^{-2}\text{BM}$$

42. [0] Molecular orbital configuration of O<sub>2</sub><sup>2-</sup> is

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2 (\pi_{2p_x}^2 = \pi_{2p_y}^2) (\pi_{2p_x}^{*2} = \pi_{2p_y}^{*2})$$

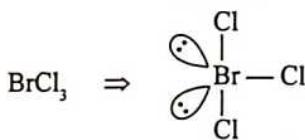
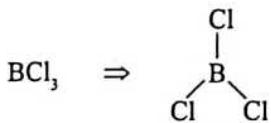
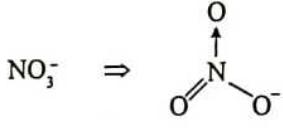
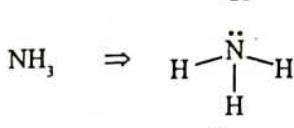
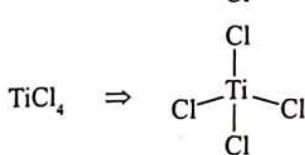
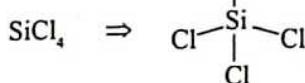
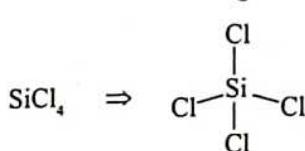
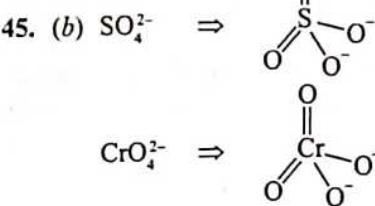
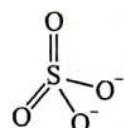
Zero unpaired electron.

43. [1]



Copper sulphate has a total of five water molecules in its structure. Four of the five water molecules found in the crystal structure of the copper sulphate molecule are coordinated to Cu<sup>2+</sup>, while one is hydrogen linked to SO<sub>4</sub><sup>2-</sup>. One Hydrogen bond H<sub>2</sub>O molecule.

44. [3] As we know that non-pyramidal species are SO<sub>3</sub>, NO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>



46. (d) [::---::---::]<sup>-</sup> Linear Shape.

47. (a) Higher the covalent character lower will be melting point.

So LiF > LiCl; MgO > NaCl

48. (c) Be<sub>2</sub> has 8 elections

Bond order of Be<sub>2</sub> is zero.

So Be<sub>2</sub> does not exist.

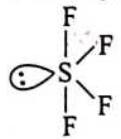
49. (a) In B2H6 terminal bond angle is greater than bridge bond angle.

$$\text{Bond angle} \propto \text{S-Character} \propto \frac{1}{\text{P-Character}}$$

So, Here in terminal bond more S-character and less P-character.

50. (c) SF<sub>4</sub>  $\Rightarrow$  Hybridisation  $\Rightarrow$  sp<sup>3</sup>d

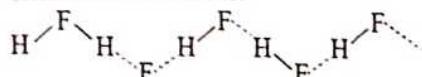
Geometry  $\Rightarrow$  T.B.P      Shape  $\Rightarrow$  See-Saw



Here 2 bonds are axial and 2 bonds are equatorial. So both bond lengths will be unequal.

51. (a) A is false but R is true

Assertion is incorrect since in hydrogen bonding. Dipole-dipole interactions are non-covalent but ion-dipole interaction can also result in H-bond formation. Reason is correct since F is most electronegative element & structure is.



Symmetrical H-bonds are present.

52. (a) Molecule Electrons Bond order

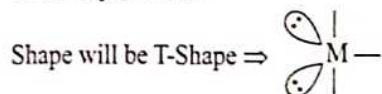
$\text{Ne}_2$	20	0
$\text{N}_2$	14	3
$\text{F}_2$	18	1
$\text{O}_2$	16	2

A → (iii), B → (iv), C → (i), D → (ii)

53. (d)  $\text{H}_2\text{O}$  bond angle is  $104.5^\circ$  bond angle is less due to lone pair-lone pair repulsion.

54. (c) Here 2 lone pairs and 3 bond pairs steric number =  $2 + 3 = 5$

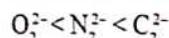
Geometry is T.B.P.



55. (b) Molecule Electrons Bond order

$\text{C}_2^{2-}$	14 e <sup>-</sup> s	3
$\text{N}_2^{2-}$	16 e <sup>-</sup> s	2
$\text{O}_2^{2-}$	18 e <sup>-</sup> s	1

Correct order of bond order.



56. (b) Nitrogen does not have d-orbitals in its valence shell so. It can't form  $\text{NCl}_5$ .

57. (a) Both statement I and Statement II are correct

Due to presence of double bond alkanes are highly reactive than alkanes.

Therefore, alkanes are less stable than alkenes.

There is more energy required to break double bond than a single bond. So that, strength of double bond is greater than carbon-carbon single bond.

58. [3]  $\text{BeF}_2$ ,  $\text{BF}_3$  and  $\text{CCl}_4$  has zero dipole moment.

$\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{HCl}$  has non-zero dipole moment.

59. (c)  $\text{NO}$ ,  $\text{O}_2$  has last electron in anti-bonding orbital.

So, here if we remove last electron bond order will increase.

60. (c)  $\text{B}_2\text{H}_6$  and  $\text{BCl}_3$  is electron deficient.

61. (b)  $\text{NO}_2$  contains odd electron.

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62. (b,c)

Lone pairs on the central atom in  $\text{BrF}_5$  = 1

Lone pairs on the central atom in  $\text{ClF}_3$  = 2

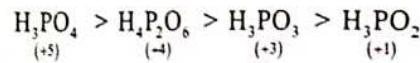
Lone pairs on the central atom in  $\text{XeF}_4$  = 2

Lone pairs on the central atom in  $\text{SF}_4$  = 1

63. (a,c)  $\text{C}_2^{2-}$  is 14 e<sup>-</sup>s species and diamagnetic

$\text{O}_2^{2+}$  (B.O. = 3) have shorter bond length than  $\text{O}_2$  (B.O. = 2)

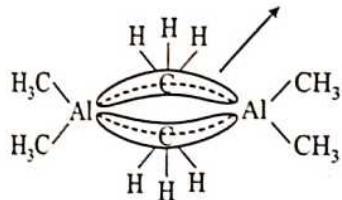
64. (b) Correct order



65. (a,b,d)

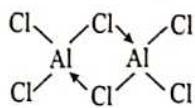
Structure of  $\text{Al}_2(\text{CH}_3)_6$

3 centre-2 electron bond



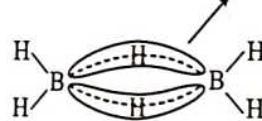
$\Rightarrow \text{BCl}_3$  is stronger lewis acid due to small size of boron.

$\Rightarrow$  Structure of  $\text{Al}_2\text{Cl}_6$

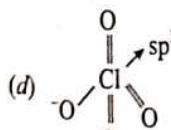
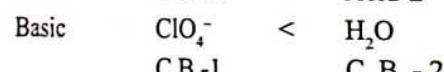
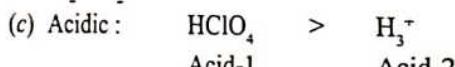
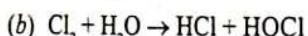
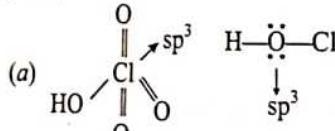


Structure of  $\text{B}_2\text{H}_6$

3 centre-2 electron bond



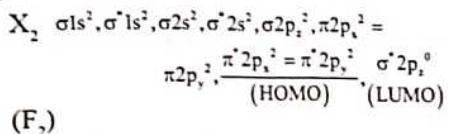
66. (a,c,d)



Resonance stabilization



67. (a,d)

Down the group  $\pi^*$  to  $\sigma^*$  excitation become easy.

68. [6]

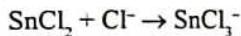
Species Lone pair on central atom

TeBr<sup>2-</sup> : 1BrF<sub>2</sub><sup>-</sup> : 2SNF<sub>3</sub> : 0XeF<sub>3</sub><sup>-</sup> : 3

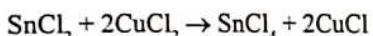
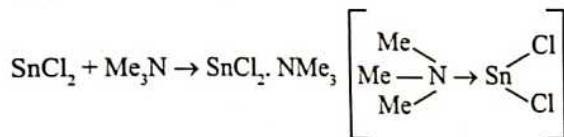
Total Number of lone pair = 6

69. [6] (H<sub>2</sub>, Cl<sub>2</sub>, Be<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, F<sub>2</sub>)H<sub>2</sub> :  $\sigma^1 s^2$ He<sub>2</sub><sup>-</sup> :  $\sigma^1 s^2, \sigma^* 1s^2$ Li<sub>2</sub> :  $\sigma^1 s^2, \sigma^* 1s^2, \sigma^* 2s^2$ Be<sub>2</sub> :  $\sigma^1 s^2, \sigma^* 1s^2, \sigma^* 2s^2, \sigma^* 2s^2$ B<sub>2</sub> :  $\sigma^1 s^2, \sigma^* 1s^2, \sigma^* 2s^2, \sigma^* 2s^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$ C<sub>2</sub> :  $\sigma^1 s^2, \sigma^* 1s^2, \sigma^* 2s^2, \sigma^* 2s^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$ N<sub>2</sub> :  $\sigma^1 s^2, \sigma^* 1s^2, \sigma^* 2s^2, \sigma^* 2s^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$ O<sub>2</sub><sup>-</sup> :  $\sigma^1 s^2, \sigma^* 1s^2, \sigma^* 2s^2, \sigma^* 2s^2, \sigma^* 2p_z^2 = \pi^* 2p_x^2$   
 $= \pi^* 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$ F<sub>2</sub> :  $\sigma^1 s^2, \sigma^* 1s^2, \sigma^* 2s^2, \sigma^* 2s^2, \pi^* 2p_z^2 = \pi^* 2p_x^2$   
 $= \pi^* 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$ 

70. (a,d)



(Q) (X)



(Q) (Z)

71. (b,d)

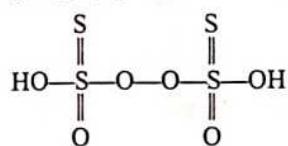
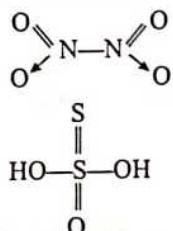
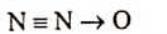
Polar molecule

CHCl<sub>3</sub>, SO<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>Cl,H<sub>2</sub>Se, BeF<sub>3</sub>, O<sub>3</sub>, XeF<sub>6</sub>,

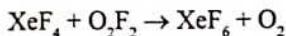
Non-polar molecule

BeCl<sub>2</sub>, CO<sub>2</sub>, BCl<sub>3</sub>, SF<sub>6</sub>NO<sub>2</sub>, NH<sub>3</sub>, POCl<sub>3</sub>, CH<sub>3</sub>Cl

72. [4.00]



73. [19.00]



Y

Y has 3 lone pair of electron in each fluorine and one lone pair of electron in xenon.

$$6 \times 3 + 1 = 19$$

Hence total lone pair of electrons is 19.

74. [6]

Here polar molecules in the liquid form will be attracted/deflected near charged comb.

Polar molecules : HF, H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, CHCl<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>Cl  
(6-polar molecules)Nonpolar molecules : O<sub>2</sub>, CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>

75. (a,d)

(a)  $\sigma$  orbital has a total of two nodal places.(d)  $\pi^*$  orbital has one mode in the xy plane the molecular axis.

# CHAPTER

# 9

# Hydrogen and Its Compounds

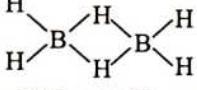
## Exercise-1 (Topicwise)

1. (b)  $\boxed{1} + e^- \rightarrow \boxed{1}$ , helium like configuration.
2. (d) Hydrogen is an invisible gas.
3. (a)  ${}_1^3H \Rightarrow n + p = 3$ .
4. (c) It can gain or lose its outermost  $e^-$ .
5. (d) Electrolysis.
6. (d)  $Ca + H_2 \rightarrow CaH_2$  (Hydrolith)  
 $CaH_2 + H_2O \rightarrow Ca(OH)_2 + H_2 \uparrow$
7. (b) The ionization energy of hydrogen is  $1312 \text{ kJ mol}^{-1}$
8. (b) Alkali metals have very low I.E.
9. (d) Hydrogen molecule cannot participate in coordinate bond formation but chlorine molecule can.
10. (d) Loss of an electron from hydrogen atom results in a nucleus of very small size as compared to any other atoms or ions.
11. (a)  $H < H^+ < H^-$ ,  $H^-$  has helium like configuration which is a noble gas, which has highest ionization energy.
12. (c) Hydrogen can lose 1 electron or gain 1 electron or it can make a bond with itself or any other atom.
13. (b)  $CO(g) + H_2O(g) \xrightarrow[{\text{Catalyst}}]{673K} CO(g) + H_2(g)$ .
14. (d) In  $CH_4$  octate is completed.
15. (a) The metals of group 7, 8 and 9 do not form hydride.
16. (a) Interstitial hydrides are formed by the compounds of d & f-block elements
17. (c) Heavy water is chemically deuterium oxide ( $D_2O$ ).
18. (b) Washing soda can remove temporary and permanent hardness of water.
19. (b)  $D_2O$  used in nuclear reactors as a moderator.
20. (d) Temporary hardness due to bicarbonates while permanent due to chlorides & sulphates of  $Ca^{+2}$  &  $Mg^{+2}$ .
21. (a)  $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$
22. (a)  $Na_2Al_2SiO_5 \cdot xH_2O$
23. (b)  $NaZ + CaSO_4 \rightarrow CaZ + Na_2SO_4$

24. (d) The density of water is  $1 \text{ g cm}^{-3}$  at  $4^\circ C$   
 $\text{so molarity} = \frac{1000}{18} = 55.5 \text{ M.}$
25. (d)  $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$
26. (c) Produce  $H_2$ , used in reduction of others.
27. (c)  ${}_1^3H$
28. (d)  $2F_2 + 2H_2O \rightarrow 4HF + O_2$
29. (d) Water obtained from organic ion-exchange resins is free from all ionic impurities.
30. (b)  $H^0$  ion will exchange  $H^+$  ion from  $H_2O$  molecule.
31. (a)  $Ca(OH)_2$  (Clark's method)
32. (c) Passing it through cation exchange resins ( $Mg^{2+}$  &  $Ca^{2+}$ ) replaces  $Na^+$  ions.
33. (b) Due to production of nascent oxygen.
34. (b)  $Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$   
In this reaction  $H_2O_2$  works as reducing agent
35. (c)  $Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$
36. (c)  $KO_2 \rightarrow O_2^-$   
 $BaO_2 \rightarrow O_2^{-2}$
37. (c) Electrolysis of 50% sulphuric acid gives per disulphuric acid ( $H_2S_2O_8$ ) which on distillation yields 30% solution of hydrogen peroxide.
38. (b) By the action of cold and dilute sulphuric acid on hydrated barium peroxide  
 $BaO_2 \cdot 8H_2O(s) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$
39. (b) During the electrolytic oxidation of acidified sulphuric acid solutions at high current density gives peroxodisulphate, which on further hydrolysis gives hydrogen peroxide.
40. (d) Fact based.
41. (a) The laboratory preparation of  $D_2O_2$  is also done by this method  
 $K_2S_2O_8(s) + 2D_2O(l) \longrightarrow 2KDSO_4(aq) + D_2O_2(l)$
42. (c)  $BaO + CO_2 + H_2O \rightarrow BaCO_3 + H_2O_2$
43. (d)  $H_2O_2$  can be used as (a), (b) and (c).
44. (b) Only non-linear structures show dipole moment.

45. (b)  $\text{Na}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}_2$   
 46. (d) Conc.  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ .  
 47. (b) In Solye process  $\text{NaCl}$ ,  $\text{CO}_2$  and  $\text{NH}_3$  are used.  
 48. (d)  $\text{H}_2\text{O}_2$  exists in two phase gaseous and solid phase with different dihedral angle.  
 49. (c) Higher the no. of hydrogen bonding and molecular mass higher will be boiling point.  
 50. (d) Strength of hydrogen bond is greater in  $\text{H}_2\text{O}$   $\because \text{H}_2\text{O}$  has more formal negative charge on the oxygen atom than  $\text{H}_2\text{O}_2$ .

## Exercise-2 (Learning Plus)

1. (d) Hydrogen does not have lone pair of electron so it can not form coordinate bond with other atoms or molecules.  
 2. (c) The ratio of protium, deuterium and tritium in nature is not certain.  
 3. (c)  $\text{H}-\text{Be}-\text{H}$
- 
4. (b)  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O} + \text{Ca}^{2+} \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O} + 2\text{Na}^+$   
 5. (b) In bosch process water gas is used for production of  $\text{H}_2$ .  
 6. (c) At Anode  
 $2\text{H}^- \rightarrow \text{H}_2 + 2\text{e}^-$   
 7. (a) Due to Ca and Mg salts.  
 8. (b)  $\text{Mg}_3\text{N}_2 + 6\text{D}_2\text{O} \rightarrow 3\text{Mg}(\text{OD})_2 + 2\text{ND}_3$   
 9. (d) Each oxygen atom attached with four hydrogen, two by covalent bonds and two hydrogen bonds in ice.  
 10. (d) Fact based.  
 11. (b)  $\text{Na}_2\text{O}_2 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O}_2$   
 $\text{Na}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}_2$   
 12. (c)  $\text{H}_2\text{O}_2$  acts as reducing agent in acidic medium  
 $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$   
 13. (c) It undergoes autoxidation on prolonged standing.  
 14. (b)  $\text{CO}_2$  is stronger acid than  $\text{H}_2\text{O}_2$  and water is weaker acid than  $\text{H}_2\text{O}_2$ .  
 15. (c) 30% (w/v)  $\text{H}_2\text{O}_2$ .  
 16. (a) Hydrogen position in the periodic table is not certain and unsatisfactory. Hydrogen exhibits properties similar to both alkali metals (Group (a)) and halogens (Group 17).  
 17. (b) Tritium is radioactive and emits low energy beta-particles  
 18. (c) The ionization energy of hydrogen ( $1312 \text{ kJ mol}^{-1}$ ) is of nearly same order as that of the halogens ( $\Delta H$  of F is  $1680 \text{ kJ mol}^{-1}$ ).

19. (a) Atomic hydrogen is very unstable it readily combines with another hydrogen atom to form hydrogen molecule which is highly stable hence energy is released.  
 20. (d) Dihydrogen gets dissociated into atomic hydrogen by an electric arc and so the hydrogen atoms which are produced are allowed to combine on the surface to be welded to generate the temperature of 4000 K.  
 21. (b)  $\text{MgH}_2$  is covalent polymeric hydride.  
 22. (c) Molar mass of  $\text{D}_2\text{O}$  and  $\text{HTO}$  is 20 g/mole  
 23. (c)  $\text{H}_2$  and  $\text{D}_2$  are isotopes. Its have same atomic number therefore bond length is same.  
 24. (a) On reaction with water Ionic hydrides will give basic solution  
 $\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$   
 25. (c) Boron hydride  $\text{BH}_3$  is electron deficient because its octet is incomplete.  
 26. (c) d and f block elements form interstitial metal's hydride.  
 27. (d)  $2\text{R}-\text{COO H} + \text{Ca}^{2+} \rightarrow (\text{RCOO})_2\text{Ca} + 2\text{H}^+$   
 28. (a) Hydrogen peroxide is diamagnetic molecule.  
 29. (a) Volume strength of  $\text{H}_2\text{O}_2 = N \times 5.6$   
 $= 1.5 \times 5.6 = 8.4 \text{ vol}$   
 30. (a)  $\text{F}_2$  is more reactive than  $\text{Cl}_2$  which is further more reactive than  $\text{Br}_2$  and least reactive amongst halogens is  $\text{I}_2$  which requires a catalyst for the reaction.  
 31. (b) Oxygen liberated from 1000 ml of  $\text{H}_2\text{O}_2 = 20,000 \text{ ml}$ .  
 $\therefore$  Oxygen liberated from 15 ml = 300 ml  
 32. (c) The adsorption of hydrogen by metals is called occlusion.  
 33. (b) Hydrogen is adsorbed by certain metals like Fe, Au, Pt & Pd.  
 34. (b) Deuterium forms strong bond with oxygen as compare to hydrogen. So the bond energy of O-H is lesser as compare to O-D bond energy in water.  
 35. (b)  $\text{H}_2\overset{-1}{\text{O}}_2 + 2\text{HI} \xrightarrow[\text{Oxidation}]{\text{Radiation}} \overset{0}{\text{I}}_2 + 2\text{H}_2\overset{-2}{\text{O}}$   
 $\therefore \text{H}_2\text{O}_2$  is an oxidising agent.  
 $\text{HO}\overset{+1}{\text{Cl}} + \text{H}_2\overset{-1}{\text{O}}_2 \xrightarrow[\text{Radiation}]{\text{Radiation}} \text{H}_3\text{O}^+ + \overset{-1}{\text{Cl}} + \overset{0}{\text{O}}_2$   
 $\therefore \text{H}_2\text{O}_2$  = Reducing agent.  
 36. (a) In group 6, only chromium forms  $\text{CrH}$ .  
 37. (a) Pd, Pd adsorbs hydrogen.  
 38. (d) 50% dilute  $\text{H}_2\text{SO}_4$  on electrolysis produces  $\text{H}_2$ .  
 39. (c)  $\text{H}_2$  and  $\text{D}_2$  have same bond length.  
 40. (a)  $\text{H}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{e}^-$ ; at anode.

## Exercise-3 (JEE Advanced Level)

1. (d)  $\text{CaH}_2$  (hydrolith)
2. (d) Ion-exchange method (Permutit process) is used for removing the permanent hardness of the water.
3. (c) Ionic hydride is formed by s-block elements. Which contains  $\text{H}^-$  ions that's why they are a good reducing agents.
4. (d) Vegetable oil +  $\text{H}_2 \xrightarrow[473\text{K}]{\text{Ni}}$  Fat  

Liquid	Solid
--------	-------
5. (c) Ortho and para-hydrogen have the same chemical properties but different physical properties.
6. (b) Ionic hydride is formed by s-block elements which are very high electropositive metals.
7. (d) s-block elements formed ionic hydride ( $\text{NaH}$ ).
8. (a,b,d)  

Ortho & para hydrogen are called as nuclear spin isomers because they are different w.r.t their nuclear spins.
9. (a,c,d)  

Bosch process used water gas ( $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)}$ ).
10. (a,b,c)  

Clark's method uses calcium hydroxide to remove the temporary hardness of water.
11. (a,c,d)
  - (a)  $\text{Fe} + 2\text{H}^+ (\text{dil}) \rightarrow \text{Fe}^{2+} + \text{H}_2$
  - (c)  $\text{Zn} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$   

Sodium	
zincate	

(d) During electrolysis, the following reactions takes place

At anode :  $2\text{Cl}^- (\text{aq}) \rightarrow \text{Cl}_2 (\text{g}) + 2\text{e}^-$

At cathode :  $2\text{H}_2\text{O} (\text{l}) + 2\text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq})$

Overall reaction:  $2\text{Cl}^- (\text{aq}) + 2\text{H}_2\text{O} (\text{l}) \rightarrow \text{Cl}_2 (\text{g}) + \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq})$
12. (a,b,d)  

Protium, deuterium and tritium are isotopes. They have only one electron in the shell. The mass number ratio is : 1: 2: 3
13. (a,c)
  - (a)  $\text{H}_2 (\text{g}) \xrightarrow[\text{Electric arc}]{5000\text{K}} 2\text{H} (\text{g}) : \Delta H = 436 \text{ KJ}$
  - (c) Palladium in the powdered state can occlude nearly 1000 times its own volume of hydrogen
14. (c) 6% (w/v) of  $\text{H}_2\text{O}_2$ .
15. (a) Protium is most common isotopes
16. (d)  

(a-c) Interstitial hydrides are non-stoichiometric hydrides and thus deficient in hydrogen. Transition and

innertransition elements at elevated temp. absorb hydrogen into the interstices of their lattices to yield metal like hydrides.

17. (a,b,c)  

Metallic hydrides are non-stoichiometric hydrides so, they are deficient of hydrogen and conduct electricity. ionic hydrides are crystalline non-volatile and non-conducting in solid state.
  18. (a,b,c)  

Hydrogen can attain stability by using an electron, gaining an electron or forming a bond with itself or another atom.
  19. (a,b,c,d)
 
$$\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$$

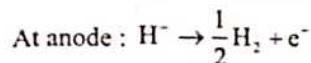
$$2\text{Al} + q\text{NaOH} \rightarrow q\text{Naiv}_2 + 3\text{H}_2$$

$$\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$$
  20. (c) Interstitial hydrides are non-stoichiometric in nature.
  21. (b)  $\text{SiH}_4$  is electron precise hydride (As it's octate is complete).
  22. (d)  $\text{Na} + \frac{1}{2}\text{H}_2 \rightarrow 2\text{NaH}$ . Along the row, electro negativity So, hydride becomes more acidic. Metallic hydrides are good conductors of electricity and have high thermal conductivity.
  23. (c)  ${}^3_1\text{H}$
  24. (b) ∵ the earth's gravity field is too small to hold such a light element.
  25. (a)  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  Highly exothermic occupies very less space and have high thrust.
  26. (c) Perhydrol '100V'  $\text{H}_2\text{O}_2$  not used to removal of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  from the sample of water.
  27. (d) permutit is a  $\text{Na}_2\text{OAl}_2\text{O}$ .
  28. (c) Zeolite is  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$
  29. (a)  $\text{D}_2\text{O}$  is heavy water, temporary hard water is bicarbonates of Mg and Ca permanent hard water contains sulphates and chlorides of Mg and Ca.
  30. (c) Calgon are polymetaphosphate of Na. Metallic hydrides are non-stoichiometric compound.  $\text{CH}_4$  is covalent hydride.
  31. (b) H-atom can be used in cutting and welding.
- $$\text{R}-\text{C}-\text{CO} + \text{H}_2 \xrightarrow{\text{Rh/PPH}_3} \text{R}-\text{CHO} + \text{R}-\text{CH}_3$$

(Hydrotormylation)  $\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$ .  
Perhydrol is  $\text{H}_2\text{O}_2$
32. (c)  $\text{H}_2\text{O} \xrightarrow{\text{Electrolysis}} \text{H}_2 + \text{O}_2$ .  $\text{LiAlH}_4$  is a reducing agent.  
 $\text{H}-\text{Cl}$  (polar).  $\text{D}_2\text{O}$  used in aromatic reactor.
  33. (d)  $\text{H}_2\text{O}_2$  is perhydrol and a propellant sodium hexametaphosphate used in a calgon method.



34. (a) LiH is a metallic hydride, conduct heat and electricity. Concept of hybridization is not applicable.



CH<sub>4</sub>(sp<sup>3</sup>) hybridised.

35. (c) perhydrol 100V H<sub>2</sub>O<sub>2</sub> not used to removal of Ca<sup>2+</sup>/Mg<sup>2+</sup> from the sample of water.

36. [3] H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> on completely hydrolysis gives ..... mole of H<sub>2</sub>SO<sub>4</sub> & ..... 1..... mole of H<sub>2</sub>O<sub>2</sub>.

37. [4] No. of Peroxy linkage in H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, CrO<sub>5</sub> & H<sub>2</sub>TiO<sub>4</sub> are 1, 2 and 1 respectively.

38. [4] Tritium has one proton, two neutrons, and one electron.

39. [3] Incorrect points

(ii) H<sub>2</sub> < D<sub>2</sub> (Bond energy)

(iii) H<sub>2</sub> < D<sub>2</sub> < T<sub>2</sub> (Boiling point)

(iv) H<sub>2</sub> < D<sub>2</sub> < T<sub>2</sub> (No. of neutrons)

(i) The number of protons in isotopes of hydrogen is the same.

40. [3] Incorrect Points

(i) CaH<sub>2</sub> < BeH<sub>2</sub> (Electrical conductance in molten condition)

(ii) LiH < NaH < CsH (Ionic character)

(iii) H<sub>2</sub> < D<sub>2</sub> < F<sub>2</sub> (Bond dissociation enthalpy)

(iv) Ionic character is an increase in ionic hydride down the group of s-block elements due to an increase in the size of cation.

41. [9] [H<sub>9</sub>O<sub>4</sub>]<sup>+</sup>

## Exercise-4 (Past Year Questions)

### JEE MAIN

1. (d) Highly pure hydrogen can be obtained by electrolysis of water. It is the decomposition of water into O<sub>2</sub> and H<sub>2</sub> gas by passing electric current.

2. (b) A reducing agent gets oxidized while reducing the other reactant. Hence, it should release electrons.

3. (c) Na<sub>2</sub>O<sub>2</sub> is peroxide of sodium.

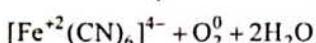
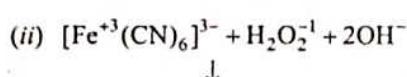
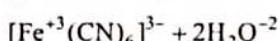
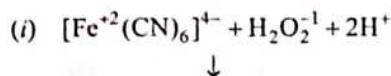
4. (a) The oxidation state of Mn in MnO<sub>4</sub><sup>-</sup> is +7. H<sub>2</sub>O<sub>2</sub> can only reduce Mn as it is in maximum O.S.

5. (c) Permanent hardness in water cannot be cured by boiling, filtration and distillation.

6. (c) H<sub>2</sub>O<sub>2</sub> can undergo oxidation as well as reduction because the oxidation number of oxygen in H<sub>2</sub>O<sub>2</sub> is -1.

7. (c) H<sub>2</sub>O<sub>2</sub> oxidises PbS to PbSO<sub>4</sub> and itself gets reduced to H<sub>2</sub>O.

8. (b)



9. (c) Temporary hardness is due to soluble Mg(HCO<sub>3</sub>) and bicarbonates of calcium and magnesium.

10. (d)

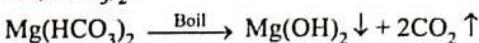
I. H<sub>2</sub> produces less combustion because it doesn't produce carbon monoxide.

II. Because it has high calorific value.

III. Dihydrogen is stored in tanks of metal alloys.

IV. LPG produces less energy than liquid dihydrogen.

11. (c) Temporary hardness is due to soluble Mg(HCO<sub>3</sub>)<sub>2</sub> and Ca(HCO<sub>3</sub>)<sub>2</sub>.



12. (a) Temporary hardness is due to soluble Mg(HCO<sub>3</sub>) and bicarbonates of calcium and magnesium.

13. (a) Mass of CaSO<sub>4</sub> =  $10^{-3} \times 136$

$$= 0.136\text{g}$$

$$136\text{g of CaSO}_4 \rightarrow 100\text{g of CaCO}_3$$

$$0.136\text{g of CaSO}_4 \rightarrow \frac{100}{136} \times 0.136$$

$$= 0.1\text{g of CaCO}_3$$

Hardness of water (in terms of CaCO<sub>3</sub>)

$$= \frac{W_{\text{CaCO}_3}}{W_{\text{H}_2\text{O}}} \times 10^6 \text{ ppm}$$

$$= \frac{10^{-1}}{1000} \times 10^6 = 100 \text{ ppm}$$

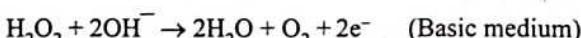
14. (d) All are isotopes of hydrogen.

15. (a) I<sub>2</sub> is least reactive among all the halogens.

16. (b) H<sub>2</sub>O<sub>2</sub> as oxidant:

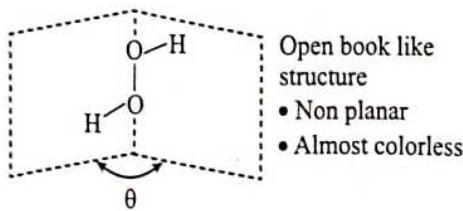


H<sub>2</sub>O<sub>2</sub> as reductant:



17. (c) Hydrogen has 3 isotopes and 1 is radioactive amongst them.



18. (c) Si has octet configuration.
19. (b) NaH is an example of ionic hydride which is also known as saline hydride.
20. (c) The synonym for water gas is syn gas.
21. (c)  $Zn + 2HCl \rightarrow ZnCl_2 + H_2$   
 $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
22. (a) Zeolite process uses the mineral zeolite as the exchange resin for cations in the hard water whereas the ion exchange process include several different resins for the ion exchange.
23. (b) (a)  $H_2O_2 \rightarrow 2H_2O + O_2$   
(b)  $KClO_3 \xrightarrow[\text{MnO}_2]{\Delta} KCl + \frac{3}{2}O_2$   
 $Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + \frac{1}{2}O_2$   
 $NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$   
(c) 2-Ethyanthraquinol  $\xrightleftharpoons[\text{H}_2/\text{Pd}]{\text{O}_2}$   
2-Ethylanthraquinone ( $H_2O_2$ )  
(d) Hydrogen peroxide is used for the manufacture of sodium perborate.
24. (d)  $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$   
 $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
25. (c) Clark's method is used to remove temporary hardness of water.
26. (d)
- 
- Open book like structure
  - Non planar
  - Almost colorless
27. (b) In water gas shift reaction, Hydrogen gas is produced economically by the reaction of carbon monoxide with water vapour at 673 K in presence of iron, chromium and copper zinc catalyst.
- $$CO + H_2O(g) \xrightarrow[\Delta]{\text{Catalyst}} CO_2 + H_2(g)$$
28. (b) To obtain  $H_2$  of high purity (> 99.95 %) electrolysis of  $Ba(OH)_2$  solution is done using Ni electrodes.
29. (c)  $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$
30. (b) (a)  $PbO_2 + 2H_2O \rightarrow Pb(OH)_4$   
(b)  $Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$  this reaction is possible at room temperature  
(c)  $SnO_2 + 2H_2O \rightarrow Sn(OH)_4$   
(d) Acidified  $BaO_2 \cdot 8H_2O$  gives  $H_2O_2$  after evaporation.
31. (a) The bond dissociation energy of  $D_2$  is greater than  $H_2$  and therefore  $D_2$  reacts slower than  $H_2$ .
32. (d)  $D_2O$  is used for the study of reaction mechanism.  $R_{25^\circ}$  of reaction for the cleavage of O-H bond > O-D bond
33. (b) Around 55% of hydrogen goes to ammonia production
34. (a) Sodium hydroxide is generally prepared commercially by electrolysis of sodium chloride in castner Kellner cell.
- At cathod:  $Na + e^- \xrightarrow{\text{Hg}} \text{Na-amalgam}$   
Anode:  $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$
- The Na-amalgam is treated with water to give sodium hydroxide and hydrogen gas:
- $$2\text{Na (amalgam)} + H_2O \longrightarrow 2\text{NaOH} + H_2 + 2\text{Hg}$$
35. (a)  $Mg(HCO_3)_2 \xrightarrow{\text{Boil}} Mg(OH)_2 + 2CO_2 \uparrow$   
 $Ca(HCO_3)_2 \xrightarrow{\text{Boil}} CaCO_3 + H_2O + CO_2 \uparrow$
36. (d) They have different neutrons and mass number.
37. (c) In option (a) and (c) reducing action of hydrogen peroxide is shown.  
In option (a) it is in acidic medium, in option (b) it is in basic medium.

### JEE-ADVANCED

38. (a) As reducing agent
- $$KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$$
- As oxidising agent
- $$NH_3OH + 3H_2O_2 \longrightarrow HNO_3 + 4H_2O$$

## CHAPTER

10

# The s-Block Elements

## **Exercise-1 (Topicwise)**



17. (c) Order of their m.p. is Li > Na > K and order of reactivity is opposite to order of m.p.

18. (c) Softness of alkali metal increases down the group due to increases in size (close packing of atoms become weak)

19. (c)  $K_2CO_3$  can not be prepared because  $KHCO_3$  is highly soluble and cannot be precipitate out.

20. (b)  $2Na + 2NH_3 \xrightarrow{\text{heat}} 2NaNH_2 + H_2$

21. (a) Greater size of  $HCO_3^-$  not stable with  $Li^+$

22. (a) In polyatomic anions stability inversely depends on polarising power of cation.

23. (d) The given compound x must be  $CaCO_3$ . It can be explained by following reactions,

$$CaCO_3 \xrightarrow[\text{(x)}]{\Delta} CaO + CO_2 \uparrow;$$

$$CaO + H_2O \xrightarrow[\text{(y)}]{} Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow Ca(HCO_3)$$

$$Ca(HCO_3)_2 \xrightarrow[\text{(x)}]{\Delta} CaCO_3 + CO_2 \xrightarrow[\text{(z)}]{\Delta} + H_2O$$

24. (c) According to Fajan's rule  $RbCl$  has greatest ionic character due to large ionic size of  $Rb^+$  ion.  $BeCl_2$  has least ionic (Maximum covalent) due to small size of  $Be^{+2}$  ion which has highly polarising.

25. (a)  $NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$   
 $NaHCO_3$  and  $NaOH$  pair can't exist in solution as they react with each other.

26. (c) Soda ash –  $Na_2CO_3$

27. (b) In Castner-keller cell wr use: At Anode – Graphite and at cathode – mercury

28. (d)  $Na \xrightarrow{\text{NH}_3} Na^+(NH_3)_x + e^-(NH_3)_y$

29. (b)  $LiCl$  has more covalent character than other alkyl halide due to which it is more soluble in non-polar solvent (pyridine)

30. (b)  $Zn(s) + 2NaOH(aq) \longrightarrow Na_2ZnO_2(aq) + H_2(g)$   
Sodium zincate      Hydrogen gas

31. (d) More the magnitude of  $\Delta H_f$  (Heat of formation), more the stability of compound



8. (a) According to Fajan rule  
solubility in polar solvent  $\propto$  Ionic character  
solubility in non polar  $\propto$  covalent character solvent
9. (c)  $\text{Na} + \text{Al}_2\text{O}_3 \rightarrow \text{Na}_2\text{O} + \text{Al}$  (Position in electrochemical series)  
 $\text{Na}_2\text{O} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3$
10. (c)  $\text{BaCO}_3$  (white ppt.)  
 $\text{CO}_3^{2-}$   
 $\text{Ba}^{2+} + \text{CrO}_4^{2-} \rightarrow \text{BaCrO}_4(s)$  Yellow ppt.  
 $\text{SO}_4^{2-}$   
 $\text{BaSO}_4(s)$  (white ppt.)
11. (b)  $\text{A} \xrightarrow[\text{Lime water}]{} \text{Ca}(\text{OH})_2$   
 $\text{Ca}(\text{OH})_2 + \text{CO}_2 \xrightarrow[\text{Lime water}]{} \text{CaCO}_3 + \text{H}_2\text{O}$  White ppt. (C)  
 $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \xrightarrow[\text{C}]{\text{B}} \text{CaCO}_3 + \text{NaOH}$
12. (b)  
(a) Ca salt imparts brick red colour to the flame.  
(b) Sr salt imparts bright crimson colour to the flame.  
(c) Ba salt imparts apple green colour to the flame.  
(d) Mg salt does not impart any colour to the flame because of high ionization energy.
13. (a)  $\text{Mg} + 3\text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$ ;  
 $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$ .
14. (c)  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+} + \text{EDTA}^{4-} \rightleftharpoons [\text{Ca}(\text{EDTA})]^{2-}$  or  $[\text{MgEDTA}]^{2-}$   
Hardness causing ion
15. (a) For alkaline earth metals,  
(i) Solubility of sulphates decreases down the group.  
(ii) Solubility of hydroxide increases down the group.  
 $\text{BeO}$  and  $\text{Be}(\text{OH})_2$  are amphoteric; so they are soluble in  $\text{NaOH}$  forming soluble  $[\text{Be}(\text{OH})_4]^{2-}$ .  
Hence metal M is Be.
16. (a)  $\text{Ba}(\text{NO}_3)_2 \xrightarrow{\Delta} \text{BaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ ;  
Alkali metal nitrates give only  $\text{O}_2$  on heating below  $500^\circ\text{C}$  according to following reaction,  
 $\text{MNO}_3 \rightarrow \text{MNO}_2 + \frac{1}{2}\text{O}_2$
17. (a)  $\text{CaCO}_3 \xrightarrow[X]{\text{X}} \text{CaO} + \text{CO}_2$ ,  $\text{CaO} + \text{H}_2\text{O} \xrightarrow[Y]{\text{Y}} \text{Ca}(\text{OH})_2$ ,  
 $\text{Ca}(\text{OH})_2 + 2\text{CO}_2 \xrightarrow[Z]{\text{Z}} \text{Ca}(\text{HCO}_3)_2$ ,  
 $\text{Ca}(\text{HCO}_3)_2 \xrightarrow[X]{\text{X}} \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$
18. (d) The solubility of most salt's decreases with increase atomic weight. But trend is reversed with the fluorides and hydroxides.  
 $\text{BeF}_2, \text{Be}(\text{OH})_2 \quad \left| \begin{array}{l} \text{Mg}(\text{OH})_2 \\ \text{Ca}(\text{OH})_2 \\ \text{Sr}(\text{OH})_2 \\ \text{Ba}(\text{OH})_2 \end{array} \right. \quad \left| \begin{array}{l} \text{K}_{\text{sp}} \downarrow \\ \text{decrease} \end{array} \right. \quad \text{BaF}_2$
19. (a) It gives a deposit of a carbonate with  $\text{CO}_2$  of atmosphere, which can jam the tap.  
(b)  $\text{LiF}$  has very large lattice energy because of the small size of both the  $\text{Li}^+$  and  $\text{F}^-$  ions. Thus its lattice energy exceeds the hydration energy and so in water it is insoluble.  
(c)  $\text{Be}^{2+}$  on account of vacant p-orbital and it high polarising power form complex with water as ligands.  
 $\text{BeCl}_2 + 4\text{H}_2\text{O} \rightleftharpoons [\text{Be}(\text{H}_2\text{O})_4]^{2+} + 2\text{Cl}^-$
20. (b)  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
21. (b) Sodium has one electron in valence shell. This requires less energy to remove the valence electron and forms  $\text{Na}^+$  ion and attains the stable electronic configuration of Ne with a completed octet. The removal of the second electron will break this stable electronic configuration and requires high energy.
22. (b) Alkali metals are very reactive so its found in combined state.
23. (d) Na – alkali metal  
Alkali metals oxide are basic in nature.
24. (b) Potassium form superoxide ( $\text{KO}_2$ ) when its reacts with oxygen.
25. (c) Castner-Kellner cell method use brine solution for manufacturing of  $\text{NaOH}$ . In this process  $\text{Cl}_2$  evolved at anode and hydrolysis of  $\text{Na}-\text{Hg}$  gives  $\text{H}_2$  gas.
26. (b) Caustic soda ( $\text{NaOH}$ ) is deliquescent because its absorb moisture.
27. (d) It is not used for baking of bread.
28. (d) Sodium bicarbonate,  $(\text{NaHCO}_3)$ .
29. (d) Potassium ions participate in the oxidation of glucose to produce ATP; helps in activation of many enzymes and used in synthesis of proteins.
30. (b)  $\text{Na}^+$  present outside the cell and  $\text{K}^+$  present in the cell.
31. (c) Fact based
32. (b) Due to high lattice energy, sulphates and carbonates of alkaline earth metals are insoluble in water.
33. (d)  $\text{NaCl}, \text{NH}_3$  and  $\text{CO}_2$  are used in manufacturing of sodium carbonate.
34. (c) For the  $\text{BeSO}_4$ ; Hydration enthalpy is higher than lattice enthalpy.



35. (c) Due to presence of  $\text{OH}^-$  ions, solution of  $\text{K}_2\text{O}$  is basic in nature.
36. (b)  $\text{Ba}(\text{NO}_3)_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + 2\text{Na}(\text{NO}_3)_2$
37. (d) In case of alkaline earth metals, down the group Hydration enthalpy decreases with increase in ion size. So,  $\text{Ba}(\text{NO}_3)_2$  undergoes minimum hydrolysis
38. (b)  $\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}$   
Quick lime Calcium carbide
39. (b) Potassium does not react with nitrogen directly,  
 $\text{Li} + \text{N}_2 \rightarrow \text{Li}_3\text{N}$   
 $\text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$   
 $\text{Ca} + \text{N}_2 \rightarrow \text{Ca}_3\text{N}_2$
40. (c) Down the group ionization potential decreases.
41. (b)  $2\text{NaNO}_2 + 6\text{Na} \rightarrow 4\text{Na}_2\text{O} + \text{N}_2$
42. (b)  $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{NaOH}$   
(A)  $\text{Na}_2\text{O} \xrightarrow[0^\circ\text{C}]{400^\circ\text{C}} \text{Na}_2\text{O}_2 \xrightarrow{\text{H}_2\text{O}} \text{NaOH} + \text{O}_2$   
(B)
43. (b) Due to High hydration in case of  $\text{AgF}$  and  $\text{BeF}_2$  they are soluble in water.  $\text{CaF}_2$  and  $\text{MgF}_2$  are insoluble in water.
44. (b) The loosely bound electron starts oscillating and goes to higher energy level when light falls on its surface. On returning back to lower level it emits light and metal have a lustrous surface.
45. (b) In solid  $\text{KHCO}_3$ ,  $\text{HCO}_3^-$  exists as dimer and it involves H-Bonding
46. (c) Due to lower melting point and high electropositive character of Na, it reacts with water more vigorously.
47. (d) Due to overvoltage for  $\text{H}_2$  in case of Hg electrode, Na is formed at cathode.
48. (b)  $I_3 >> I_2$ , hence it has 2 valence electrons so metal is Be.
49. (a)  $4\text{KO}_2 + 2\text{CO}_2 \rightarrow 2\text{K}_2\text{CO}_3 + 3\text{O}_2$
50. (b) Sulphates and chlorides of calcium and Magnesium results in hardness of water.
51. (a) Water helps in developing interlocking needle-like crystals of hydrated silicates.
52. (a) Calcined gypsum  $\rightarrow \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$   
Dolomite  $\rightarrow \text{CaMg}(\text{CO}_3)_2$   
Marble and Seashells contains  $\text{CaCO}_3$ .
53. (b)  $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$   
+1 -2 -2 +1 +2  
Oxide ion donates a pair of electron to form  $\text{OH}^-$  ion.
54. (c) -5.1 ev  
 $\text{Na}^+ + \text{e}^- \rightarrow \text{Na} (-5.1 \text{ev})$
55. (b) Magnesium prevents rusting or corrosion by providing cathodic protection.

56. (d) In case of alkali metals down the group electropositive character increases and reactivity increases.  
In case of Halogen, electronegativity decreases down the group thus reactivity decreases.
57. (c) But-2-yne does not have any acidic hydrogen.  
 $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}_3$
58. (c)  $2\text{BeCl}_2 + \text{LiAlH}_4 \rightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$

### Exercise-3 (JEE Advanced Level)

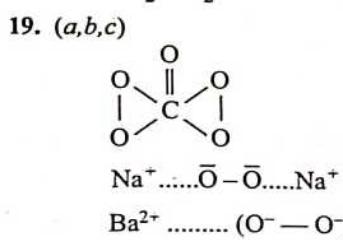
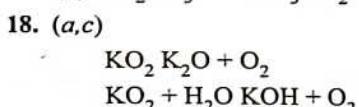
1. (b) When light falls on the surface of sodium, the free electron starts oscillating at its mean position and gets excited to higher levels. On returning back to lower levels, it emits light in all directions. Due to this sodium has a characteristic metallic lustre.
2. (d) Alkali metals have low ionisation energy.
3. (a) S1 :  $\text{Li}^+$  being smaller has high polarising power and  $\text{I}^-$  being larger has high polarisability. So it is most covalent among alkali metal halides according to Fajan's rule.  
S2 : The  $\text{IE}_1$  of potassium atom is less than sodium atom.  
S3 : The presence of transition metals like iron and other impurities catalyses the decomposition of deep blue solution forming amide and liberating  $\text{H}_2$ .  
S4 : Two opposing tendencies exist. With greater charge and smaller size of cation, lattice energy increases which tends to increase the melting point; while increase in covalent character causes a decrease in melting point. Hence, no unique generalised trend may be stated for melting points.
4. (b) The reaction of alkali metals with water becomes increasingly violent on descending the group on account of their decreasing ionisation energies with increasing atomic size. So, the order of reactivity is:  
 $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ .
5. (c) Reacts with water being more basic than water.
6. (c) Isoelectronic species have same number of electrons.
7. (b) All alkali metal hydrides are ionic in nature and react with water according to the reaction ;  
 $\text{NaH} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2$ .
8. (a) True statement. The  $\text{CsI}$ , because of bigger cation ( $\text{Cs}^+$ ) and bigger anion ( $\text{I}^-$ ), has smaller hydration enthalpy. As a result, it does not exceed its lattice energy; so  $\text{CsI}$  is insoluble in water.
9. (d)  
(a) Lithium shows exceptional behavior in reaction directly with nitrogen of air to form the nitride,  $\text{Li}_3\text{N}$ .

liberating  $\text{CO}_2$  gas. So it has the lowest thermal stability.

- (c) The solubility of the alkali metal hydroxides increases down the group from Li to Cs. This is because of the fact that down the group with increasing size of cation, the lattice energy as well as hydration energy also decreases but the change in lattice energy is more as compare to that of hydration energy.
10. (a) The reaction Follows as:  

$$2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow 2\text{NH}_3 + \text{H}_2\text{O} + \text{CaCl}_2$$
11. (b) Anhydrous sodium carbonate is stable to heat and does not decompose.
12. (a)  $\text{NaNO}_3$  is not used as gun powder because it is hygroscopic in nature and becomes wet by absorbing water molecules from the atmosphere.
13. (d) Fact based
14. (a) Dehydration is the process of removal of water from any substance.
15. (c) Alkali metals showing +1 oxidation state.
16. (c) In Down's method for the extraction of sodium, the melting point of the electrolyte is lowered by adding both calcium chloride and potassium fluoride.
17. (a,b,d)

- (a) The solubility of the alkali metal carbonates increases down the group from Li to Cs. This is because of the fact that down the group with increasing size of cation the lattice energy as well as hydration energy also decrease but the change in lattice energy is more as compare to that of hydration energy. Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.
- (b)  $\text{K}_2\text{CO}_3$  can not be prepared by Solvay process because intermediate formed,  $\text{KHCO}_3$  is appreciably soluble in water.
- (c)  $\text{Li}_2\text{CO}_3$  and  $\text{MgCO}_3$  both are not thermally stable.
- (d)  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  is a mineral called trona.



20. (a,d) Sodium when dissolved in liquid ammonia produces solvated electron which imparts blue colour to the sol.
21. (a,b,c)

- (a) The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the

stabilisation of large anions by larger cation through lattice energy effects.

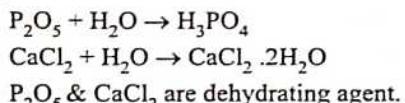
- (b) Bigger cation stabilises bigger anion and similarly smaller cation stabilises smaller anion through lattice energy effects.
- (c) The low solubility of  $\text{LiF}$  is due to its high lattice energy whereas low solubility of  $\text{CsI}$  is due to smaller hydration energy .
- (d)  $\text{NaOH}$  is deliquescent in nature. So,  $\text{NaOH}$  absorbs moisture.

22. (a,b,c)

- (A)  $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \xrightarrow{\Delta} \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$   
(B)  $4\text{S} + 6\text{NaOH} \xrightarrow{\Delta} \text{Na}_2\text{S}_2\text{O}_6 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O}$   
(C)  $3\text{Cl}_2 + 6\text{NaOH} \xrightarrow{\Delta} 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$   
(D)  $2\text{B} + 6\text{NaOH} \xrightarrow{\Delta} 2\text{Na}_3\text{BO}_3 + 3\text{H}_2$

23. (a,b,d)

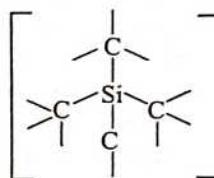
24. (a,c)



25. (c,d) For solubility

Hydration energy should be greater than lattice energy.

26. (a,b,d)



27. (a,b,c,d) Fact Based.

28. (a,b,c,d) Both become passive on reaction with  $\text{HNO}_3$  due to formation of oxide layer, their chlorides are lewis acids chlorides exist in polymeric form and hydroxides are soluble in alkali as well as in acid.

29. (b,c)  $\text{NaOH}$ ,  $\text{NaH}_2\text{PO}_4$  and  $\text{NaHCO}_3$  can not exist together in the solution as they react with each other.

30. (a,b) The solubility of a compound depends on the co-relation between lattice enthalpy and hydration enthalpy if the hydration enthalpy is equal to or greater than the lattice enthalpy then the salt is water-soluble.

31. (b,c) Alkaline earth metal sulphate gives metal oxide and  $\text{SO}_3$  on heating  

$$\text{MgSO}_4 \rightarrow \text{MgO} + \text{SO}_3$$
  

$$\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$$
  
Alkali Metal sulphates are thermally stable.

32. (a,d) Fact based

33. (a,b) Sodium nitrate decomposes to the nitrite on heating  

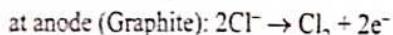
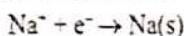
$$2\text{NaNO}_3 \text{ (heat)} \rightarrow 2\text{NaNO}_2 + \text{O}_2$$

Sodium forms an ionic hydride NaH, it is a crystalline soft metal.

Sodium carbonate is thermally stable so it doesn't decomposes on heating.

34. (a,b,d) As  $K_2CO_3$  is thermally stable so apart from this all gives  $CO_2$  gas.

35. (b,d) At cathode (iron vessel):



By electrolysis aqueous solution of  $NaCl$ , hydrogen gas produces.

Sodium is a strong reducing agent Na dissolves in liquid ammonia to give blue solution.

36. (a,b,d) Ionic mobility in aqueous solution increases from Li to Cs thermal stability of carbonate salt also increases. Reactivity towards water increases from Li to Cs.

37. (a,c,d) Milk of lime :  $Ca(OH)_2$  line water is a saturated solution of  $Ca(OH)_2$  (aq).

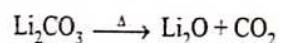
$MgO$  : it is quite stable and fuses at 2800 K hence it is used as a refractory material for lining electric furnaces. The oxides of alkaline earth metals are less basic than those alkali metals.

38. (a,b,c) The alkali metals from ionic hydrides

Alkali metals have  $ns^1$  configuration so they have low potential energy and are highly electropositive metals. Due to this configuration they do not occur in free state in nature and have high affinity towards non metals and form ionic compounds. Also due to higher radius they have low density so they are soft and can be cut with knife.

39. (a,c,d) Hydration depends upon the size of cation, lower the size higher the hydration So Cs ion have low hydration due to large size. Among the alkali metals Li, Na, K and Rb, lithium has the highest melting point due to the smaller size.

- 40 (d) As Lithium is less basic than other alkali metals so lithium carbonate decomposes into its oxide on heating unlike other elements.



Also  $LiCl$  is covalent in nature so it doesn't provide any ions in molten state and its molten state is non-conductive & due to this nature it dissolves in either. Also Li form  $Li_3N$  but none other element from group I forms a nitride.

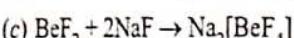
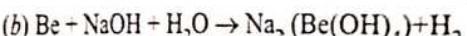
41. (a,c,d) Metal hydroxides with a highly-charged central metal atom forms amphoteric in addition to aluminium, metal such as zinc, tin, lead, and beryllium also forms amphoteric oxides the two elements have same electronegativity and their charge radius ratios.

42. (a,b) Moving down the group radius increases thermal stability of carbonates increases.

Hydration energy is proportional to  $(1/\text{cation size})^{1/3}$  decreases.

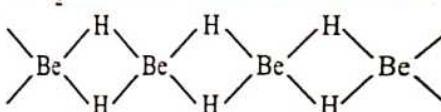
43. (a,c,d)

44. (a,b,d) (a) we know stability of carbonates increases down the group. So,  $BeCO_3$  is most unstable of all the carbonates of 2nd group and kept in the atmosphere of  $CO_2$ .



45. (a,b,d) Mg does not react with  $NaOH$  so it can not be used to generate hydrogen gas. All other reagent gives  $H_2$  gas.

46. (a,b,c,d) As we move down the group, polarization power of cation decreases so  $CaH_2$ ,  $SrH_2$  and  $BaH_2$  are ionic and beryllium and magnesium hydrides are covalent.  $BeH_2$  contains three centre two-electron bond.



47. (b)  $2CH_3COCH_3 + 6CaCOCl_2 \rightarrow 2CHCl_3 + (CH_3COO)_2Ca + 2Ca(OH)_2$  the product obtained when bleaching powder + 3  $CaCl_2$  is distilled with acetone is  $CHCl_3$  or chloroform.

48. (d) Bleaching powder -  $CaOCl_2 \cdot 2H_2O$



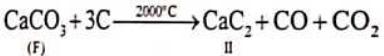
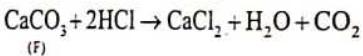
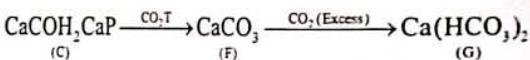
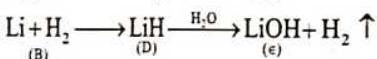
145g  $\rightarrow$  71

$$\% \text{ of available chlorine} = \frac{71}{145} \times 100 = 48.9\% = 49\%$$

49. (b) On long standing, bleaching powder undergoes auto-oxidation which results in the formation of calcium chloride and calcium chlorate



50. (b)  $Ca(S) \xrightarrow[\substack{(A) \\ (B)}]{H_2O} H_2(g) + Ca(OH)_2(aq)$



51. (c) It is  $CaHCO_3$ , which can not be obtained in solid state and causes temporary hardness.

52. (c) Fact Based.

53. (a) Fact Based.

54. (c) Fact Based.

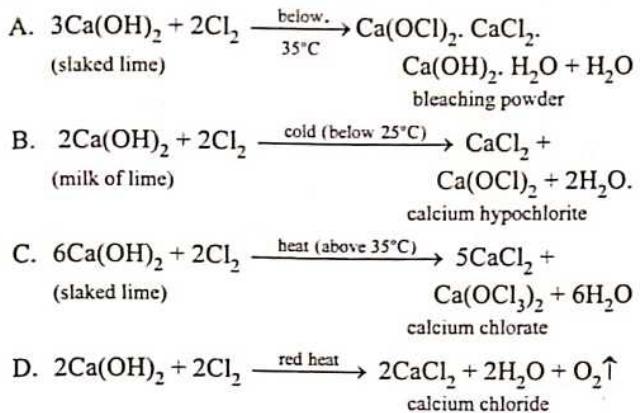
55. (a) A  $\rightarrow$  r,s; B  $\rightarrow$  r; C  $\rightarrow$  p,q,r,s; D  $\rightarrow$  q

- A. Solvay process is used for the manufacture of  $NaHCO_3$  and  $Na_2CO_3$ ; the raw material is  $NaCl$ .



- B.  $2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{CO}_2 \uparrow + \text{H}_2\text{O} \uparrow$ .
- C.  $\text{Na}_2\text{O} + \text{H}_2\text{O} \longrightarrow 2\text{NaOH}$ ; NaOH being basic turns red litmus blue.
- $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$ ; NaOH being basic turns red litmus blue but  $\text{H}_2\text{O}_2$  being oxidising agent bleaches coloured litmus.
- $\text{NaHCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{H}_2\text{CO}_3$ ; solution is alkaline and turns red litmus blue.
- $\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{NaOH} + \text{H}_2\text{CO}_3$ ; solution is alkaline and turns red litmus blue.
- D.  $\text{Na}_2\text{O}_2 + \text{CO} \longrightarrow \text{Na}_2\text{CO}_3$ ;  $2\text{Na}_2\text{O}_2 + 2\text{CO} \longrightarrow 2\text{Na}_2\text{CO}_3 + \text{O}_2$ . Hence, it absorbs CO and  $\text{CO}_2$  and liberates oxygen.

56. (c) A  $\rightarrow$  r; B  $\rightarrow$  s; C  $\rightarrow$  q; D  $\rightarrow$  p



57. [6] It is a cyclic structure having six P–O–P linkages.

58. [7] Except Be and Sr all are correctly matched.

59. [3] Except  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  all form polymeric chains.  
 $\text{AlCl}_3$  dimeric chain.

60. [15] x =  $\text{Na}_2\text{PbO}_2$  y =  $\text{Na}_2\text{SnO}_3$  z =  $\text{NaAlO}_2$

61. [10] Glauber's salt is  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

## Exercise-4 (Past Year Questions)

### JEE MAIN

1. (a) Region 2.

Just above the tip of the Primary flame.  
 $1500^\circ\text{C}$  ( $2,700^\circ\text{F}$ )

2. (d)  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}_2$ , and  $\text{KO}_2$ .

3. (a) Both form basic carbonates.

4. (b)  $\text{Al} + \text{NaOH} \rightarrow \text{Al}(\text{OH})_3$  (white ppt.)

$\text{Al}(\text{OH})_3 + \text{OH}^- \rightarrow [\text{Al}(\text{OH})_4]^-$  Solvate

$\text{Al}(\text{OH})_3 \xrightarrow{\text{heat}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$

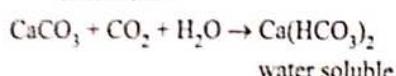
$\text{Al}_2\text{O}_3$  used as an adsorbent in column chromatography

5. (b)  $\text{Rb} + \text{O}_2 \xrightarrow{\text{excess}} \text{RbO}_2$   
superoxide  
X  $\rightarrow$  is  $\text{RbO}_2$   
 $2\text{RbO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{RbOH} + \text{H}_2\text{O}_2 + \text{O}_2$
6. (c) Be Because of its transparency to X ray
7. (d) It give a deep blue solution due to formation of ammoniated  $\text{e}^-$ .
8. (c) Saline hydride. It is an Ionic hydride
9. (d)  $\text{Ba}(\text{NO}_3)_2$   
Due to size of Ba, it doesn't crystallize with water molecule.
10. (b) Li only element in the group that react with dinitrogen to form nitride.
11. (a)  $\text{Be}(\text{OH})_2$ .
12. (d)  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$   
It depends upon ionic Potential  
(Charge/size) I.P.  $\uparrow$  es; H.E.  $\uparrow$  es.
13. (c) Mg O and  $\text{Mg}_3\text{N}_2$ .  
 $\text{Mg} + \text{O}_2 \rightarrow \text{MgO}$   
 $3\text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$
14. (c)  $\text{BeX}_2$  {Be has smallest size}
15. (a) K, 2S feels more attraction from nucleus so It has less energy.
16. (d)  $2\text{LiNO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + 2\text{NO}_2 \text{ (g)} + \frac{1}{2}\text{O}_2 \text{ (g)}$
17. (b)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{393\text{ K}} \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
18. (a) Mg and  $\text{Mg}_3\text{N}_2$   
 $3\text{Mg} + \text{N}_2 \xrightarrow{\Delta} \text{Mg}_3\text{N}_2$  (B)  
 $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$   
(B)  
 $\text{NH}_3 + \text{CuSO}_4 \rightarrow [\text{Cu}(\text{NH}_3)_4] \text{ SO}_4$  (Blue complex)
19. (d) A, C and D only.
20. (a) Li and Mg  
 $6\text{Li(s)} + \text{N}_2\text{(g)} \xrightarrow{\Delta} 2\text{Li}_3\text{N(s)}$   
 $3\text{Li(s)} + \text{N}_2\text{(g)} \xrightarrow{\Delta} \text{Mg}_3\text{N(s)}$
21. (b) (i), (ii) and (iv)
22. (d)  $\text{Be}(\text{OH})_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2\text{O}$   
Be is highly soluble in water.
23. (b) A  $\rightarrow$  q; B  $\rightarrow$  s; C  $\rightarrow$  p; D  $\rightarrow$  r
24. (d) The solubility of 2nd group element depends on their hydration energy which decreases down the group.  
So, the solubility also decreases down the group  
Be and Mg are 2<sup>nd</sup> and 3<sup>rd</sup> group elements hence the solubility of their sulphate is high.

25. (a) Both A and R are correct but R is not the correct explanation of A.

26. (d)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaSO}_4$  and  $\text{CaSO}_4 \frac{1}{2} \text{H}_2\text{O}$   
No. of  $\text{H}_2\text{O}$     2        0        and    0.5

27. (b)  $\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 \downarrow$   
slaked lime



28. (d) A  $\rightarrow$  t; B  $\rightarrow$  r; C  $\rightarrow$  q; D  $\rightarrow$  p

29. (a) Baking soda, sodium bicarbonate. It contains Sodium, Oxygen, Hydrogen and Carbon.

30. (a) A  $\rightarrow$  p; B  $\rightarrow$  q; C  $\rightarrow$  r; D  $\rightarrow$  s

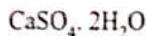
31. (a) Li < K < Na < Rb < Cs.

K is lighter due to unusual tension atomic size of K.

32. (a) Mg

Li  $\xrightarrow{\text{diagonal relationship}}$  Mg.

33. (b) Portland cement contains gypsum



### JEE ADVANCED

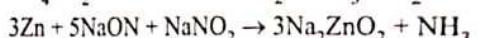
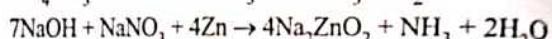
34. (a)  $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$

When  $\text{CO}_2$  dissolved in water in water It gives  $\text{H}_2\text{CO}_3$ .  
On ionisation give  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ion.

35. (a)  $\text{MgSO}_4 + \text{Na}_2\text{HPO}_4 + \text{NH}_4\text{OH} \rightarrow \text{Mg}(\text{NH}_4)\text{PO}_4$   
 $+ \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$

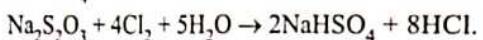
36. (b) Blue colour is due to ammoniated  $\text{e}^-$ .

37. (a,b)

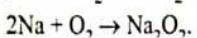


38. (b)  $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3$   
So O.S. of P in  $\text{P}_4$ ,  $\text{NaH}_2\text{PO}_2$  and  $\text{PH}_3$  is 0, +1, -3,

39. (b)  $\text{NaHSO}_4$



40. (a,b)  $4\text{Na} + \text{O}_2 \rightarrow 2\text{Na}_2\text{O}$



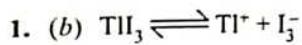
41. (b)  $2\text{K}\text{O}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{KOH(aq)} + \text{H}_2\text{O}_2(\text{aq}) + \text{O}_2(\text{g})$

## CHAPTER

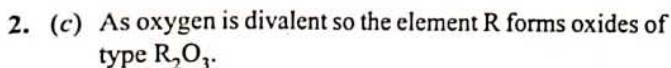
# 11

# The p-Block Elements-I

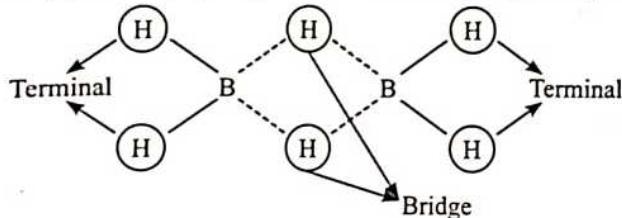
## Exercise-1 (Topicwise)



Tl is in +1 oxidation state because of inert pair effect  
(b) is correct.

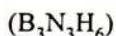


3. (b) 2 bridge hydrogens and 4 terminal hydrogen are present



A mixture of boric acid with ethyl alcohol burns with green edged flame due to the formation of ethyl borate.

5. (a) Borazine



6. (c) Large sized chlorine atom do not fit in between the small boron atom whereas small sized hydrogen atom get fitted in between boron atoms. So  $BCl_3$  does not exist as dimer but  $BH_3$  as dimer ( $B_2H_6$ ).

7. (a) Electron deficient molecules.



9. (c) Al is called self-protecting metal because when it comes in contact with the atmosphere it is covered entirely with a layer of aluminium oxide which stage of further corrosion.

10. (a) Al

11. (b) 1 : 1 : 2

The formula of alum



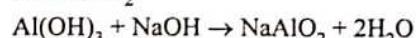
2 → Monovatent cation

2 → Trivatent cation

and 4  $SO_4^{2-}$  ion

True Ratio  $\rightarrow 1 : 1 : 2$

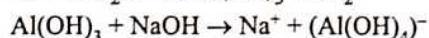
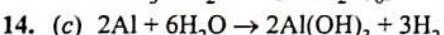
12. (c) Aluminium hydroxide react with excess of NaOH and forms  $AlO_2^-$



So, the  $NaAlO_2$  forms  $AlO_2^-$



$AlCl_3$  is covalent but in water it becomes ionic due to large hydration energy of  $Al^{3+}$



15. (a)  $AlCl_3$  can form dimer and exist as  $Al_2Cl_6$  aluminium have vacant d-orbital which can accomodate electron from chloride atom

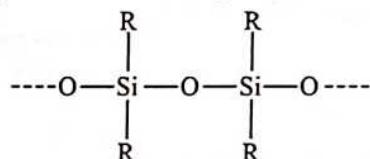
16. (a)  $Ge > Sn > Pb$

17. (b) 12 Pentagons and 20 hexagons.

18. (c)  $CO_2$  is acidic oxide and thus more effectively absorbed by an alkali. SO, cold and solid calcium hydroxide is the best absorbing material for the  $CO_2$ .

19. (a) Calcium phosphide

20. (c) Organic polymers containing silicon in them are called as silicons. Silicons have general formula of  $R_2SiO$ , an empirical formula analogous to Ketone ( $R_2CO$ ).



21. (b) HF

22. (c) Lead pipes are not suitable for drinking worm because lead reacts will water containing air to form  $Pb(OH)_2$  which poisonous for our health.



24. (b) Due to inert pair effect.

25. (c)  $Pb_3O_4$  is a mixed oxide. It can be represented as  $2PbO \cdot PbO_2$

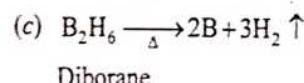
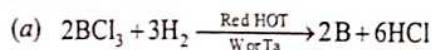
26. (c) When tin is treated with conc. nitric acid, it is converted into-metastannic nitrate ( $H_2SnO_2$ ).  
 $Sn + Conc. HNO_3 \rightarrow NO_2 + H_2SnO_2$
27. (c) White lead is the basic lead carbonate. It is a complex salt containing both carbonate and hydroxide ions. It is also known as hydrate of carassite. It causes lead poisoning.
28. (a) Litharge is one of the natural mineral formed by lead that is lead (II) oxide,  $PbO$ .
29. (a) No lead in pencils Rather, the core is made up of a non-toxic mineral called graphite. Therefore % of lead in lead pencil is zero.
30. (d) Lead (II, IV) oxide, red lead or triplumbic tetroxide, is a bright red or orange crystalline or amorphous solid pigment. Chemically, red lead is  $Pb_3O_4$  or  $2PbO \cdot PbO_2$  it is used in the manufacture of lead glass, rust proof paints and in sindur.



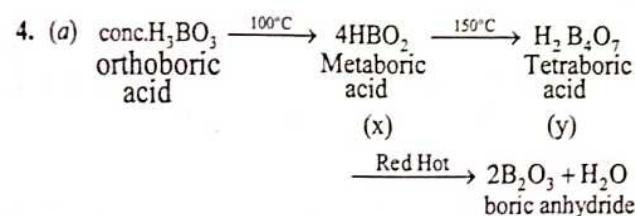
## Exercise-2 (Learning Plus)

1. (b) The reluctance of S-subshell electrons to participate in the chemical bonding.

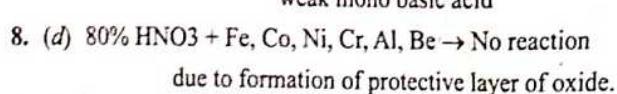
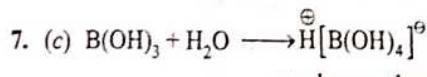
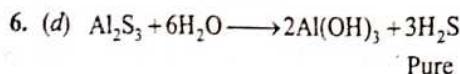
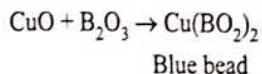
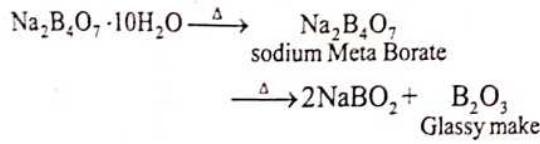
2. (d) All of these



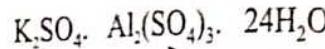
3. (d) Formula of Borax is  $Na_2B_4O_7 \cdot 10H_2O$



5. (d) Borax bead test

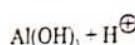
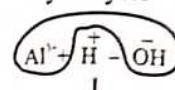


9. (b) Acidic



Strong base cation  
and strong acid anions  
are always soluble in  
water as medium for M  
neutral.

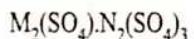
Weak base cation  
hydrolysis



In, aq. medium  
acidic in nature

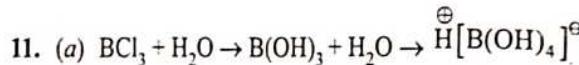
10. (d) Alum's

General formula



IA  $\Rightarrow Na^+, K^+, Rb^+, Cs^+, NH_4^+$  due high P.P.

N  $\Rightarrow (+3)$  O.S. &  $Cr^{3+}, Fe^{3+}, Al^{3+}$



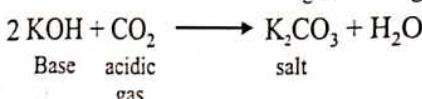
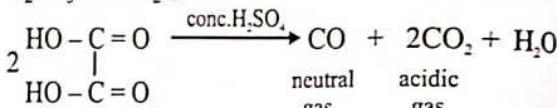
weak acid due to  
presence of  $H^+$

12. (b) Group-14  $\Rightarrow +2$  and  $+4$  (O.S.)

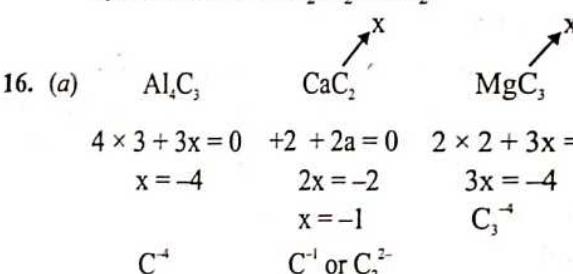
13. (d) Methanides

$Be_2C$  and  $Al_4C_3$  form methanides.

14. (a)  $K_2CO_3$  and  $CO_2(g)$



15. (b) Coal gas is a mixture of  $H_2$ . Saturated and unsaturated hydrocarbons  $CO, CO_2, N_2$  and  $O_2$ .



17. (a)

$\rightarrow$  Interstitial carbides form only silicon metalloids form covalent carbides.

$\rightarrow$  CO and  $CN^-$  both are fatal due to complex formation with Fe (III) present in blood.

$\rightarrow$  SiC is called carborundum

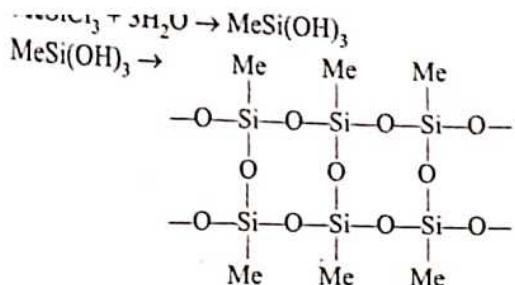
18. (c)  $Sn^{2+} \Rightarrow$  (amphoteric)

19. (c) Due to inability of bromine and iodine to oxidise  $Pb^{2+}$  to  $Pb^{4+}$

20. (d)  $PbI_4$  due to inert pair effect.

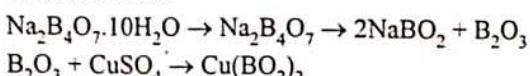






19. (b)  $\text{CH}_3\text{SiCl}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{Si(OH)}_3 + \text{HCl}$   
 (Hydrolysis of  $\text{CH}_3\text{SiCl}_3$ )  
 $\text{CH}_3\text{Si(OH)}_3$  form complex crosslinked polymer  
 $\text{SnCl}_4 + \text{H}_2\text{O} \rightarrow \text{Sn(OH)}_4\text{Cl}_2$

**20. (c) Barox bead test**



21. [6] Four 'H' atoms, two on the left and two on the right, known as terminal hydrogens and two boron atoms lie in the same plane.

Total atoms =  $4 + 2 = 6$

$$\text{Total atoms} = 4 + 2 = 6$$

22. [4] Compound having higher lattice energy than NaBr are:  
LiF, MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>,

23. [3]  $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3 + 3\text{H}_2$   
 1 mol  $\text{B}_2\text{H}_6$  yields 3 moles  $\text{H}_2$  gas.

24. [4]  $C_{60}$  contain 12 five membered ring and 20 six-membered rings. Graphite is diamagnetic in nature and thermodynamically more stable than diamond.  
Coke is the impure form of carbon.

25. [21] B, Al, In, Tl are solid at 40°C while Ga is at 30°C. So,  
 $x = 4$

L.E. B > Al > Ga > In > Tl

y = 4

Al → 4

z = 3

$$x + 2y + 3z = 4 + 2 \times 4 + 3 \times 3 = 21$$

- $$26.[26] C_{60} \text{ contains } 12 \text{ five-membered rings} \Rightarrow a = 12 \\ C_{60} \text{ contains } 20 \text{ six-membered rings} \Rightarrow b = 20 \\ C_{60} \text{ contains } 30 \pi\text{-bonds} \Rightarrow c = 30 \\ 2a - 2b + c = 3 \times 12 - 2 \times 20 + 30 = 26$$

27. [26]  $B_{10}C_2H_{12}$  is isostructural and isoelectronic with borate ion of  $B_{12}H_{12}^{2-}$   
 $x + y + z = 12 + 12 + 2 = 24 + 2 = 26$

28. [7] Amphoteric nature are those nature which react from both acid as well as base.  
 $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{BeO}$  are amphoteric nature.

29. [3]  $Mg + B \rightarrow MgB_2 \xrightarrow{HCl} 3MgCl_2 + B_2H_6$  Diborane  
 $x = 1$   
 $y = 2$   
 $x + y = 1 + 2 = 3$

## **Exercise-4**

19. (d) Electron deficient species are  $\text{BCl}_3$  and  $\text{B}_2\text{H}_6$ .

20. (a) Cs - Photoelectric effect

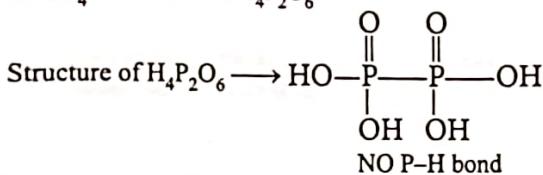
Ga - High temperature thermometer

B - Bullet proof vest

Si - Water repellent sprays.

21. (b) White  $\text{P}_4$  + alkali  $\rightarrow \text{H}_3\text{PO}_2$

Red  $\text{P}_4$  + alkali  $\rightarrow \text{H}_4\text{P}_2\text{O}_6$



22. (b)  $\text{Br}_2 + 5\text{F}_2 \rightarrow 2\text{BrF}_5$   
(Excess)

23. (b)  $\text{P}_4 + 8\text{SOCl}_2 \rightarrow 4\text{PCl}_3 + 4\text{SO}_2 + 2\text{S}_2\text{Cl}_2$   
White Phosphorus

24. (b)  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow{\Delta} \text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{\Delta} 2\text{NaBO}_2 + \text{B}_2\text{O}_3$   
 $\text{B}_2\text{O}_3 + \text{CoO} \rightarrow \text{Co}(\text{BO}_2)_2$  cobalt metaborate  
(Blue bead)

25. (b,d)

When orthoboric acid react 1,2 dihydroxy or polyhydroxy compounds, they form chelate ring which removes  $[\text{B}(\text{OH})_4^-]$  and produces a maximum number of  $\text{H}_3\text{O}^\oplus$  or  $\text{H}^\ominus$

(d)  $\text{H}_3\text{BO}_3$  is weak electrolyte in water as it's  $pK_a$  is 9.25.

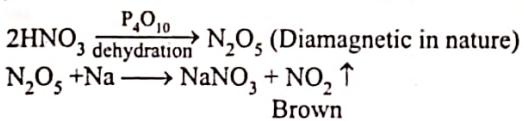
26. [2]  $\text{B}_2\text{H}_6 + 6\text{MeOH} \rightarrow 2\text{B}(\text{OMe})_3 + 6\text{H}_2$   
Hence answer is 2 moles of boron containing product.

27. (b) The hydrolysis of  $(\text{H}_3\text{C})_2\text{SiCl}_2$  produces silane diol which produces linear polymer on condensation. Trimethylchlorosilane can't undergo polymerisation. Hence it is used for chain termination.

28. (a,c,d)

Crystalline  $[\text{B}_4\text{O}_5(\text{OH})_2]^{2-}$  have  $\text{sp}^2$  and  $\text{sp}^3$  hybridised boron atoms it also contains one terminal hydroxide per boron unit.

29. (b,d)



30. (b)  $2\text{KO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2\text{O}_2 + \text{O}_2 \uparrow$

Whereas  $\text{Na}_2\text{O}_2$  and  $\text{Li}_2\text{O}_2$  produces  $\text{H}_2\text{O}_2$  and  $\text{Pb}_3\text{O}_4$  do not react with water.

31. (a,b,c)

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is a reducing agent since  $\text{Sn}^{2+}$  tends to convert  $\text{Sn}^{4+}$ .

(b)  $\text{SnO}_2 + 2\text{KOH} \text{ (aq)} + 2\text{H}_2\text{O} \rightarrow \text{K}_2[\text{Sn}(\text{OH})_6]$   
(Amphoteric)

(c) Filterate of first group contain solution of  $\text{PbCl}_2$  in  $\text{HCl}$  which contains  $\text{Pb}^{2+}$  and  $\text{Cl}^-$   
However in conc.  $\text{HCl}$  it produces  $\text{H}_2[\text{PbCl}_4]$

(d)  $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \rightarrow \text{PbO}_2 \downarrow + 2\text{Pb}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$   
( $2\text{PbO} \cdot \text{PbO}_2$ ) Not a redox reaction

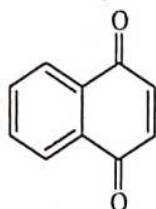
# CHAPTER

# 12

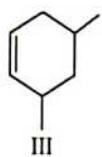
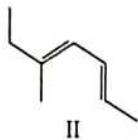
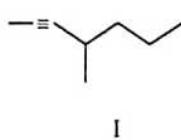
# IUPAC Nomenclature

## Exercise-1 (Topicwise)

1. (c) For molecular formula, we add all atom A of particular elements available in the organic compound and denotes each in subscript.



2. (c) If we see, all the given compounds have molecular formula

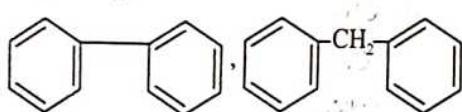


It is clear that I, II, III are not identical structure hence correct option will be (C).

3. (b) is aromatic Hydrocarbon.

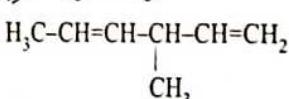
4. (b) is unsaturated Hydrocarbon since contain  $\pi$ -bonds.

5. (a) has only 2° Hydrogen.



6. (c) Fact Based

7. (d) has terminal double bond which the



8. (a)

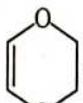


No. of  $\pi$ -bonds = 6

No. of ring = 1

D.O.I = 6 + 1 = 7

9. (c) Fact based.

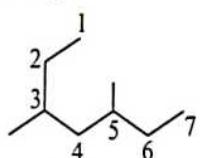


10. (c) has heteroatom in ring hence it is heterocyclic compound.

11. (b) Alkanal has  $C_nH_{2n}O$  general formulae.

12. (c)  $H_3CCH_2CHO$  is third member of homologous series of aldehyde.

13. (b)

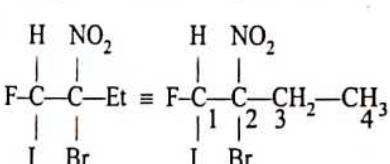


3, 5 Dimethylheptane

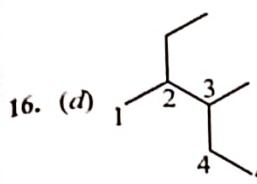
We start numbering of substituent from that end where substituent comes at locast locant.

14. (c) 6- ethyl - 2, 3, 5 trimethyl nonane

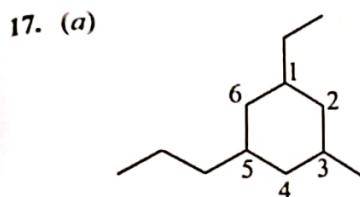
15. (c)



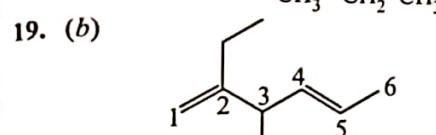
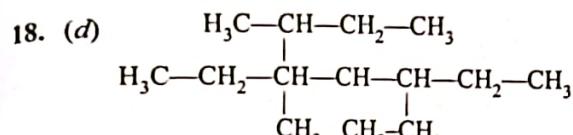
2-Bromo-1-fluoro-1-iodo-2-nitroethane



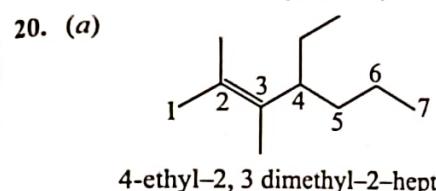
2-ethyl-3-methylpentane.



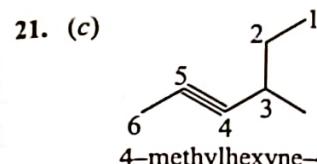
- (i) Followed lowest locant rule.  
(ii) Followed alphabetical order of substituents.



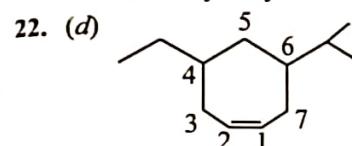
2-ethyl-3-methyl hexa 1, 4 diene



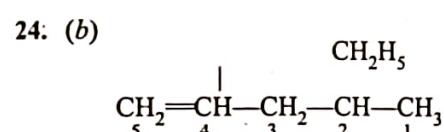
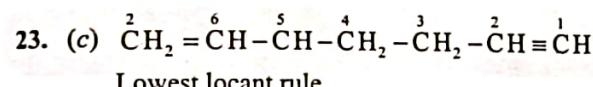
4-ethyl-2, 3 dimethyl-2-heptene



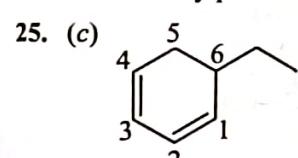
4-methylhexyne-4



4-ethyl-6-(isopropyl) cycloheptene.

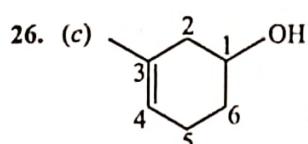


s2-Ethylpent-4-ene

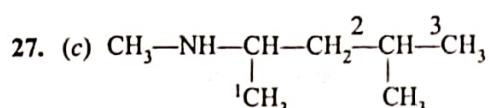


6-Ethenylcyclohexa-1, 3-diene

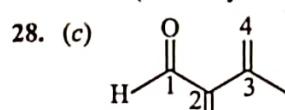
$$\begin{aligned} \text{Mg}^+ \rightarrow \text{Mg}^{+2} + e^- & \quad \text{IP}_1 = 348 \text{ K cal mol}^{-1} \\ \text{Mg} \rightarrow \text{Mg}^{+2} + 2e^- & \quad \text{IP} = \text{IP}_1 + \text{IP}_2 \\ & = 348 + 178 = 526 \text{ K cal} \end{aligned}$$



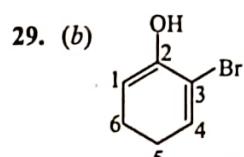
3-methyl cyclohex-3-enol



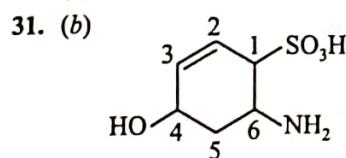
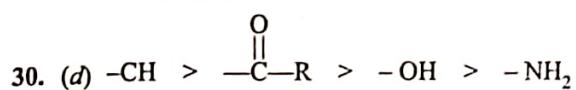
2-(N-methylamino)-3-isopropylpropane



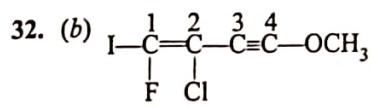
3-Methyl-2-methylidene but-3-enal



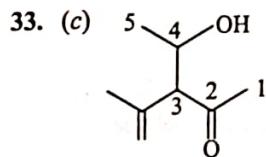
$$2 + 3 = 5$$



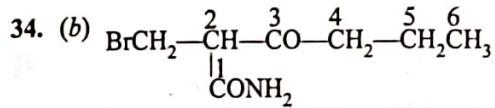
6-Amino-4-hydroxycyclohex-2-ene



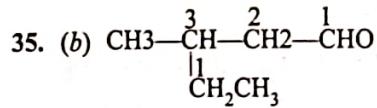
4-methoxy-2-chloro-1-fluoro-1-iodobuten-3-yne



3-(1-Methylethyl)-4-hydroxy pentan-2-one

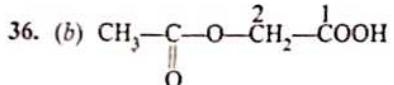


2-(Bromomethyl)-3-oxohexanamide

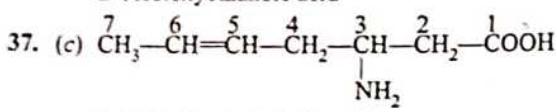


Correct Name: 3-methyl-pentanal

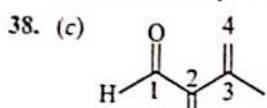
Given Name: 3-ehtyl-butanal in question



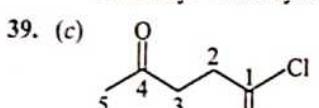
2-Acetoxyethanoic acid



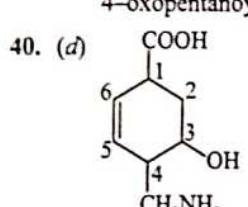
3-Aminohept-5-enoic acid



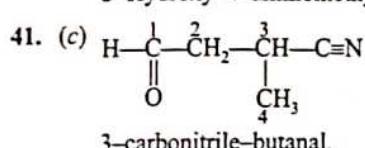
3-Methyl-2-methylenebut-3-enal.



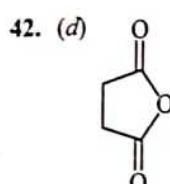
4-oxopentanoyl chloride



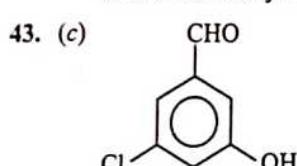
3-Hydroxy-4-aminomethylcyclohex-5-en-1-oic acid



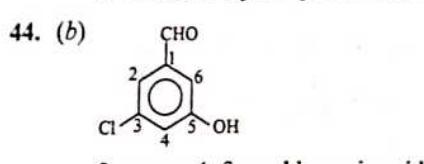
3-carbonitrile-butanal.



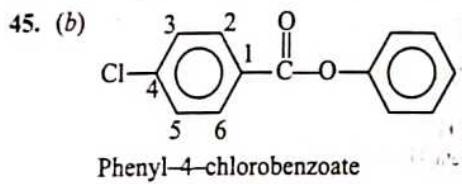
Butanedioic anhydride



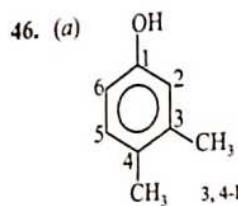
3-chloro-5-hydroxybenzene carbaldehyde



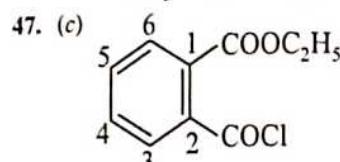
3-cyano-4-formyl benzoic acid



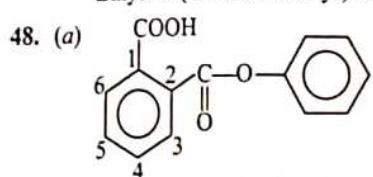
Phenyl-4-chlorobenzoate



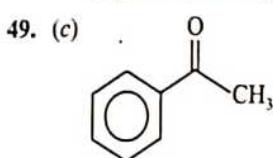
3,4-Dimethylphenol.



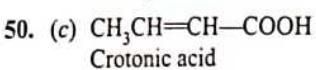
Ethyl-2-(Chlorocarbonyl)benzenecarboxylate.



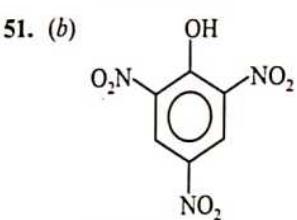
2-phenoxy carbonylbenzenecarboxylic acid.



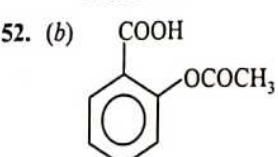
Acetophenone



Crotonic acid



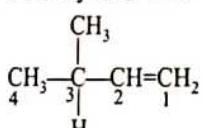
Picric acid



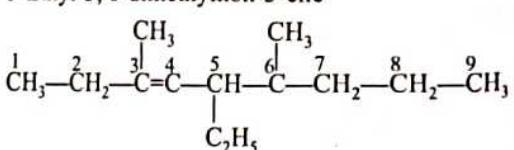
Aspirin

## Exercise-2 (Learning Plus)

1. (c) 3-Methyl-1-butene



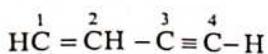
2. (a) 5-Ethyl-3,6-dimethylnon-3-ene



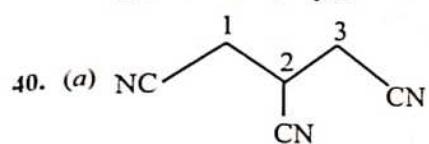




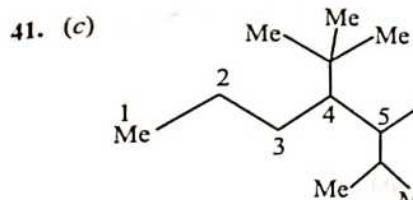
39. (c) Vinylacetylene



But - 1 - en - 3 - yne

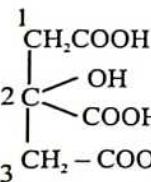


Propane - 1, 2, 3 - tricarbonitrile



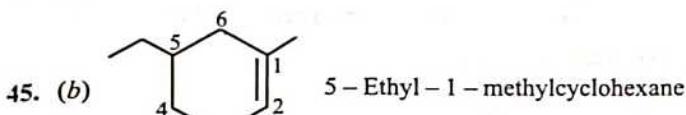
4 - t - Butyl - 5 - isopropyloctane

42. (d) All members have the same physical properties.



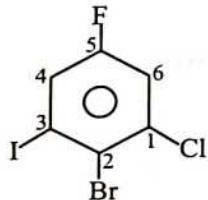
2 - Hydroxypropane - 1, 2, 3 - tricarboxylic acid

44. (c)



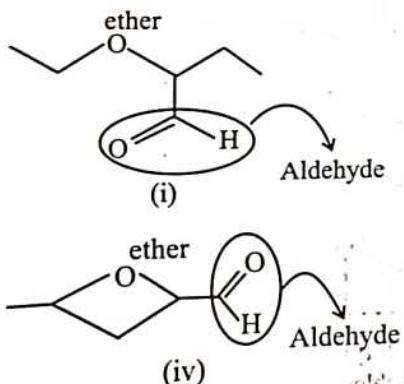
5 - Ethyl - 1 - methylcyclohexane

46. (b)

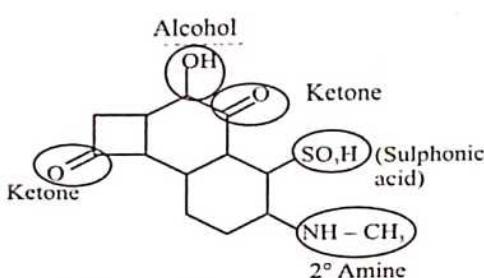


2 - Bromo - 1 - chloro - 5 - fluoro - 3 - iodobenzene

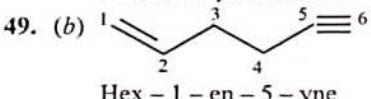
47. (b)



48. (d)

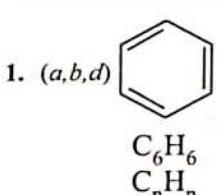


Alcohol is present here.

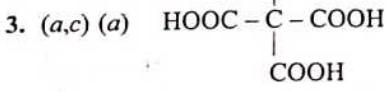
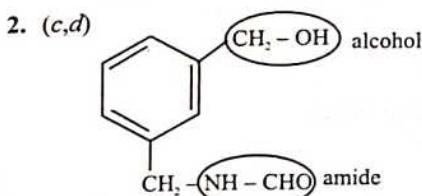
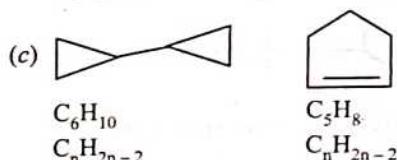
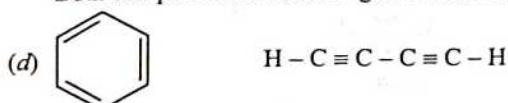


Hex - 1 - en - 5 - yne

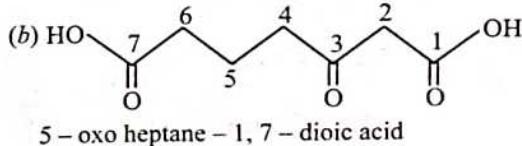
### Exercise-3 (JEE Advanced Level)

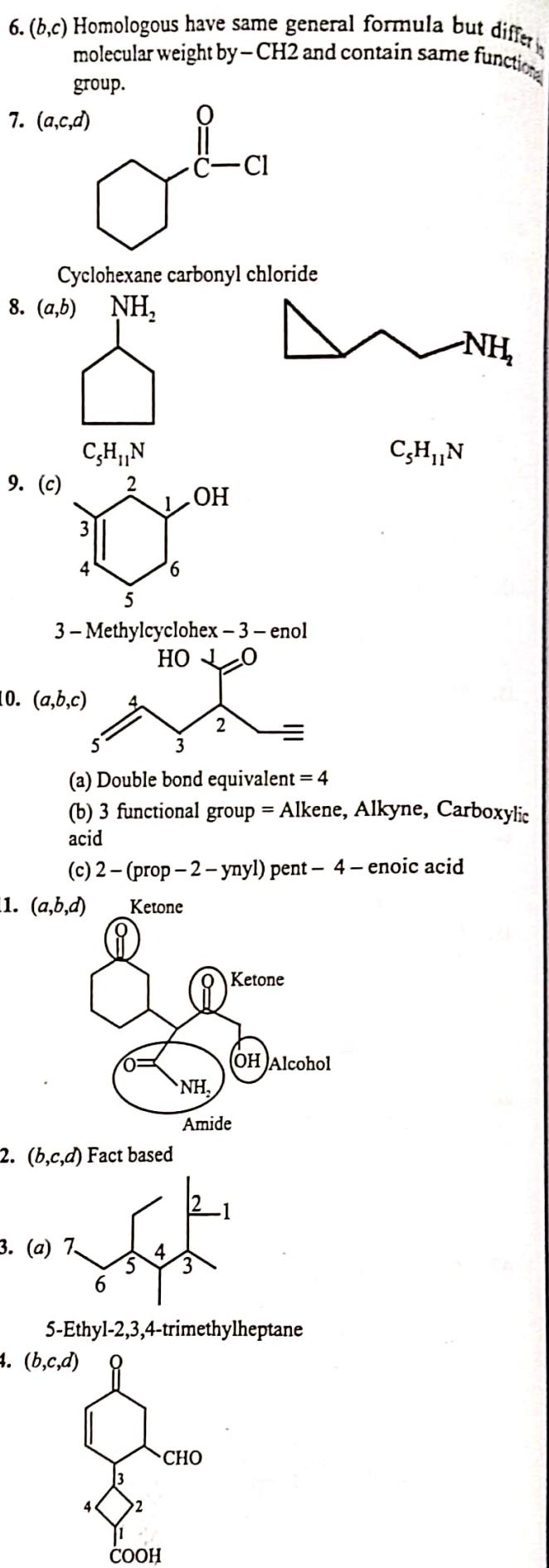
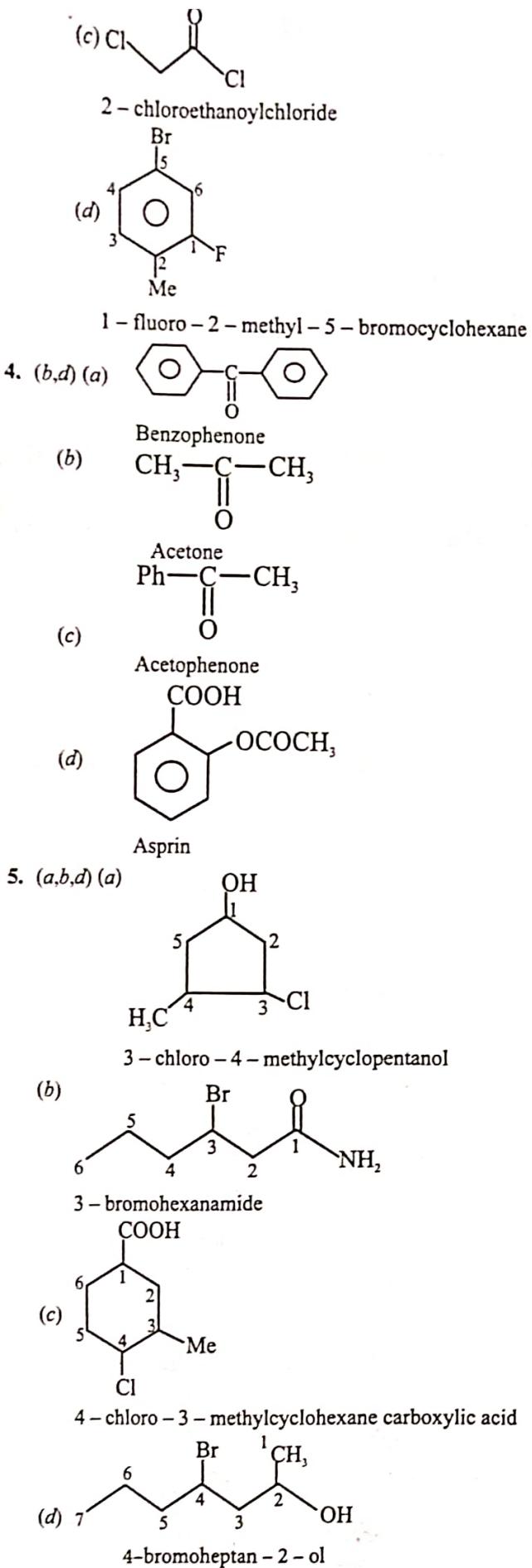


Both compounds have same general formula.



Methane - 1,1,1,1 - tetracarboxylic acid



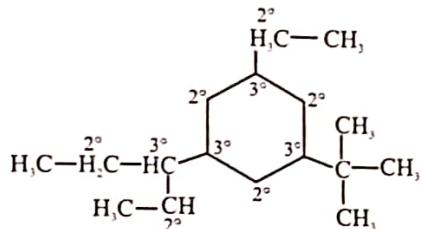


(b) Carbon in parent chain = 4

(c) IUPAC name is 3 - (6 - formyl - 4 - oxocyclohex - 2 - enyl) cyclobutane carboxylic acid

(d) Number of 2° carbon are 6.

Sol. 15 - 17

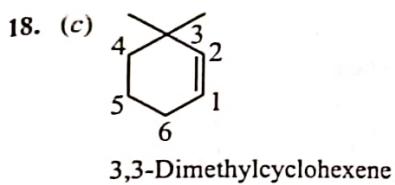


15. (c) 3° hydrogen = 4

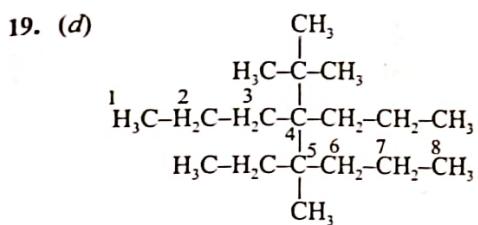
16. (c) 2° hydrogen = 12

17. (c) 3 substituents → Ethyl ; 1-ethylpropyl ; 1, 1 - dimethyl ethyl

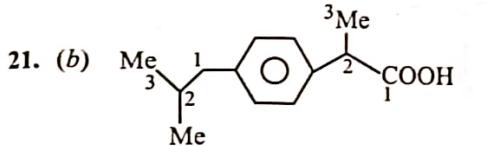
\* 1 - (1, 1-Dimethylethyl) - 3 - ethyl - 5 - (1 - ethylpropyl) cyclohexane



3,3-Dimethylcyclohexene



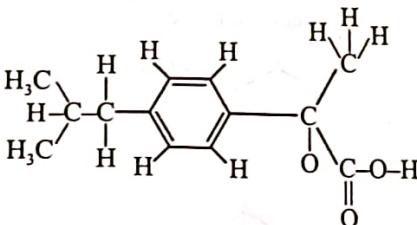
20. (b) -COOH group



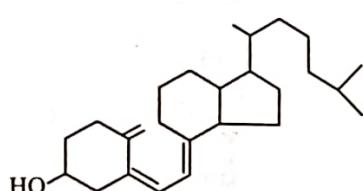
2-(p-Isobutylphenyl)propanoic acid

22. (c) No. of π bonds = 4

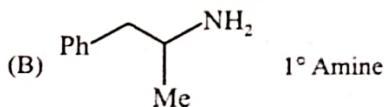
23. (d) No. of σ bonds = 33



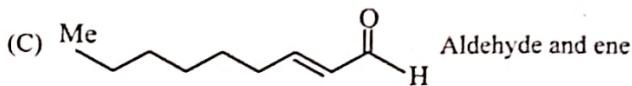
24. (a) (A)



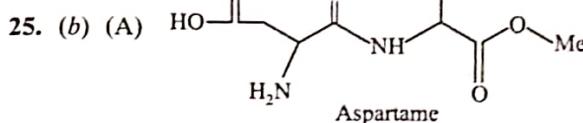
2° Alcohol and Triene



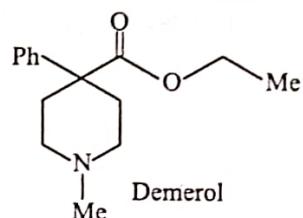
1° Amine



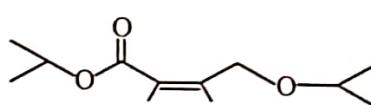
Aldehyde and ene



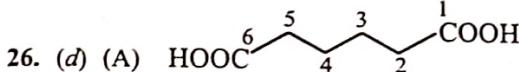
q, r



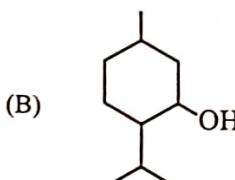
r,s



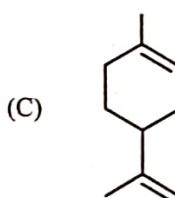
r



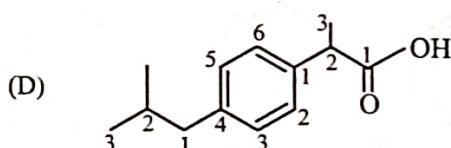
p, s



p, s

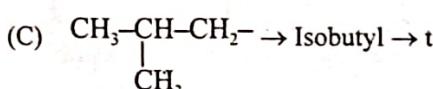
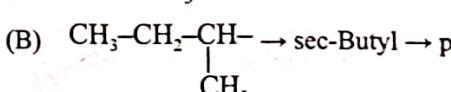
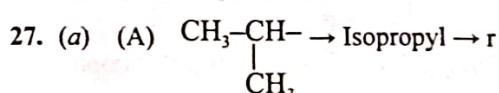


p, s

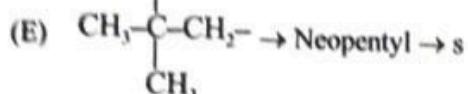
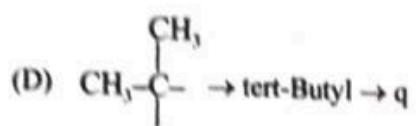


q, r, t

2-[4-(2-methyl propyl)phenyl]  
Propanoic acid



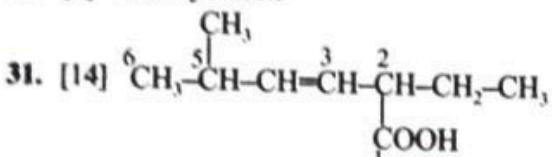
155



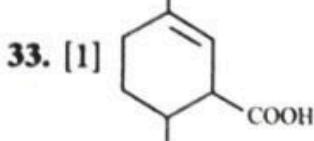
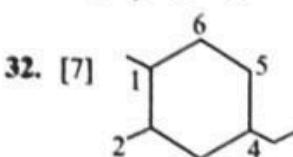
28. (d) Fact based

29. [6] Do it yourself

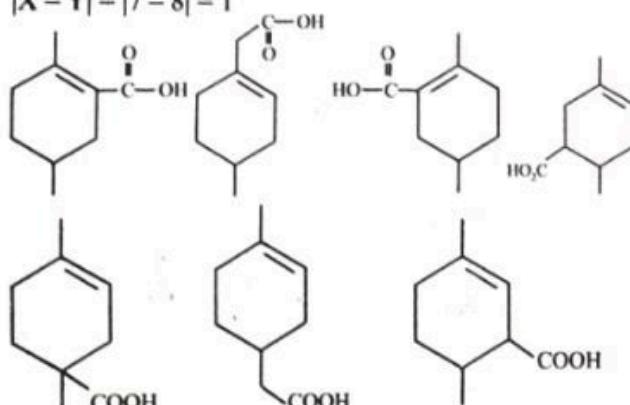
30. [5] Do it yourself



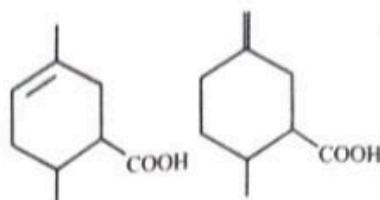
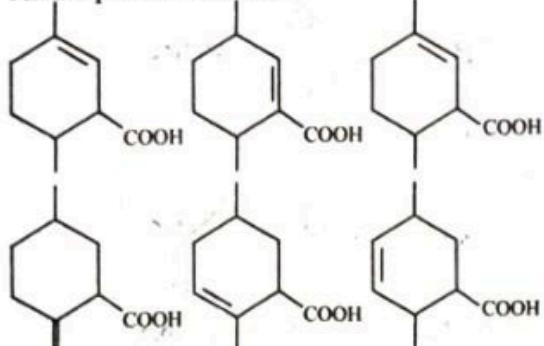
$$\begin{aligned}x &= 6 \\y &= 5 \\z &= 3 \\x + y + z &= 14\end{aligned}$$



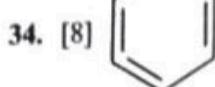
$$\begin{aligned}X &= 7 \\Y &= 8 \\|X - Y| &= |7 - 8| = 1\end{aligned}$$



All are positional isomers



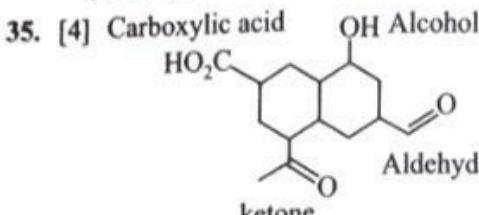
All are positional isomers



$$\sigma = 11$$

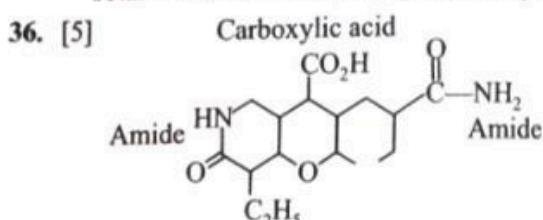
$$\pi = 3$$

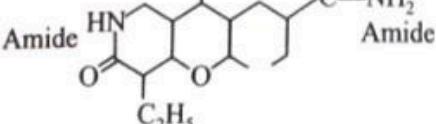
$$\sigma - \pi = 8$$



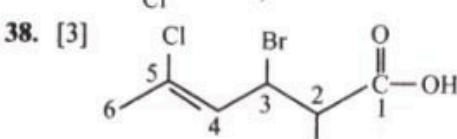
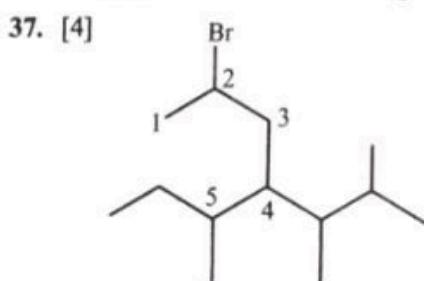
Aldehyde  
ketone

Total 4 different functional groups are present.

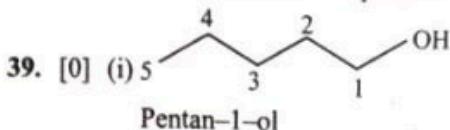


Amide 

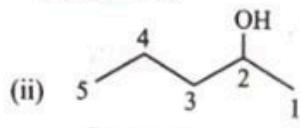
Total 3 different functional groups are present.



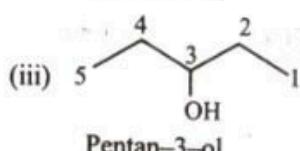
Total 3 substituent are present



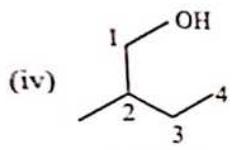
Pentan-1-ol



Pentan-2-ol



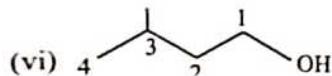
Pentan-3-ol



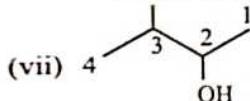
2-Methylbutan-2-ol



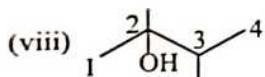
2, 2-Dimethylbutan-1-ol



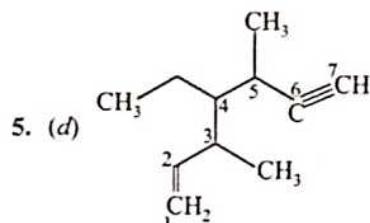
3-Methylbutan-1-ol



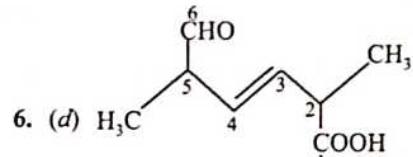
3-Methylbutan-2-ol



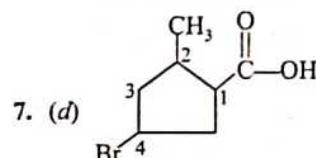
2, 2-Dimethylbutan-2-ol



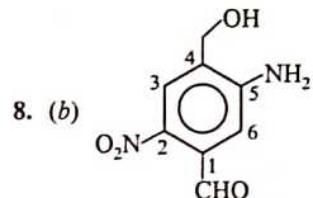
3,5-Dimethyl-4-propylhept-1-en-6-yne



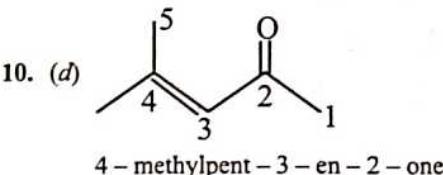
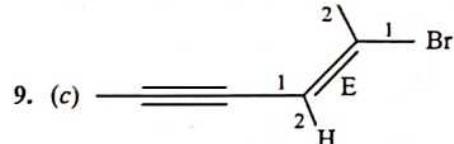
2, 5-Dimethyl-6-oxo-hex-3-enoic acid.



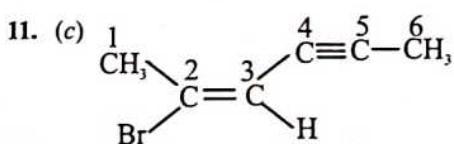
4-Bromo-2-methylcyclopentane carboxylic acid.



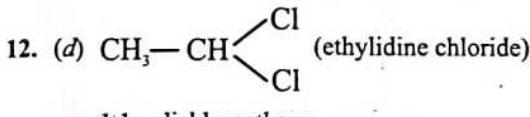
5-Amino - 4 - hydroxymethyl 1 - 2-nitrobenzaldehyde



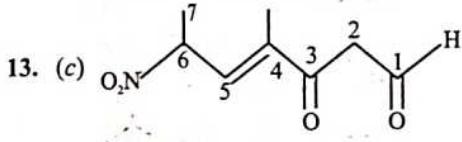
4 - methylpent - 3 - en - 2 - one



(2E)-2-bromo-hex-2-en-4-yne



1,1 - dichloroethane



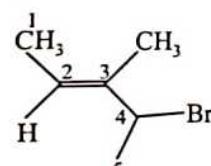
4 - Methyl - 6 - nitro - 3 - oxohept - 4 - enal

## JEE MAIN

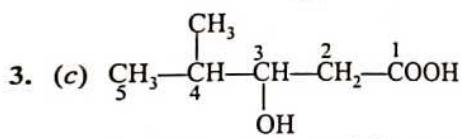
1. (d) Glycerol which decomposes at its boiling point can be purified by distillation under reduced pressure.

At normal pressure, boiling point of glycerol is 563 K, at this temperature it decomposes.

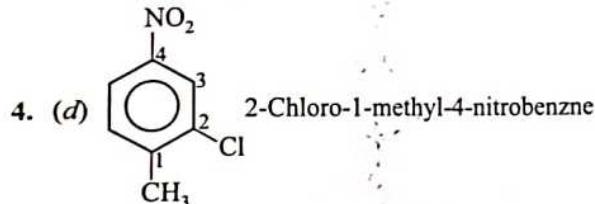
But at reduced pressure of 12 mm Hg, glycerol can be distilled at 453K without decomposition.



4-Bromo-3-methylpent-2-ene

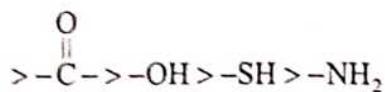
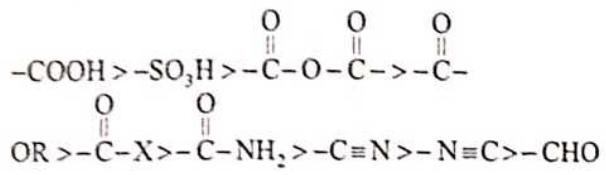


3 - Hydroxy - 4 - methylpentanoic acid

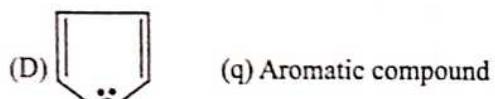
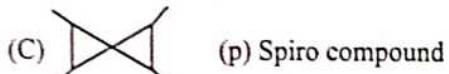
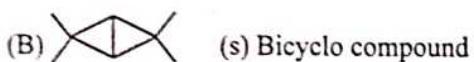


2-Chloro-1-methyl-4-nitrobenzene

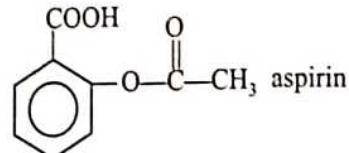
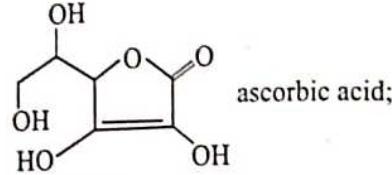
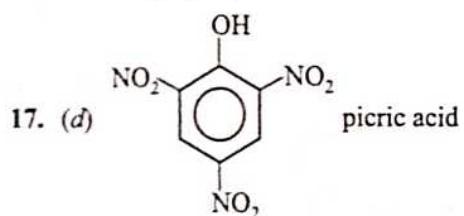
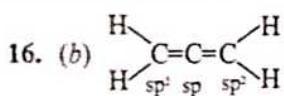
14. (b) Priority order



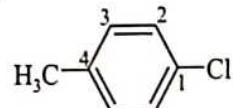
15. (c) (A)  (r) Non planar Heterocyclic compound



### JEE ADVANCED

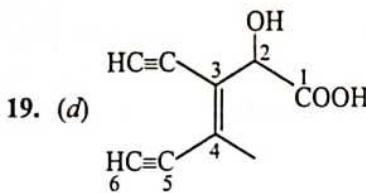


18. (b,c)



1-Chloro-4-methylbenzene

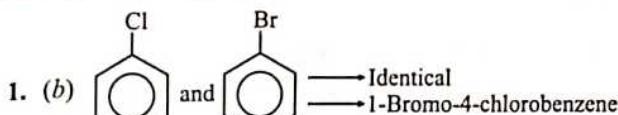
4-Chlorotoluene



3-Ethynyl-2-hydroxy-4-methyl-hex-3-en-5-yonic acid

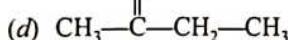


### Exercise-1 (Topicwise)



2. (d)  $\text{CH}_3\text{---CH}_2\text{---O---CH}_2\text{---CH}_3$  (Diethylether)

- (a)  $\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---O---CH}_3$
- (b)  $\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---OH}$
- (c)  $\begin{matrix} \text{CH}_3 \\ | \\ \text{CH}_3\text{---CH---CH}_2\text{---OH} \\ | \\ \text{CH}_3 \end{matrix}$



For isomerism molecular formula must be same.

For isomerism molecular formula must be same.

Molecular formula of diethylether is  $\text{C}_4\text{H}_{10}\text{O}$

Molecular formula of butanon is  $\text{C}_4\text{H}_8\text{O}$

3. (b) For position isomerism

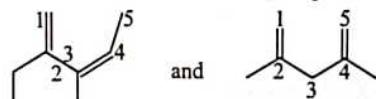
(a) Molecular formula = same

(b) Parent chain = same

(c) Substituent = same

(d) Function group = same

(e) Position of substituent/Function group = different



4. (a) 2-Ethyl-3-methylpenta-1,3-diene 2,4-Dimethylpenta-1,4-diene

IUPAC name = different

Molecular formula = same

Parent chain = same

Substituent are different

Chain Isomers

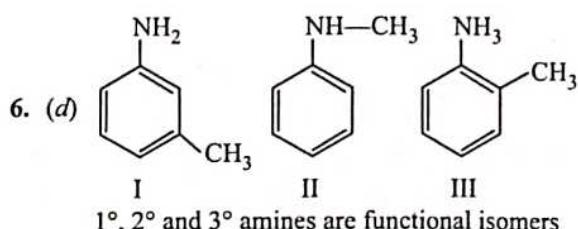
5. (d) Molecular formula = same

Parent chain = same

Substituent/Function group = same

Position of substituent/Function group = different

Position Isomers



7. (b) For chain Isomer

Molecular formula (M.F) = same

PC = different

Substituent = different

Functional group (F.G) = SAME

8. (d) For isomers molecular formula = same

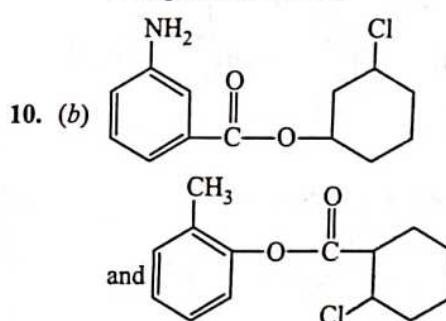
Degree of unsaturation = same

9. (d) For metamer: Molecular formula (M.F) = same

F.G. = same but polyvalent

Alkyl group = different

All option are correct



Molecular formula = same

Functions group = same but polyvalent

Alkyl group = different

Metamers

11. (d) For metamer

Functional group = bivalent or polyvalent.

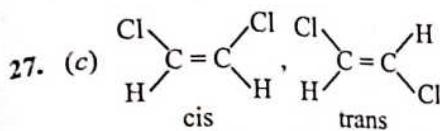
12. (b) Molecular formula = same

Functional group = same but polyvalent

Alkyl group = different

Metamers

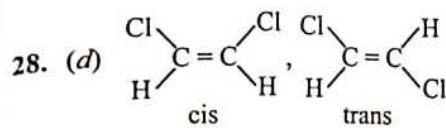




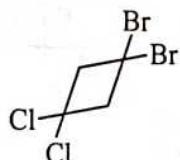
Condition for G.I.

Restriction rotation about double bond

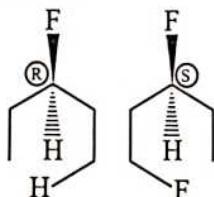
Double bonded C-atom should have different valency.



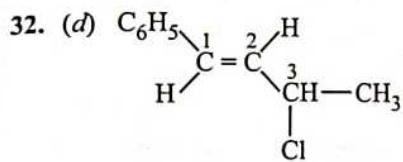
29. (a) Restricted rotation but the groups attached with C-atom is not different no. G.I.



30. (a) Ring structure having double bond less than 8C- atom does not show G.I.



31. (b) Bisubstituted cycloalkane having different position of substituents.

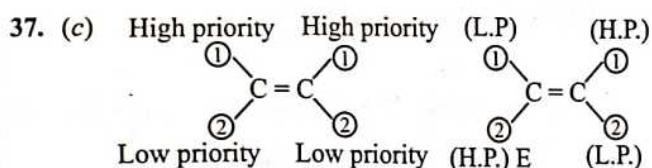


33. (d) Fact based

34. (d) Fact based

35. [2] Fact based

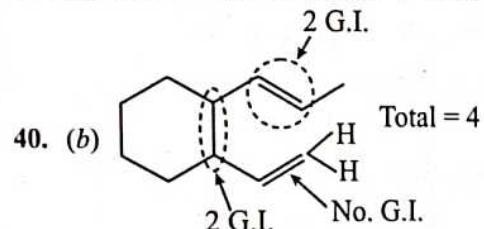
36. (a) Fact based



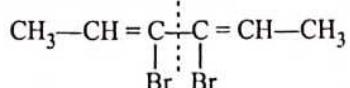
38. (c) Syn → -OH group and bulky group same side.

i.e. -OH and Et group same side.

39. (a) In Z configuration higher priority atoms on same side.

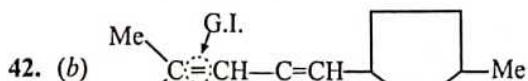


41. (b) For symmetrical molecule



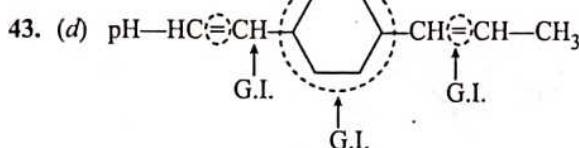
$$\begin{aligned} \text{G.I.} &= 2^{n-1} + 2^{p-1} \\ &= 2^{n-1} + 2^{p-1} \\ &= 2^1 + 2^0 \\ &= 2 + 1 = 3 \end{aligned}$$

$$\left( P = \frac{n}{2} \text{ if } n = \text{even} \right)$$



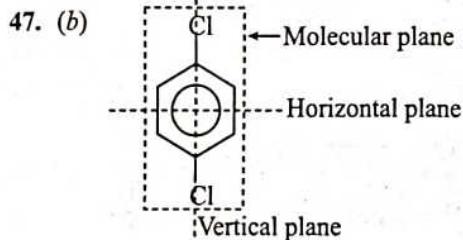
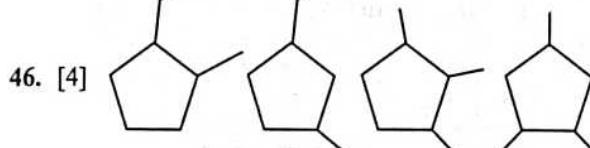
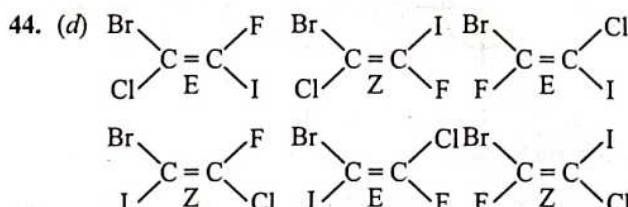
Unsymmetrical molecules

$$\text{No. of G.I.} = 2^n = 2^3 = 8$$



Unsymmetrical molecules

$$\text{No. of G.I.} = 2^n = 2^3 = 8$$

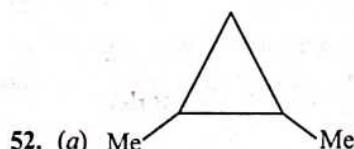
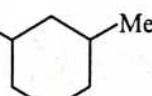


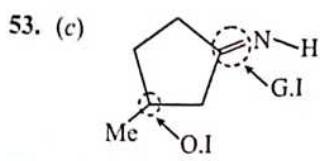
48. (d) Fact based

49. (c) Fact based

50. (a) Correction in Y structure Me

51. (a) Fact based

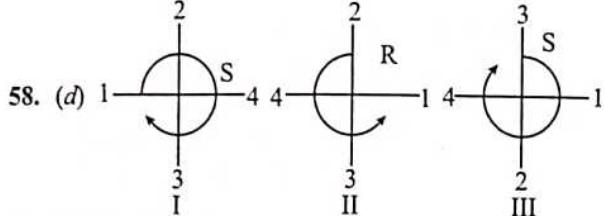
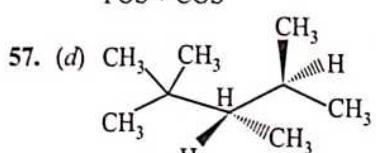
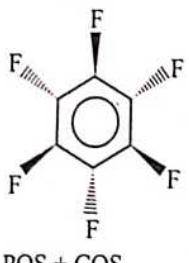




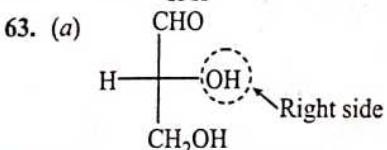
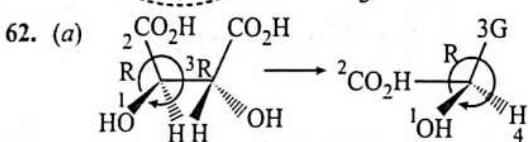
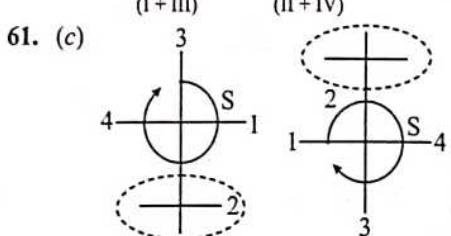
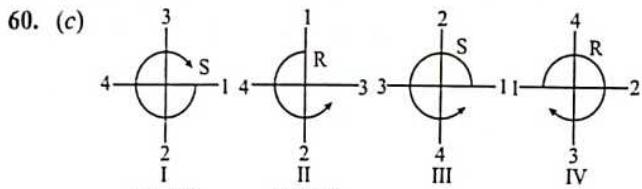
54. (c) Fact based

55. (d) Fact based

56. (c)



59. (d) Fact based



64. (c) Fact based

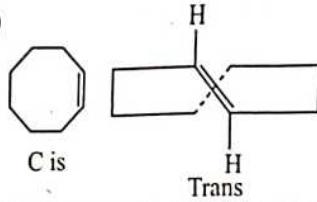
65. (c) Cis and trans Diastereomer

8 members ring containing double bond show G.I.

Less than 8 members ring contain double bond do not show G.I.

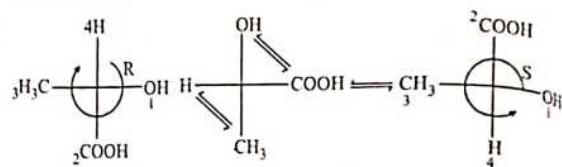
66. (a) Fact based

67. (a,d)

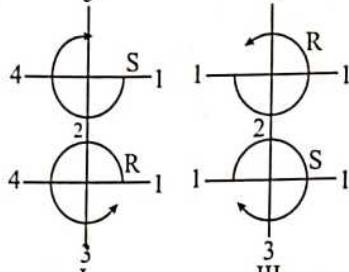


Cis, trans are diastereoisomer/geometrical isomer

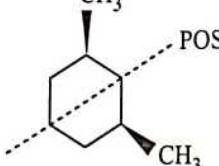
68. (b)



69. (a)



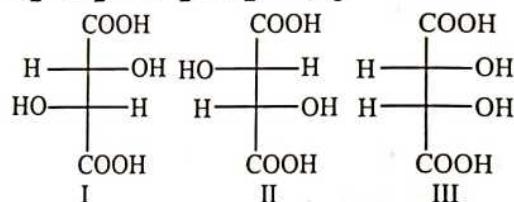
70. (b)



71. (c) Fact based

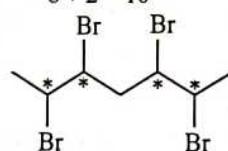
72. (b) Compound having even number of chiral centre with similar ends stereoisomer = O.I. + Meso

$$= 2^{n-1} + 2^{n/2-1} = 2^{2-1} + 2^{2/2-1} = 3$$

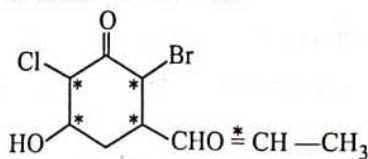


73. (c) Stereoisomer =  $2^{n-1} + 2^{n/2-1} = 2^{4-1} + 2^{4/2-1}$

$$= 2^3 + 2^{2-1} = 8 + 2 = 10$$

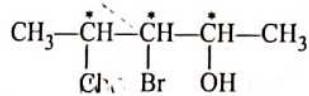


74. (d) Stereoisomer =  $2^n = 2^5 = 32$

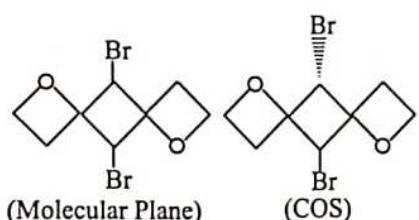
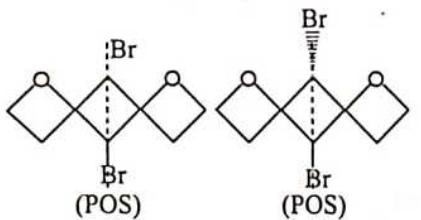


75. (d) Compound having no mirror image

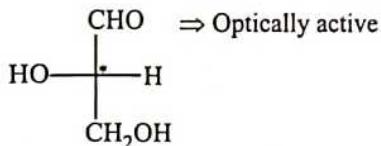
76. (c) Stereoisomer =  $2^n = 2^3 = 8$



77. (a) All isomers are optically inactive



78. (c)  $\begin{array}{c} \text{CHO} \\ | \\ \text{HO}-\text{CH}_2\text{OH} \end{array} \Rightarrow \text{Optically active}$



Unsymmetrical compound =  $2^n$

$n = 3$

Total stereoisomers =  $2^3 = 8$

79. (a) Case of Pseudo chiral centre

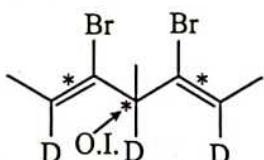
C R T

T R C

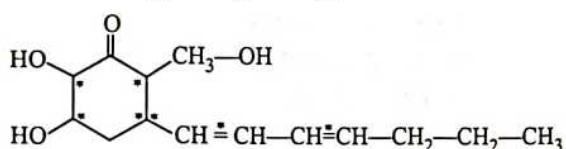
C S T

T S C

$$2^{n-1} = 2^{3-1} = 2^2 = 4$$

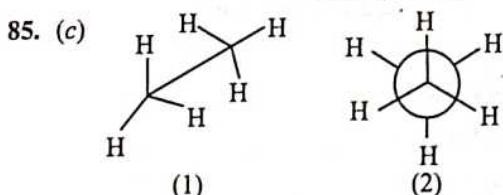
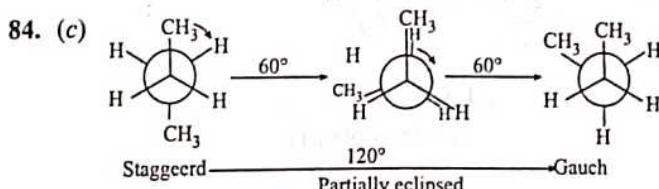
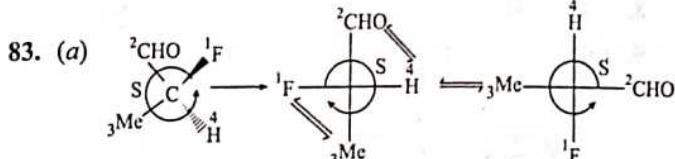
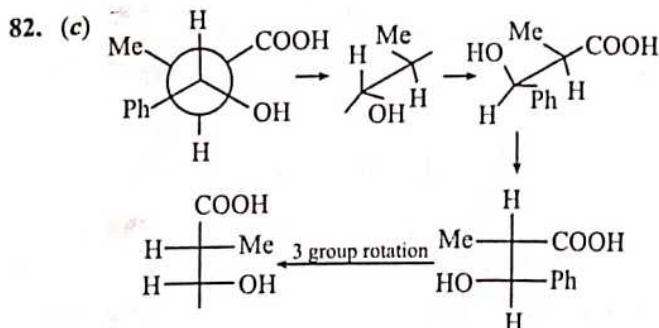
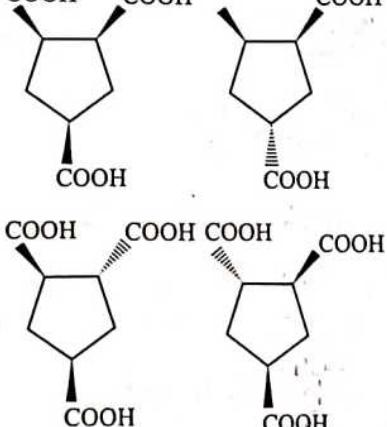


80. (d)



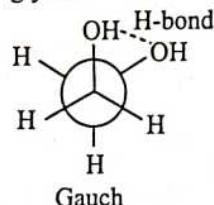
Total Stereoisomer =  $2^n = 2^6 = 64$

81. (c)



Both are staggered conformation of ethane.

86. (c) Due to intra H-bond in Gauch is more stable than anti in ethylene glycol.



87. (a) Conformer

88. (d) Due to intra H-bonding.

89. (d) Flag pole interaction.

90. (d) PE.(Chair) < PE.(Twist boat) < PE(Boat) < PE(Calf Chair)

91. (c) Stability = Chair form > Boat form

Equatorial conformer > Axial conformer.

92. (b) Theory based

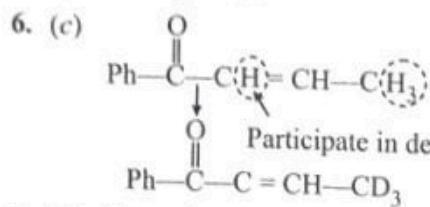
93. (d) Stability equatorial > Axial

## Exercise-2 (Learning Plus)

1. (b) For isomer molecular formula should be same.
2. (c) Theory based
3. (c) Theory based

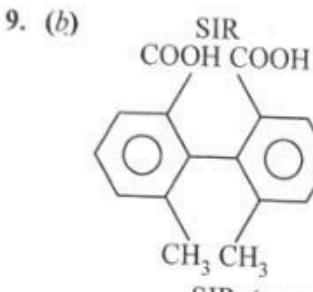


5. (c) Theory based



7. (c) Theory based

8. (c) 2s, 3s

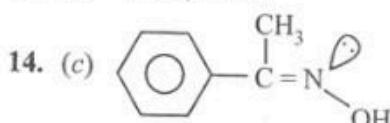


10. (a) Due to SIR molecule is non-planar

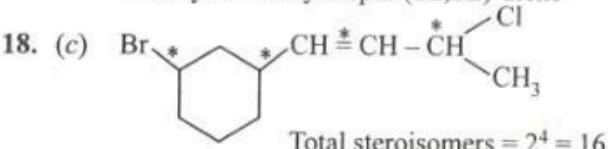
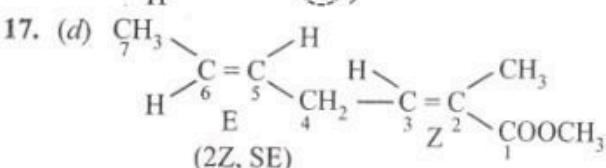
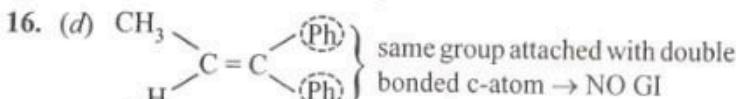
11. (a) Theory based

12. (b) Theory based

13. (d) Theory based



15. (d) Theory based

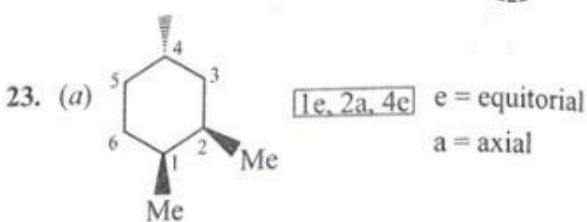
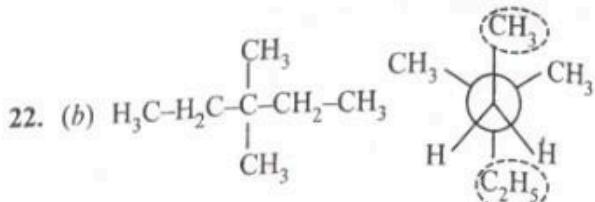
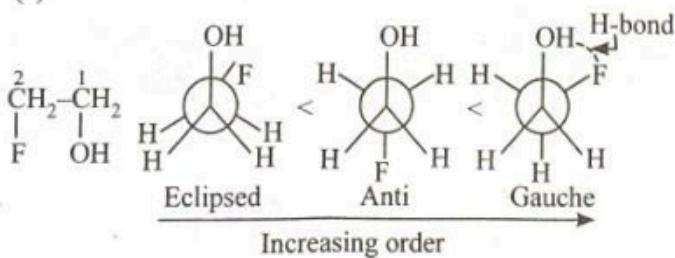


19. (a,b,c) Molecular formula = same

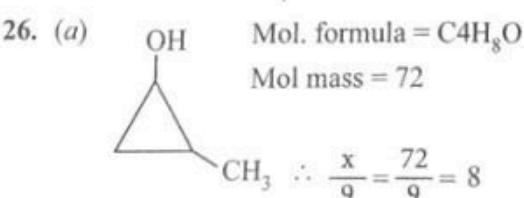
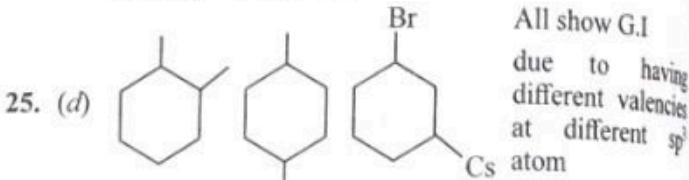
DBE or Du = Same for structural isomers

20. (a) Theory based

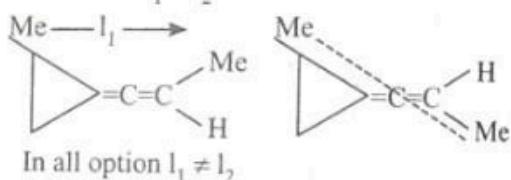
21. (c)



24. (d) Theory based  
Dipole moment = Cis > trans  
B.P = Cis > Trans (d.p-dp interaction moreno cis)  
M.P. = Trans > cis (symmetrical str. of tRNA)  
Stability = trans > cis



27. (a) for G.I  $\rightarrow l_1 \neq l_2$



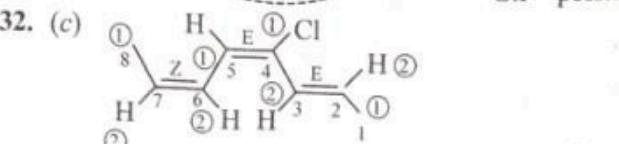
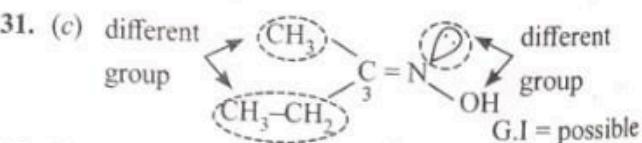
28. (d) Theory based

29. (d) NO G.I  $\rightarrow$  if Total double bond and ring = even

Terminal end = different

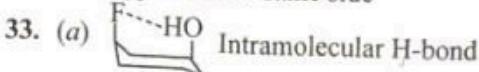
Show G.I  $\rightarrow$  if Total double bond and ring = odd  
Terminal = different

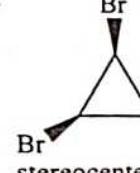
30. (d) I and III = G.I



$\downarrow \quad \downarrow \quad \downarrow$   
H.P H.P H.P

opposite side same side



34. [3] 

35. (c) stereocenter = 10  
stereocentre = CC + GC  
1 GC = 2

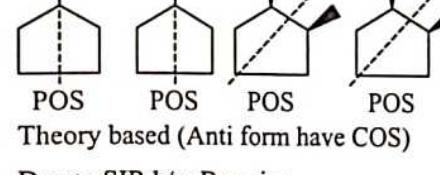
I = 3  
II = 4  
III = 1  
IV = 2

Total = 10

36. (b) Total chiral C-atom = 8

37. (d) Total chiral C-atom = 8

38. (d) Both  $C_3$  + POS

39. (b) 

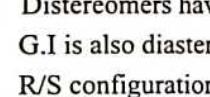
40. (a) Theory based (Anti form have COS)

41. (a) Due to SIR b/w Bromine.

42. (b) All having POS but option 'b' having POS + COS

43. (a) (A) - POS  
(B) - POS, chiral centre, optically in active but will show optical isomer.  
(C) - COS  
(D) -  $C_2$  axis of symmetry

44. (d) 2nd C = 5, 3rd C = R 4th C = S  
(2S, 3R, 4S)

45. (d) 

I and II conformers

46. (b) Distereomers having no mirror image + CC  
G.I is also diastereomers  
R/S configuration  $\rightarrow$  RR + RS } Pass  
(A) 2S, 4R                      SS + RS } Pass  
(a) 2S, 4R } diastereomers of A  
(d) 2R 4S }

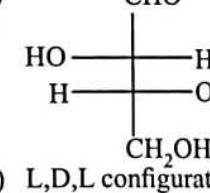
47. (a,b) (A)  $sp, sp^2$       (B)  $C_1$  P-orbital =  $C_4$  P-orbital

48. (c) POS is present = achiral.

49. (c) For meso there should be chiral carbon and POS

50. (a) Compound (II), (V), (IX), (X) are chiral

51. (b) No POS

52. (d) 

53. (b) L,D,L configuration of respective compounds

54. (b)  $2^n = 2^4 = 16$  ( $n$  = chiral centre)

55. (c)  $2^n = 2^3 = 8$  ( $n$  = chiral centre + geometrical centre)

**Exercise-3**  
**(JEE Advanced Level)**

1. (a,c) Fact based
  2. (a,c) Fact based
  3. (a,b) Fact based
  4. (b,c) Different valency at double bonded c-atom
  5. (c) Not show G.I
  6. (a,b,c)  
Fact based
  7. (b,d) Fact based
  8. (a,b,d)  
Fact based
  9. (a,b) Fact based
  10. (a,c,d)  
In option (b) Allene system with  $n = \text{even}$   
 $L_1 = L_2$  not show G.I
  11. (a,b,c,d) Fact based
  12. (b,c,d)  
For R/S configure molecule should have at least 1 chiral centre.
  13. (b,c,d)  
a → conformers  
b → G.I  
c → O.I  
d → O.I
  14. [3] Enantiomers → non superimposable mirror image  
→ different R/S configuration  
(a) S/R  
(b) S/R  
(c) R/S  
(d) R/R  
(e) Non superimposable mirror image  
(f) 2S, 3S/ 2S, 3S  
(g) nos mirror image i.e. diastereomers
  15. [2] (i), (ii), (v) = diastereomers = 3  
(iii) = enantiomers  
(iv) structures isomers having different IUPAC difference = 3 - 1 = 2
  16. (a) A-S, B-P, C-S, D-R
  17. (b,c)  
(iii) no POS, no COS, optical active
  18. [6] (b, c, d, e, f, i) chiral compounds
  19. [32] Total stereoisomers =  $2^n = 2^5 = 32$
  20. (a,d) a = 2, b = 0 c = 3 d = 2 - even

21. (b,c,d)  
Theory based

22. (b, d)  
Theory based

23. (d)  $\alpha_H/\alpha_D$  containing molecules

24. (b) In enol form double bonded c-atom having different valency

25. (a) % enol  $\propto$  aromaticity  
 $\propto$  H-bonding

26. (c) stability  $\rightarrow$  Anti > gauche > Partial eclipsed > eclipsed  
of there is intra H-bond gauche > Anti  
Anti + Intra H-bond  $\rightarrow$  most stable

27. (d) Infinite conformer possible

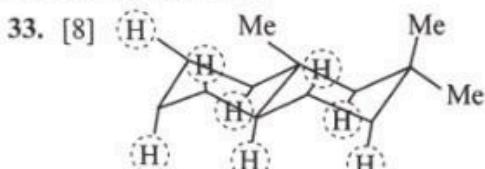
28. (a) Theory based

29. (a) Theory based

30. (d) Theory based

31. (c) A-(p,s); B-(q,s,t); C-(r,s,t); D-(q,s,t)

32. (d) Theory based



34. [0] (i) 2CC (ii) 2CC (iii) no. CC (iv) 2CC  
(v) 2CC (vi) 2CC (vii) 4CC (viii) 4CC  
(ix) 4CC (x) 2CC

35. [2] Theory based

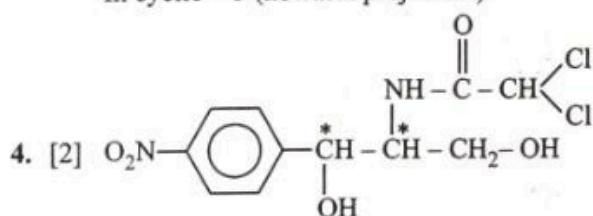
## Exercise-4 (Past Year Questions)

### JEE MAIN

1. (c) Angle between H'-C-C-H" is  $149^\circ$ .

2. (b) Theory based

3. (a) In linear = 4 (Fischer)  
In cyclic = 5 (howarth projection)



5. [3] Structure based

6. [5] C-sp<sup>3</sup> having four different group are chiral carbon.

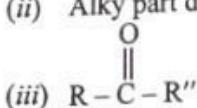
7. (c,d) c  $\rightarrow$  G.I. due to ring  
d  $\rightarrow$  G.I due to double bonded C-atom.

8. (d) Double bonded c-atoms having different valency

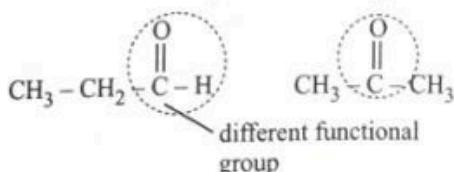
9. (d) meso comp.  $\therefore$  T.S.I =  $2^{n-1} = 2^2 - 1 = 3$   
compounds having chiral center + POS are called me compounds

10. (c) (i) Having no chiral c-atom  
(ii) double bonded c-atom having same valency

11. (d) For metamors  
(i) F.G = same and bivalent or polyvalent  
(ii) Alky part different



12. (d)  $\text{C}_3\text{H}_6\text{ODU} = \frac{2+2\text{c}-\text{H}}{2} = \frac{2+2\times 3-6}{2} = \frac{2+6-6}{2}$



different functional group

[Enol form is not stable so don't consider that structu

13. (c) Theory based

14. (b) Conformers/Rotamer

15. (b) P.E  $\propto \frac{1}{\text{stability}}$

16. (c) Staggered

17. (d) Theory based (i) sp<sup>3</sup> c-atom having different group

18. [7] Fact based

19. [60°]

### JEE ADVANCED

20. (b) Fact Based

21. (a) Fact Based

22. (a, b, c,)

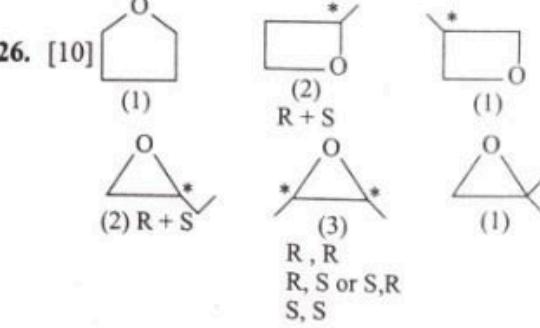
M & N  $\rightarrow$  Diasteromers, M & O  $\rightarrow$  Identical

M & P  $\rightarrow$  Enantiomer, M & Q  $\rightarrow$  Diasteromers

23. (a,c,d)

24. [3]

25. [7] Theory based



Total = 1 + 2 + 1 + 2 + 3 + 1 = 10

27. (c) The conformer having same IUPAC name are identical

28. (b) a & b = meso compound b having intra-molecular H - bond.

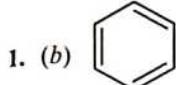
29. [2] Theory based

# CHAPTER

# 14

# General Organic Chemistry

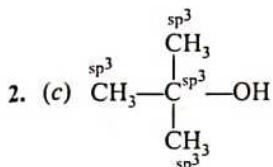
## Exercise-1 (Topicwise)



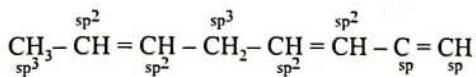
Benzene

Each carbon atom has  $3\sigma$  and  $1\pi$ .

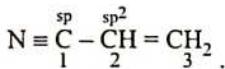
It has  $3\sigma$  bond so  $sp^2$ .

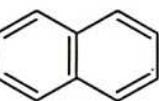


3. (d)



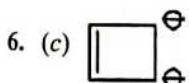
4. (c)  $sp$  and  $sp^2$



5. (c) 

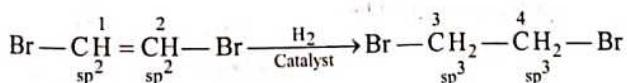
$\pi$  bonds = 5

hence electrons are double.

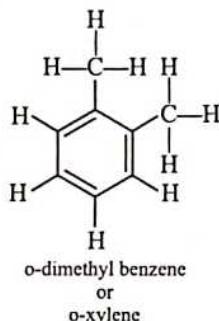


Total  $\pi e^- = 6$

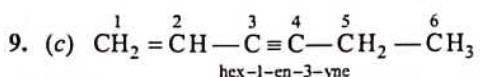
7. (a)



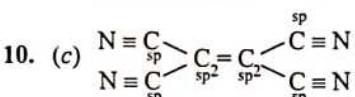
8. (d)



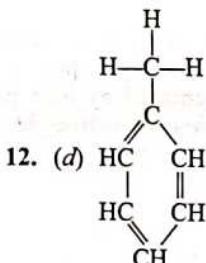
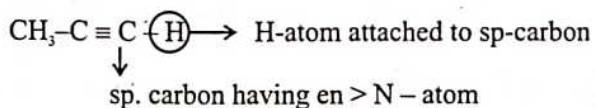
It has  $18\sigma$  bonds and  $3\pi$  bonds.



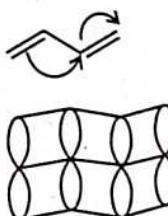
Three  $\pi$  bonds.



11. (c)



13. (b)



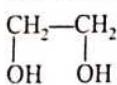
14. (a)  $\text{C}_2\text{H}_5\text{OH}$  (H attached to O atom)



15. (b)  $\text{CH}_3-\text{C}=\text{CH}_2$

9σ, 1π and 2L.P

16. (a) 1,2 - ethandiol

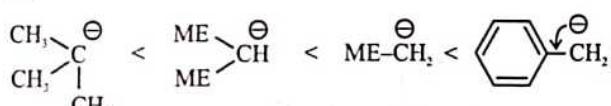


17. (c) Theory based

18. (b) Theory based

19. (c)  $-\text{NR}_2 < -\text{OR} < -\text{F}$

20. (b)



3°C

2°C

1°C

Involve in resonance

21. (a)  $-\text{NH}_3^\oplus > -\text{NO}_2 > -\text{CN}$

22. (b) (a) Has 6α - H

(b) Has 2α - H

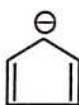
(c) Has 9α - H

(d) Resonance

23. (c)  $-\text{CH}_3 \Rightarrow +\text{I - effect}$

24. (d) Resonance structure of molecule does not have identical bonding.

25. (d)

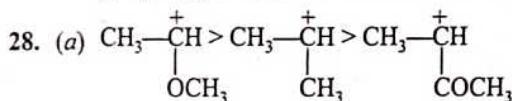


Envolve in resonance so total

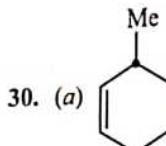
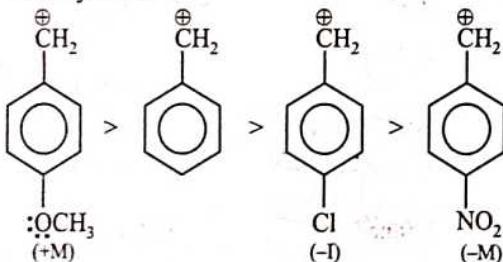
$\pi e^- = 6$  and follow's Huckel's Rule

26. (a) Triphenyl methyl cation has three benzene resonating ring so it is most stable compound.

27. (c) The octet of all atoms are complete in structures (a) and (b). In structure (d) electron deficiency of positively charged carbon is duly compensated by lone pair electrons of adjacent oxygen atom while such neighbour group support is not available in structure (c).

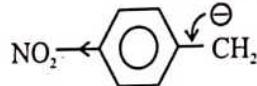


28. (c) Stability order :



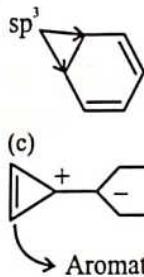
30. (a) (Resonance + hyperconjugation)

31. (d)



32. (c) Aromatic compound follows Huckel's rule of aromaticity  $[4n + 2]\pi e^-$

33. (b)



34. (d) (I)  $\alpha - \text{H} \Rightarrow 9$

(II) Resonance (conjugation)

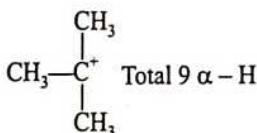
(III)  $\alpha - \text{H} \Rightarrow 2$

(IV) no  $\alpha - \text{H}$



36. (a) Fact Based

37. (b)



38. (b) More α - H

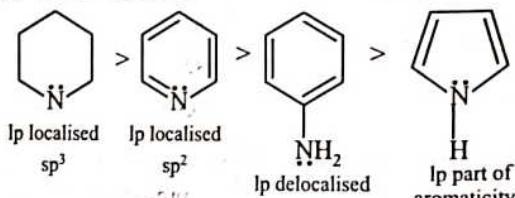
39. (b) Acidity  $x > y > z$  (-I effect of x support y)



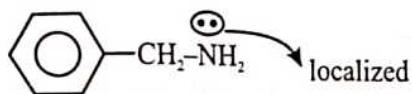
$\text{NO}_2 \Rightarrow -\text{M}, -\text{I effect}$

$\text{NO}_2$  increases the stability of anion.

41. (d) Basic strength :



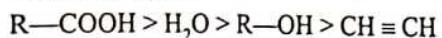
42. (d)



43. (d) Aromatic compound follows  $(4n+2)\pi e^-$  [Huckel's rule]

44. (a)  $e^-$  with drawing group decreasing basic strength

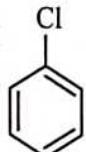
45. (b) Acidic strength :



stable the conjugate base, stronger the acid

46. (b)  $H-\ddot{O}-H$ ,  $:NH_3$ ,  $R-\ddot{O}-R$  — nucleophiles  $SO_3^-$   
has electron deficient centre (a reagent which can accept an electron pair in a reaction, is called an electrophile)

47. (d) upcoming group is decided by  $+M$

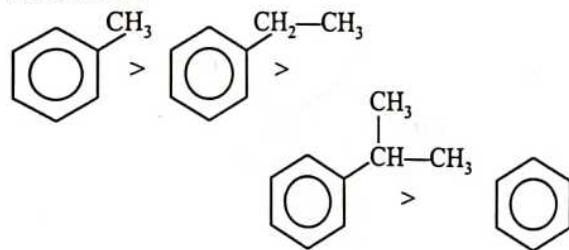


48. (d) When methane gas is treated with chlorine in the presence of sunlight, one hydrogen of methane replaced by the chlorine atom and forms methyl chloride. The mechanism involved in this reaction is free radical mechanism. So it is an example of free radical substitution reaction.

49. (a)  $AlCl_3$  is lewis acid i.e., electron deficient compound. So it is electrophile.

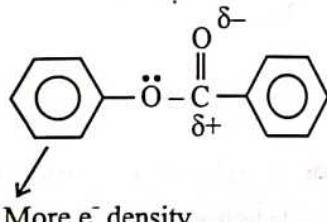
50. (d)  $CH_3-O^-$  is the strongest nucleophile which is capable of acting as donor of electron pair.

51. (b) ESR order :



due to hyper conjugation effect.

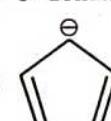
52. (c)



53. (c) Characteristic reaction of aromatic hydrocarbon is ESR.

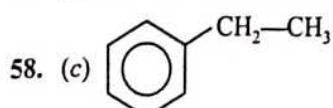
54. (c)  $e^-$  donating group increases ESR

55. (b)  $e^-$  donating group increases ESR



56. (c) 6 $\pi$  electrons are present in compound

57. (d) In benzene all C—C bond lengths are same.



Benzyllic carbon has 2 hydrogen ethyl benzene.

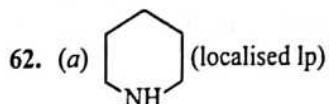
58. (c)  $R-\ddot{N}H_2$

N has 3 $\sigma$  and 1 L.P.

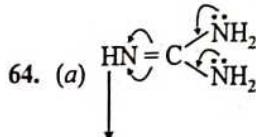
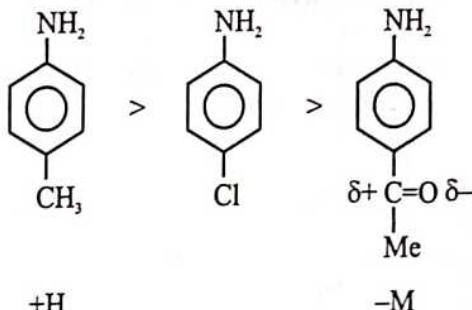
so,  $sp^3$

59. (a)  $e^-$  drawing group decreases basic strength

60. (a) Fact based



61. (a)

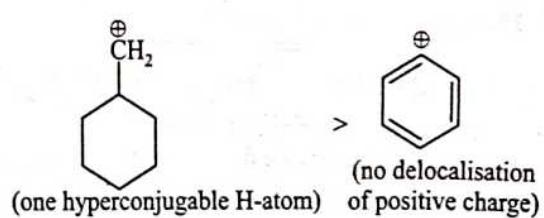
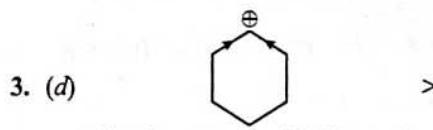
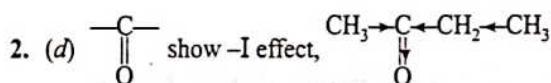


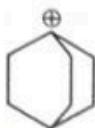
Electron-density will be maximum at this position.

62. (a) It is picric acid because it has three  $-NO_2$  group are arranged which are ortho and para position

## Exercise-2 (Learning Plus)

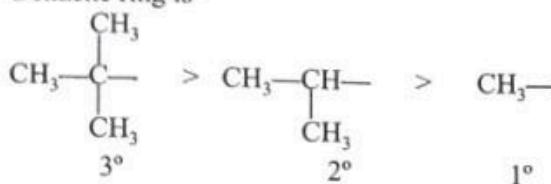
1. (b) Partial displacement of  $\sigma$ -electrons.



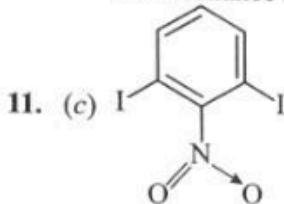


(bridgehead carbocation)

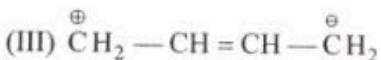
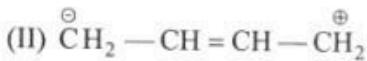
4. (b) The correct order of these groups were attached with Benzene ring is-



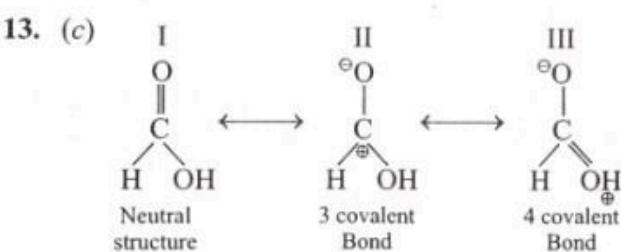
5. (d) (a) is secondary and (b) is primary alcohol  
 6. (b) Due to presence of conjugated system.  
 7. (d) (a), (b) and (c) all are conjugated.  
 8. (b) Do it yourself  
 9. (c) Nitrogen does not have vacant d-orbital, so cannot form five bonds.  
 10. (c) Equivalent resonating structures contribute equally to the resonance hybrid.



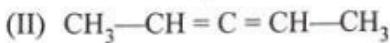
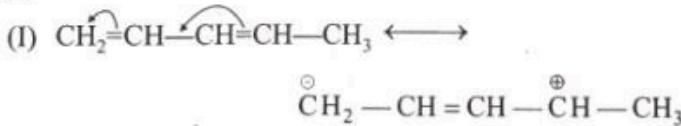
12. (d) (I)  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$   
 I, II, III are canonical structures to each other.



All

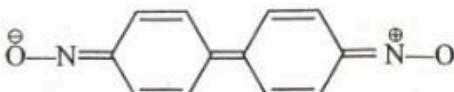


14. (a)



Here in str. (I) Resonance occurs But not in II<sup>nd</sup>.

15. (d)



Complete octate &  
 Extended conjugation

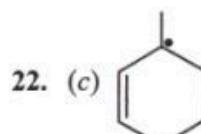
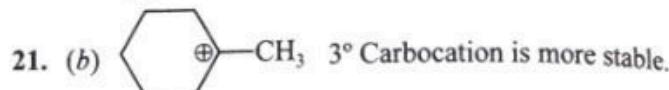
16. (d) Do it yourself

17. (a) Do it yourself

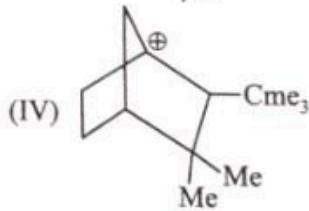
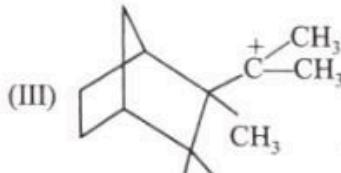
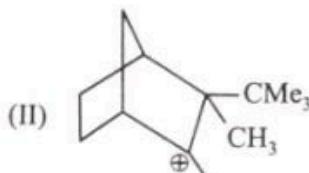
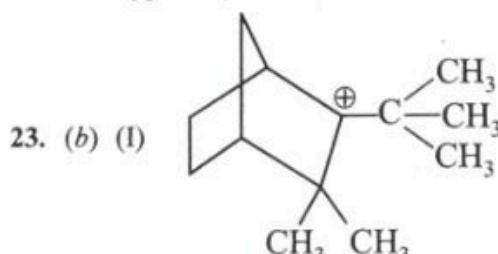
18. (d)  $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$  has two  $\alpha$ -hydrogen for hyperconjugation.

19. (d) Has maximum number of hyperconjugation structure.

20. (b) (I) & (III) has delocalisation (III has better delocalisation)  
 (II) & (IV) has hyperconjugation. (II has better hyperconjugation).



hyperconjugation and delocalisation with +I effect.



Bredt rule

- (IV) III > II > I > IV

24. (d) Conjugate base of (4) has negative charge on oxygen.

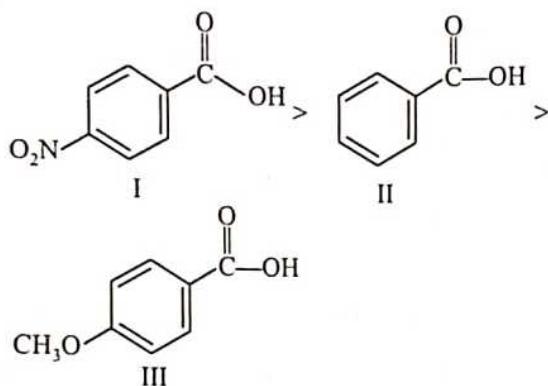
25. (a) On the basis of Inductive effect.

26. (a) On the basis of Inductive effect.

27. (b)  $\text{H}_3\text{N}^\oplus-(\text{CH}_2)_2-\text{COOH}$  has strongest acid due to strong -I effect of  $\overset{\oplus}{\text{NH}_3}$ .

28. (a) On the basis of Inductive effect.

29. (c)



(Strong  $-I$ ,  $-M$  effect of  $-NO_2$  group) (+ $M$  effect of  $-OCH_3$  group)

30. (b) Conjugate base of (2) has three equivalent resonating structures.

31. (a) II  $\rightarrow$  Hyperconjugation III  $\rightarrow -M$  effect

Due to Hyperconjugation basicity increases and due to  $-M$  basicity decreases

32. (a) Nucleophilicity  $\propto \frac{1}{\text{electronegativity}}$  (in a period).

33. (a) Nucleophilicity  $\propto$  size (in a group).

34. (d) As increases delocalisation of negative charge nucleophilicity decreases.

35. (b) Nucleophilicity  $\propto$  Size (in group)

36. (c) Weaker bases are better leaving group.

37. (c) Carbocation Stability  $\text{CH}_3\text{CH}_2^+ > \text{C}_6\text{H}_5^+$

leaving group ability is  $\text{Br}^- > \text{Cl}^-$

over all reaction order  $r_1 > r_3 > r_2$

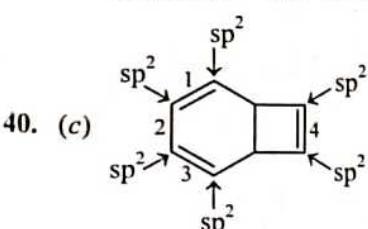
38. (c) On the basis of carbocation stability.

39. (b)  $\xrightarrow{\text{AgNO}_3}$  S<sub>N</sub>1 Reaction

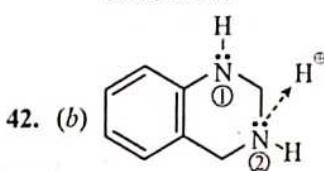
Reaction Intermediate — Carbocation :

III will give most stable carbocation  $\Rightarrow$  stabilised by + $M$  effect of  $-\ddot{\text{O}}-$

I will give stable carbocation  $\rightarrow$  3° carbocation so order of reaction = III > I > II.



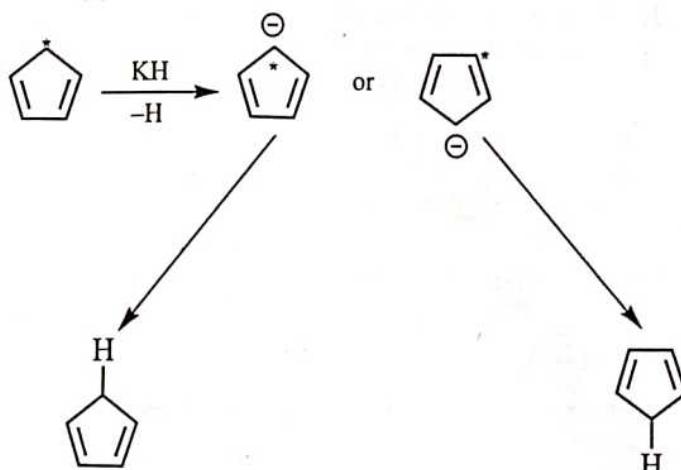
41. (a) Stability of carbocation = 3° > 2° > 1° (a) has 3° carbocation.



Lone pair N-1 is delocalised with benzene ring but N-2 is not so N-2 is more basic and protonation will occur at N-2.

43. (d) Hint: Look for stability of conjugate base using general concept of organic chemistry.

44. (d)



So correct options are (b) and (c) both.

45. (c) Heat of combustion  $\propto$  No. of carbon atom.

46. (d) Remove most acidic proton and look for its stability. In option IV negative charge is stabilized by 3 carbonyl groups so is most acidic.

So correct option (d) ii < iii < i < iv.

47. (c) After dehydrating carbocation is formed and the species with most stable carbocation will be most easily dehydrated.

II upon dehydration forms aromatic compound the most stable.

I Antiaromatic 5-membered Ring Least Stable

III Non Aromatic 7 membered ring.

So order of dehydration ii > iii > i.

48. (d) In (a) and (c) Lone pair undergo resonance in b and d  $\rightarrow$  d is 2° Amine.

49. (b) In option 'b' it is 2° carbocation in first and i carbocation is second.

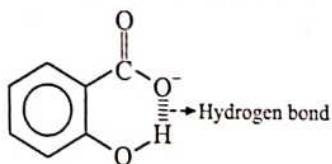
50. (d) Alkenes with highest Number of  $\alpha_H$ -are most stable option 'd' has 8- $\alpha_H$ .

51. (a) Option II has  $-R$  group so most acidic option III and I has electron releasing groups among I and III, I is more acidic as in III there is +R of oxygen atom.

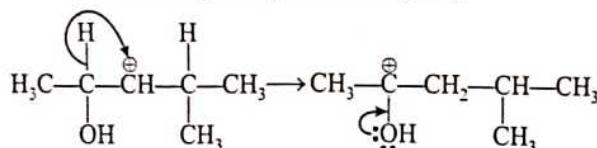
So correct order iii < i < iv < ii

~~positive~~ charge is isolated so most basic. Between A and B, B has higher number of resonating structures so is more stable so correct order is C > A > B.

53. (a) Half life of carbocation  $\propto$  stability of carbocation in option 'a' cyclopropyl ring shows dancing resonance due to ring strain so is most stable among all other carbocations.
54. (d) Negative charge on electronegative atom is more stable. So correct order of stability p > r > q.
55. (a) Electron density  $\propto$  no. of  $\alpha_H$  with respect to phenyl ring 'a' has maximum that is  $3\alpha_H$  (b)  $2\alpha_H$  (c) has  $1\alpha_H$  and (d) has zero  $\alpha_H$ .
56. (c) Orthohydroxy benzoic acid is most acidic as conjugate base is stabilized by hydrogen bond.

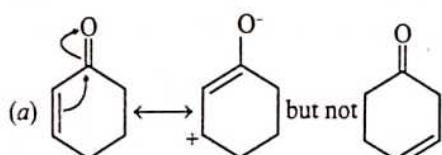


57. (d) H at C<sub>2</sub> as after migration carbocation is stabilized by resonance by lone pair of -OH group.

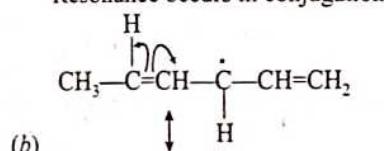


### Exercise-3 (JEE Advanced Level)

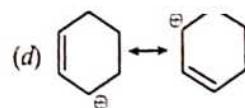
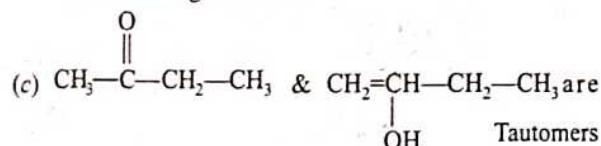
1. (a,b,d) Based on definition of inductive effect.
2. (a,c,d) Fact based on the concept of Resonance.
3. (b,d)



Resonance occurs in conjugation.



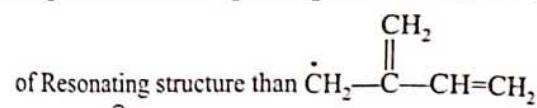
are Resonating structure.



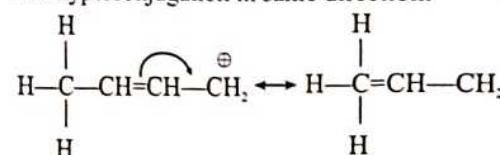
4. (b,d)

(a) Conjugated systems are more stable than non-conjugated system so option 'a' incorrect.

(b)  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2-\text{CH}_2$  will show higher number



(c)  $\text{CH}_2=\overset{\oplus}{\underset{\ominus}{\text{C}}}-\text{CH}_2$  hyperconjugation and resonance are not in same direction but in  $\text{CH}_3-\overset{\oplus}{\underset{\ominus}{\text{C}}}=\text{CH}-\overset{\oplus}{\underset{\ominus}{\text{CH}}}_2$  resonance and hyperconjugation in same direction.



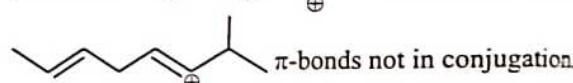
So incorrect stability order.

(d) In  $\text{CH}_3-\overset{\oplus}{\underset{\ominus}{\text{C}}}-\text{O}^-$  negative charge is delocalised on two electronegative atoms. So it is correct.

5. (b,c,d)

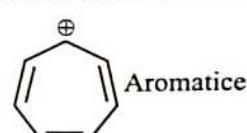
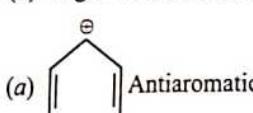
(b) In option 'b' higher number of resonating structure possible

more stable



(c)  $\text{CH}_3-\overset{\oplus}{\underset{\ominus}{\text{O}}}-\text{CH}_2-\text{CH}_3$  more stable due to Resonance.

(d) Higher no of Resonating structure is more stable.



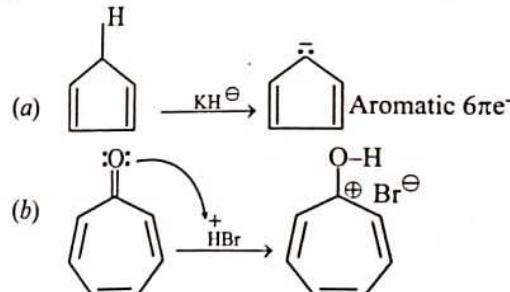
6. (c,f)

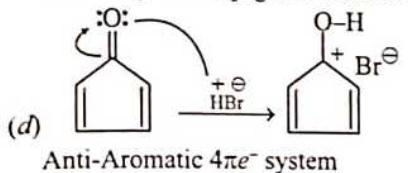
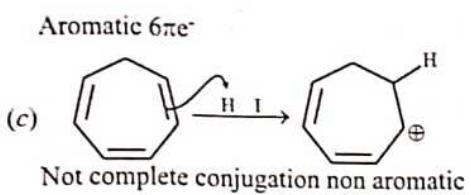
Electron donating groups are  $-\ddot{\text{O}}-\text{COCH}_3$ ,  $-\ddot{\text{N}}\text{HCOCH}_3$

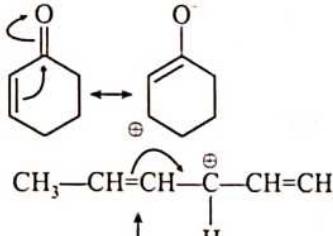
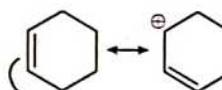
7. (b,d,e)

Lone pair in conjugation will undergo Resonance so correct options are b, d, e.

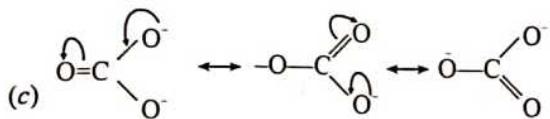
8. (a,b)





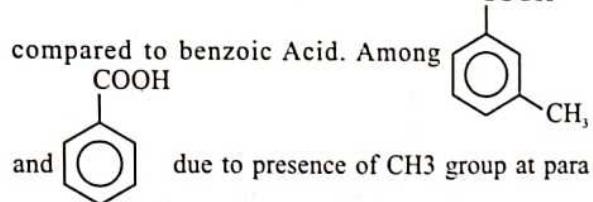
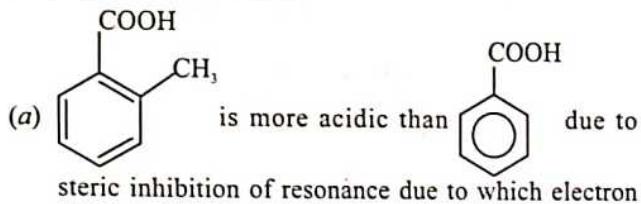
9. (b,d)
- (b) 
- (c) Shown structure are tautomers.
- (d) 

10. (a,c) All canonical forms do not always contribute equally to the resonance hybrid.

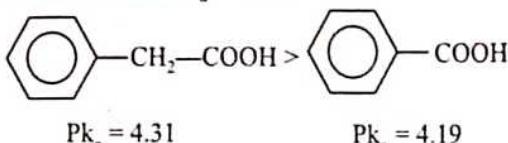


All are equivalent resonating structures so all C—O bond lengths are equal.

11. (a,c)  $K_a \propto$  Acidic strength.



(b) Acetic acid has  $PK_a = 4.74$ .



12. (a,b,c,d)

(a)  $PK_a$  of carbonic Acid is 6.37.

$PK_a$  of CH<sub>3</sub>COOH is 4.74.

(b) Boiling points of acids are higher than Alcohol due to higher extent of hydrogen bonding in Acids.

(c) Chloroacetic Acid is stronger acid than acetic acid due to presence of -I group i.e. chlorine.

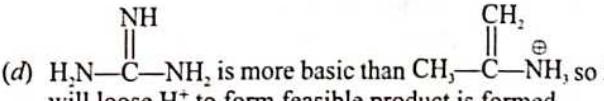
(d) In phenol conjugate base is Resonance stabilized.

13. (a,c,d) Less stable conjugate base will be stronger base so correct options are a, c, d.

14. (c,d) In option 'a' lone pair of N is in conjugation so protonation will not occur and reaction not feasible.

(b) In Aniline Lone pair will undergo conjugation so will not be protonated and infisible reaction.

(c) After reaction a stable aromatic product is obtain from anti-aromatic so feasible reaction.

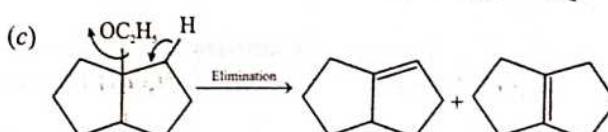
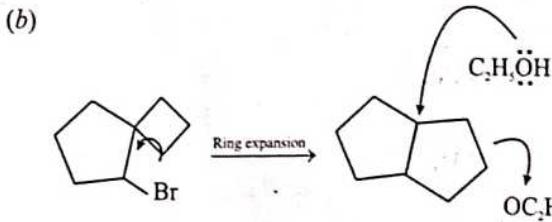
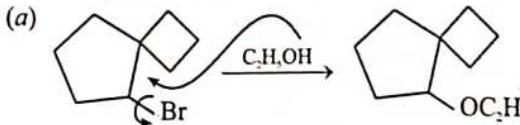
(d) 

15. (a,b)

Weaker bases are good leaving group or stable Anion are good leaving group.  is more stable than . So it is correct. CF<sub>3</sub>-SO<sub>3</sub><sup>-</sup> is more stable than CCl<sub>3</sub>SO<sub>3</sub><sup>-</sup> so it is good leaving group.

16. (a,b,c,d)

All are possible products.



17.(a,b,d)

a, b and d are Resonance stabilized as carbocation is in conjugation with  $\pi$ -bond. (Allyl carbocation is stabilized by Resonance)

18. (c) In option a, b and c after rearrangement more stable carbocation is formed on rearrangement so  $\Delta G$  will decrease.

19. (d) In case of singlet conbene there is presence of one vacant orbital and there is possibility of backbonding and get stabilized.



Extent of backbonding is more in :CF<sub>2</sub> than :CCl<sub>2</sub> due to 2P-2P overlap in :CF<sub>2</sub> and 2P-3P overlap in :CCl<sub>2</sub>.

Triplet :CH<sub>2</sub> is more stable than singlet :CH<sub>2</sub> as per hunds rule.

(c) Singlet CH<sub>2</sub> has planar geometry as two electrons will present in one orbital and from trigonal planar geometry.

(d) electron affinity of CH<sub>3</sub> radical is greater as, after getting one electron octet is completed.

20.(a,c) H<sub>a</sub> is abstracted more rapidly as it forms stable radical. H<sub>b</sub> is more acidic than H<sub>c</sub> as H<sub>b</sub> is in conjugation with  $\pi$ -bond and is resonance stabilized.

21.(b,c,d)

(a) Due to resonance, second is more stable.

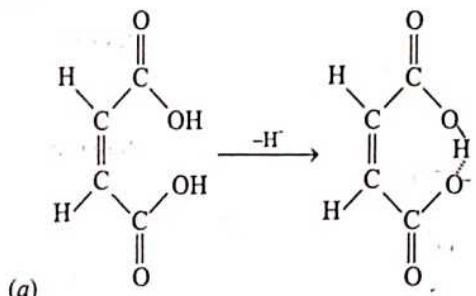
(b) First has 5 $\alpha$ H, Second has 4 $\alpha$ H.

(c) Oxygen is more electronegative.

(d) Second is not resonance stabilized.

22. (b) Only a and b are more stable than . In 'a' -NO<sub>2</sub> group is -R and 'b' negative charge delocalize to oxygen a more electronegative atom. (c) is Anti-aromatic. (d) has lesser number of Resonating structure than .

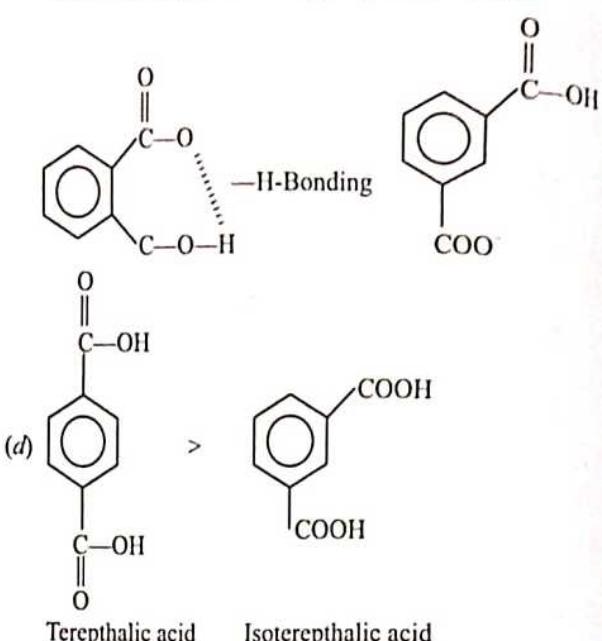
23.(a,c)



Negative change stabilized by H-bond so is more acidic than fumaric acid. So PK<sub>1</sub> of Maelic acid < PK<sub>1</sub> of fumaric acid.

(b) PK<sub>a2</sub> of Maelic Acid is 6.5 and that of fumaric acid is 4.5.

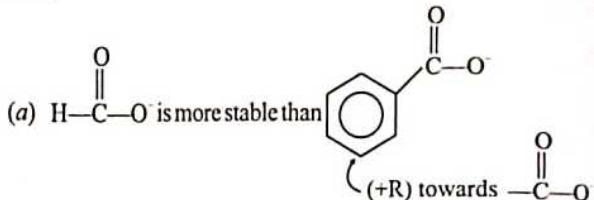
(c) Phthalic acid is stronger acid than isophthalic acid due to Intramolecular H-bonding in phthalate anion.



Terephthalic acid      Isoterephthalic acid

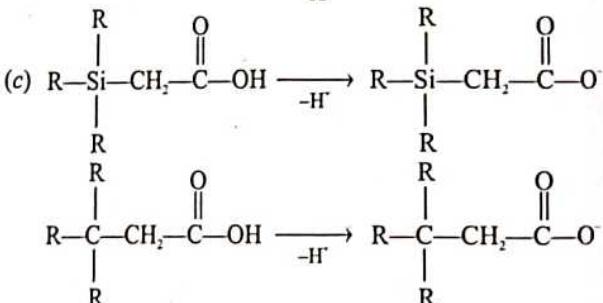
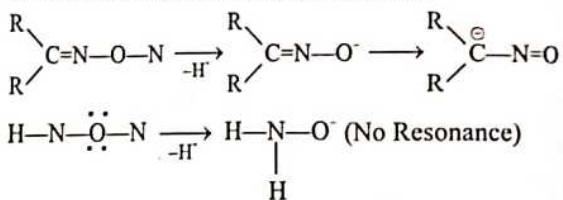
Due to -R Nature in Terephthalic acid so Terephthalic is more acidic.

24. (a,b,c)



so HCOOH is more acid.

(b) In oxime oxide ion is Resonance stabilized

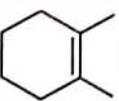


Si is less electronegative than carbon. So, R<sub>3</sub>SiCH<sub>2</sub>COOH is less acidic than R<sub>3</sub>CCH<sub>2</sub>COOH.

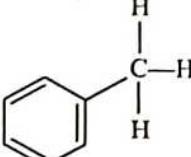
(d) Highly branched carboxylic acids are less acidic than unbranched acids.

25. In 3,4,5-trinitroaniline due to the steric crowding of bulky Nitrogroup, the nitrogroup in para position rotates out of plane hence it can't take part in Resonance with phenyl ring. This phenomenon is called steric inhibition of Resonance (SIR). This phenomenon affects the basicity of compound.  $\text{NO}_2$  being  $-I$  and  $-R$  withdraw electron towards itself. But due to SIR lone pair of Nitrogen cannot come towards ring and is more available for donation and is more basic.

There is no steric inhibition of Resonance in 4-cyano-3,5-dinitro aniline due to linear  $-\text{C}\equiv\text{N}$  group. So correct options are *a, c, d*.

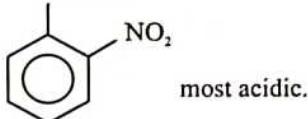
26. (d) Number of hyperconjugation structure is directly proportional to number of  $\alpha_{\text{H}}$ . (d)  has maximum number of  $\alpha_{\text{H}} = 10$ .

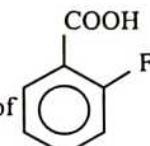
27. (c) In 'c' there is no  $\alpha$ -H so hyperconjugation not possible.

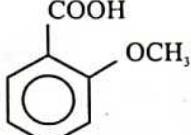
28. (d)  will show hyperconjugation.

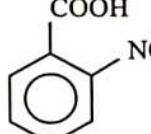
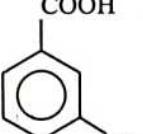
29. (a)  $K_a \propto$  Acidic strength.

$\text{NO}_2$  being strong electron withdrawing group makes



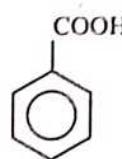
In case of  'F' being smallest will produce lowest ortho effect and will be less acidic than bromo and chloro derivative. So correct order is I>II>III>IV

30. (d)  will be strongest acid due to highest ortho effect.

31. (d)  (i)  (ii)



(iii)



(iv)

Correct order of Acidity is I>III>II>IV.

In (i)  $-\text{NO}_2$  group is more closer as compared to (iii) so will withdraw more electron and make the molecules more acidic.

32. (d) Stability of carbonion follows  $1^\circ > 2^\circ > 3^\circ$ . So correct option is (d).

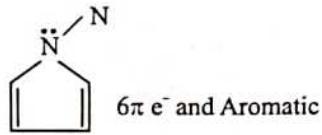
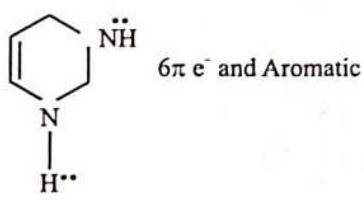
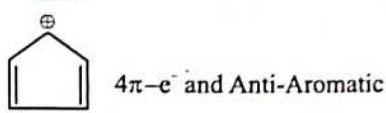
33. (d) Stability of free radical  $\propto +\text{I}/+\text{R}$  and inversely proportional to  $-I$  or  $-R$ .

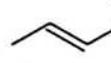
In ph— $\text{CH}_2 \rightarrow$  phenyl stabilize the radical by resonance so is most stable.

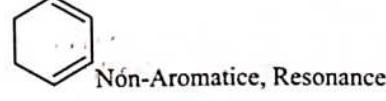
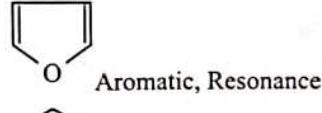
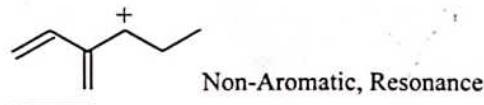
In ph— $\text{CH}_2-\dot{\text{C}}\text{H}_2$ , Ph act as  $-I$  so is less stable than  $\text{CH}_3-\text{CH}_2-\dot{\text{C}}\text{H}_2$ . So, correct order is III>II>I>IV.

34. (a) Stability of carbocation  $\propto +\text{R}$ . with increase in steric crowding at orthoposition extent of Resonance decreases. So, correct order is I>II>III.

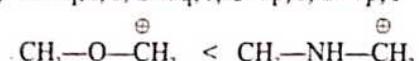
35. (b)   $\longrightarrow$  6- $\pi$  Electron and Aromatic



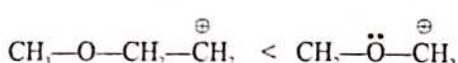
36. (c)  Non-Aromatic, Resonance



37. (a) A $\rightarrow$ q, r, s; B $\rightarrow$ q, r; C $\rightarrow$ p, r; D $\rightarrow$ p, r



Less electronegative of N.



No Resonance

Resonance occur

- (c) due to steric crowding in second there is no resonance and hence is less stable.

38. (d) A $\rightarrow$ s; B $\rightarrow$ q; C $\rightarrow$ r; D $\rightarrow$ p

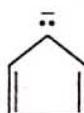
39. [4] Electrophiles are electron accepting species So, CO<sub>2</sub>, SnCl<sub>2</sub>, FeCl<sub>3</sub> and BF<sub>3</sub> are electrophile NH<sub>4</sub><sup>+</sup> is not electrophile because there is no any vacant orbital for accepting electron.

40. [4] NO<sub>2</sub>, :CCl<sub>2</sub>, AlCl<sub>3</sub>, SO<sub>3</sub>

↑

Incomplete octet

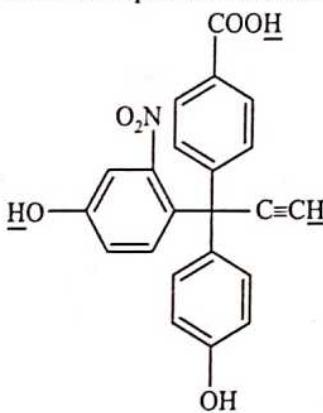
41. [6] No. of Hyperconjugative structure = no. of  $\alpha_H$   
(CH<sub>3</sub>)<sub>2</sub>CH has 6  $\alpha_H$  so 6 hyperconjugative structure.



42. [6] 6-conjugated electrons.

43. [4] Number of mole of NaNH<sub>2</sub> Required = No. of Acidic proton.

Here acidic protons are indicated below



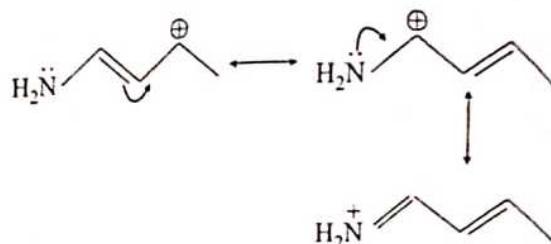
44. [2] HCOOH and ClCH<sub>2</sub>COOH are stronger than CH<sub>3</sub>COOH.

45. [3] -NO<sub>2</sub>, -CHO and CH<sub>2</sub><sup>+</sup>

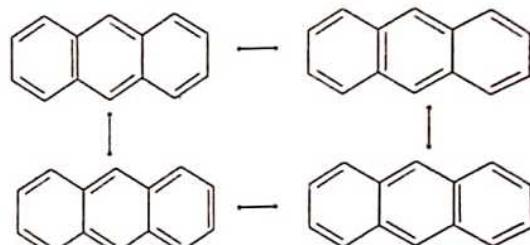
46. [6] Compounds having No any  $\alpha$ -H will not show Hyperconjugation.

47. [9] No. of H.C. structure = No. of  $\alpha_H$ . There are 9 $\alpha_H$ .

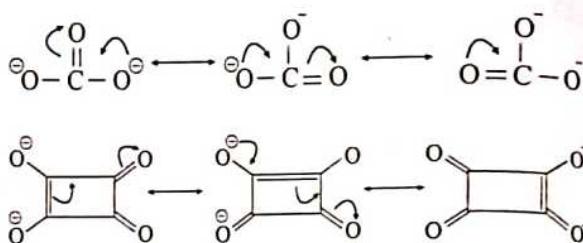
48. [3] 3 Resonance structure can be drawn.



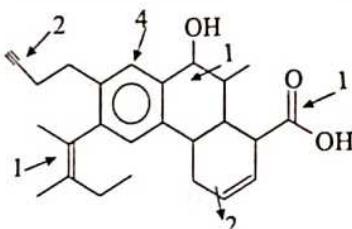
49. [4]



50. [3] R-C(=O)-O<sup>⊖</sup>  $\longleftrightarrow$  R-C=O equivalent structure



51. [11] DU = Number of double bond + Ring



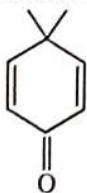
52. [4] 'b', 'd', 'e', 'g'

53. [3] - H = 3 = There are three lone pairs of e<sup>-</sup> in the given molecule.

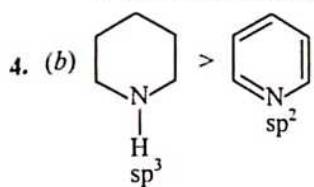
## Exercise-4 (Past Year Questions)

### JEE MAIN

1. (d) Least Resonance stabilized

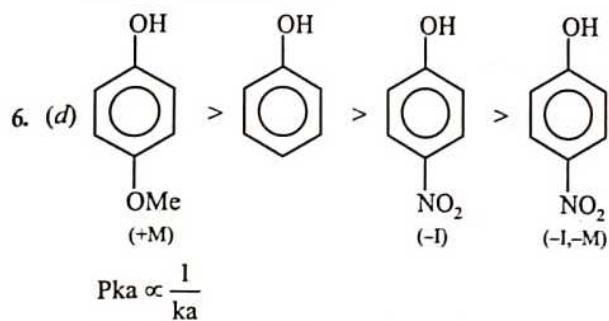


2. (b) Basicity depends upon electron density → which is also directly proportional to number of N-atoms basic order increase with +i group.
3. (d)  $\text{CH} \equiv \text{CH}_{\text{sp}} > \text{CH}_3 - \text{C} \equiv \text{CH}_{\text{sp}} > \text{CH}_2 = \text{CH}_{\text{sp}}$   
S-char. α E.N. α acid strength.



Basic strength of amine increases with electron donating capacity.

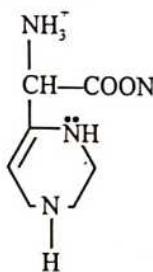
5. (d) In option 'd' only vander waals interaction will operate but in other option H-Bonding dipole-dipole/ion dipole interaction will occur.



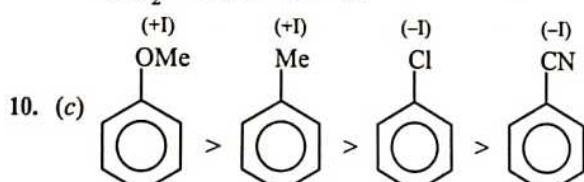
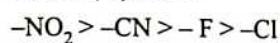
7. (c)  $\text{CH}(\text{CN})_3$

Due to high E.N. of  $\text{CN}^-$ .

8. (c) In strongly acidic medium Lone pair of nitrogen which are localized will undergo protonation  
so correct structure is



9. (d) Due to (-I) effect

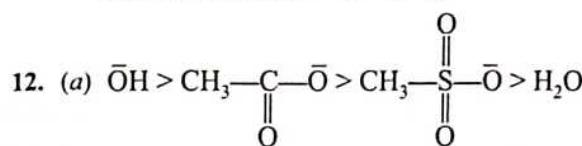


11. (b)  $P_{\text{K}_b} \propto \frac{1}{\text{Basic Nature}}$  Basic Nature  $\propto \frac{1}{-R}$

$$P_{\text{K}_b} \propto -R$$

$-\text{NO}_2$  is  $-R$  so least basic

so correct order is ii < iv < i < iii



Nucleophilicity reduces with l.p. donating tendency of oxygen reduced.

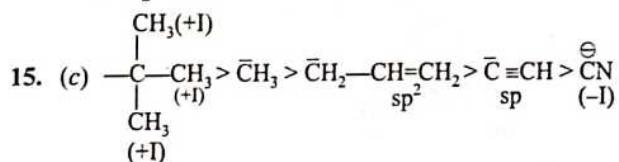
13. (c)  $P_{\text{K}_b} \propto \frac{1}{\text{Basicity}} \propto \frac{1}{k_b}$

$$k_b \Rightarrow \text{B} > \text{A} > \text{C}$$

$$P_{\text{K}_b} \Rightarrow \text{C} > \text{A} > \text{B}$$

14. (a)  $\text{C} > \text{B} > \text{A}$

(c)  $\Rightarrow$  -ve charge is in conjugation with (=) bond and  $\text{NO}_2$ .



16. (c) Heat of combustion  $\propto \frac{1}{\text{stability}}$   $\text{C} > \text{B} > \text{A}$

17. (a)  $\bar{\text{C}}\text{l}-\text{CH}=\text{CH}-\bar{\text{N}}\text{O}_2$

Conjugation

Double Bond char. ↑ B.L. ↓

18. (c) Do it yourself

19. (b) Benzene contains  $6\text{sp}^2$  carbon and on each carbon there are  $3-\sigma$  bonds means  $3\text{sp}^2$  hybrid orbitals per carbon atom so total  $\text{sp}^2$  hybrid orbitals =  $6 \times 3 = 18$

20. (a) Proton with carboxylic acid will be most acidic  $-\text{OH}_2$   
 $\Rightarrow$  is at para position with respect to  $-\text{NO}_2$  so is most acidic after 'b'

21. (a) In option 'd' the negative charge is stabilized by resonance with two oxygen atom.

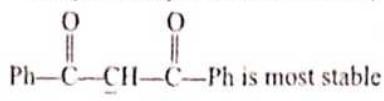
22. (b) In 'b' lone pair of chlorine is in conjugation with double bond, so will undergo resonance and bear partial double bond between  $\text{Cl}-\text{C}$  so has shortest bond length

23. (a) use concept of aromaticity and localization and delocalization of lone pair of  $e^-$  in 'b' lone pair is delocalized and makes the ring aromatic

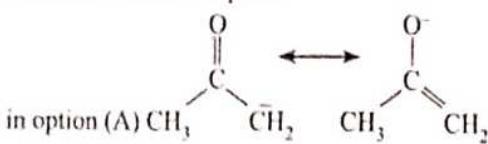
so correct order is  $\text{B} < \text{A} < \text{D} < \text{C}$

D.B. char. ↑ B.L. ↓

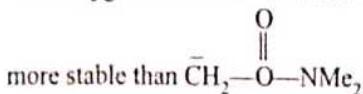
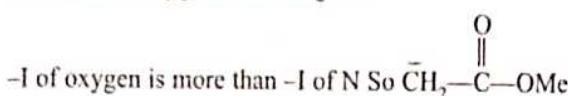
24. (a) Acidity of H depends on the stability of conjugate base



So is most acidic in option

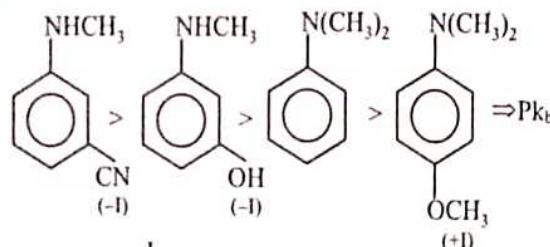


in option (A)  $\text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{||}}} \text{CH}_2-\text{CH}_3$   
only +I of  $\text{CH}_3$  group operates to increase electron density and it is further increased by resonance from lone pair of oxygen and nitrogen.



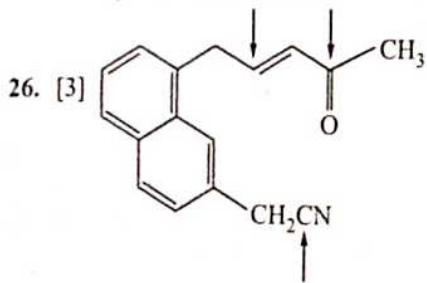
So correct order is D < C < A < B

25. (a)

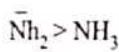


$$\text{P}_{\text{k}_b} \propto \frac{1}{k_b} \propto (-\text{I})$$

$$k_b \propto \text{Basicity.} \propto (+\text{I})$$



27. (d) More stable anion less nucleophilic charged species are more nucleophilic



28. (c)

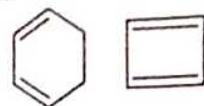
: Bicyclo Compound

: Spiro Compound

: Aromatic Compound

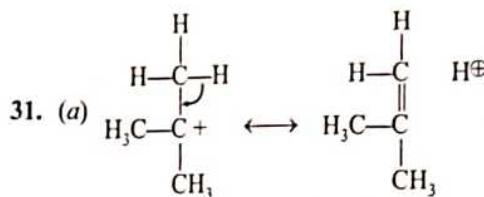
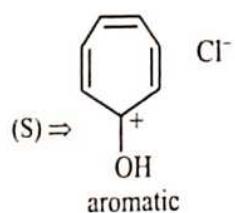
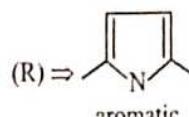
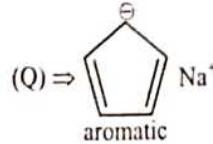
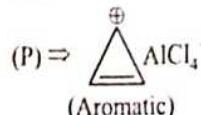
## JEE ADVANCED

29. (b,c)

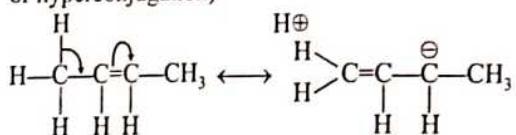


Antiaromatic ( $4\pi e^\ominus$ )  
so unstable.

30. (a,b,c,d)



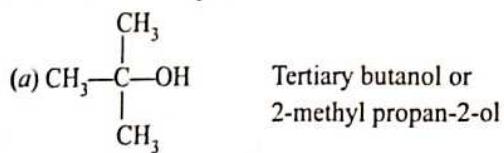
In tert butylation, carbon bearing positive charge has one vacant p-orbital hence it is  $\sigma-p$  (empty conjugation or hyperconjugation)



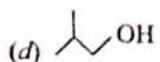
In 2-butene, hyperconjugation is between  $\sigma-\pi^*$  orbital.

32. (a,c,d) We need to draw all the structures of compound given.  
D.U. = 0. Indicates no any double bond. The alcohol contain -OH

So here are all the possible structures



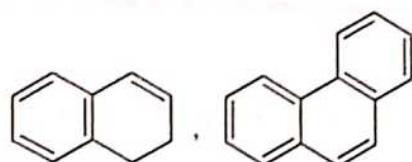
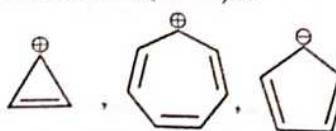
(c)  $\swarrow\searrow\text{OH}$  and  $\nwarrow\nwarrow\text{OH}$



2-methyl propan-1-ol  
and iso butyl alcohol

So correct answers are (a, c, d)

33. [5] Aromatic  $\Rightarrow (4n + 2)\pi e^\ominus$



34. (d) Correct order of basicity of the given compounds is iv > i > ii > iii

In compound iv when lone pair of electron on N-atom is donated to suitable acid conjugate acid is stabilized by resonance by two NH<sub>2</sub> group

In (I) conjugate acid is stabilized by resonance by one NH<sub>2</sub> group

In (III) conjugate acid is stabilized by resonance by one NH group

35. (d) Acidity  $\propto$  stability of conjugate base among I and II, I is more acidic as triple bond has higher s-character.

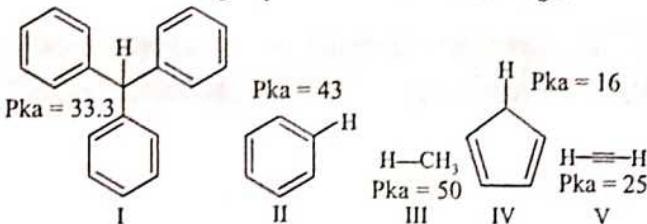
So I > II acidic

between III and IV, III will be more acidic because —COOH group is attached with sp<sup>2</sup> carbon where as in IV COOH group is attached with sp<sup>3</sup> carbon so III is more acidic than IV

- 36.(a,b,c) The conjugate base of compound I is stabilized by delocalization as negative charge is in conjugation with the phenyl rings.

Conjugate base of compound IV is aromatic and is most stable

- R or -i group increases the acidic strength



37. (\*) IV is strongest base due to SIR effect.

III is weakest base due to -M group of three -NO<sub>2</sub> present at ortho and para position.

II is more basic than I due to +I group present. IV is approximately 40,000 times more basic than III.

Where as I and III have little difference in basic strength so correct options are c and d



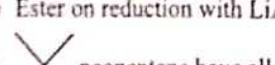
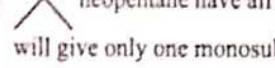
## CHAPTER

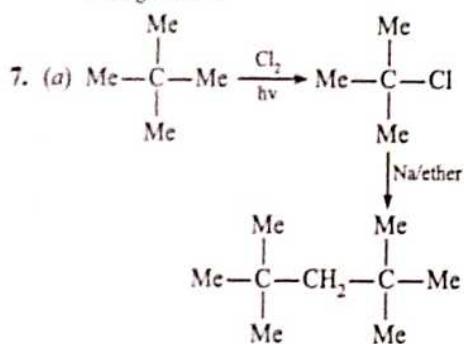
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### Hydrocarbon

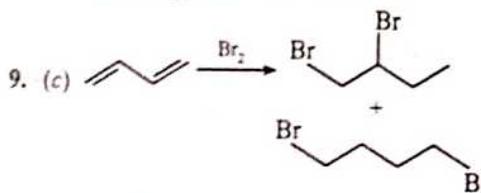
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## **Exercise-1 (Topicwise)**

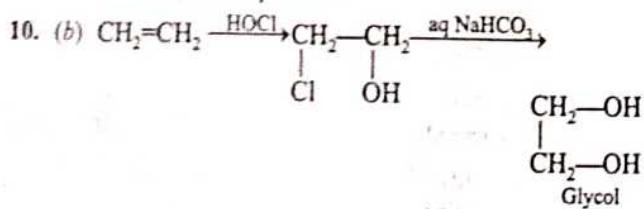
- (c) Unsymmetrical alkane.  
Covery-Hons Synthesis
  - (d)  $C_3H_{16}(C_nH_{2n+2})$
  - (a) Boiling Point  $\propto$  Van Der Walls force.
  - (d) Ester on reduction with  $LiAlH_4$  produces alcohol.
  - (b)  neopentane have all equivalent H-atoms. Hence will give only one monosubstituted alkyl Halide.
  - (d) 



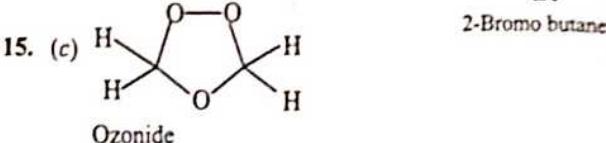
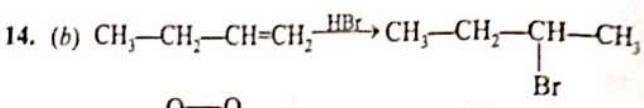
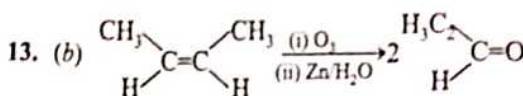
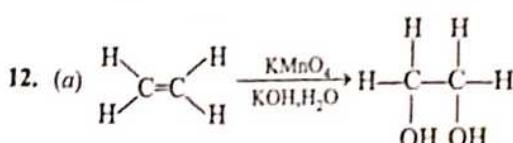
8. (d) Anti addition to trans alkene gives meso compound and bromine gives trans addition.



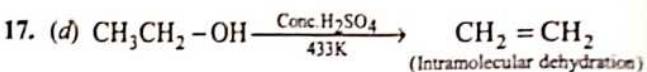
Since formed carbocation can rearrange and will give 1, 2 & 1, 4 both product.



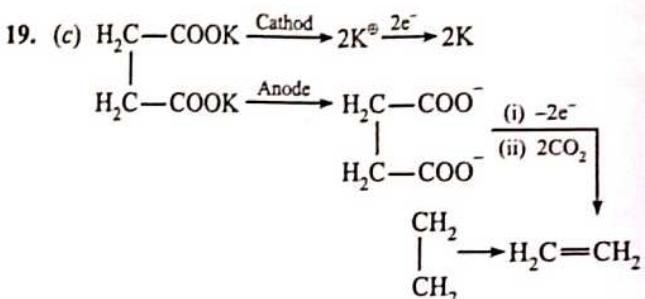
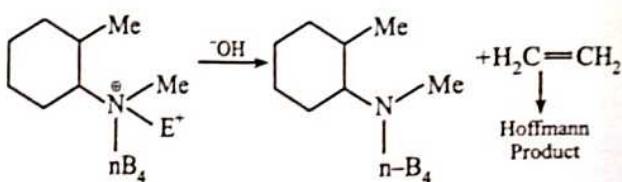
- $$11. (d) \text{C}_2\text{H}_5\text{I} + \text{alc. KOH} \rightarrow \text{C}_2\text{H}_4 + \text{KI} + \text{H}_2\text{O}$$



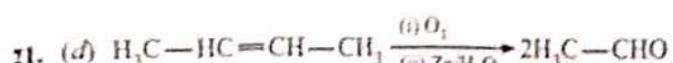
16. (b) Markovnikov's rule can not be applied for symmetrical alkene.



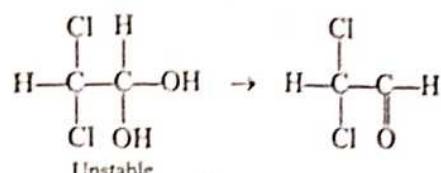
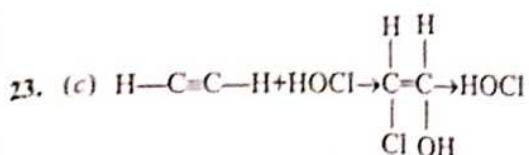
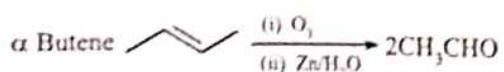
18. (b)



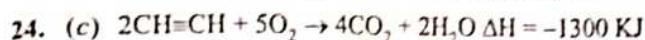
20. (d) Dehydration of Alcohol can be done by (i) conc.  $H_2SO_4$  and Heat (ii)  $H_3PO_4$  (conc.) and Heat



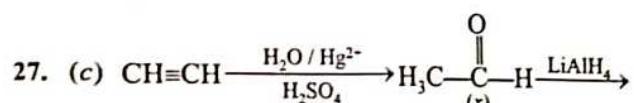
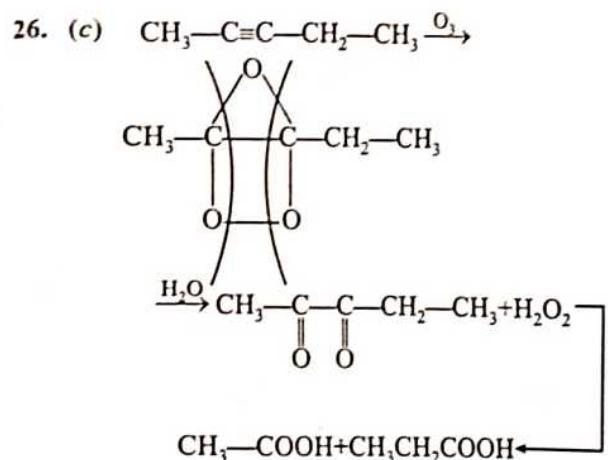
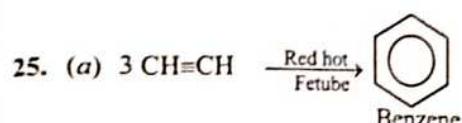
Hence symmetrical alkene should be



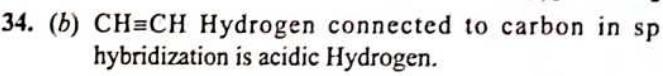
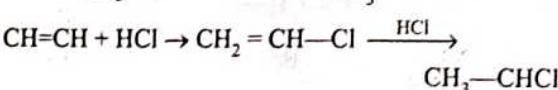
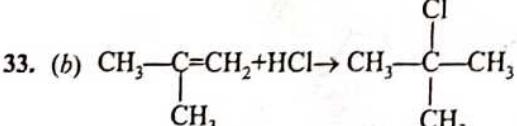
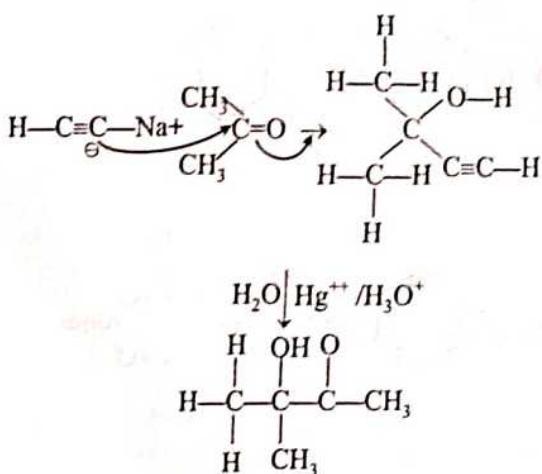
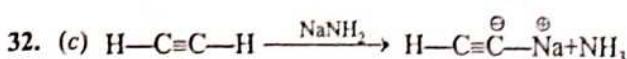
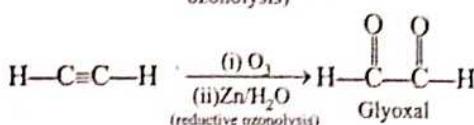
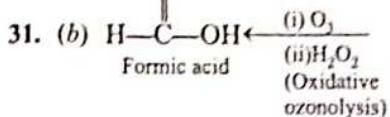
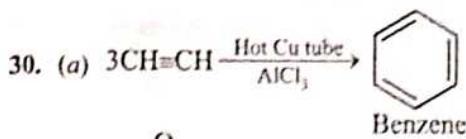
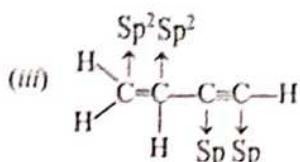
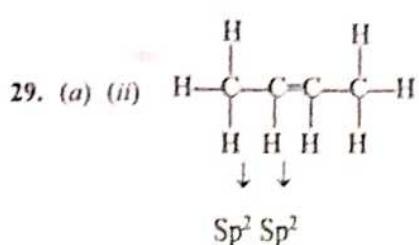
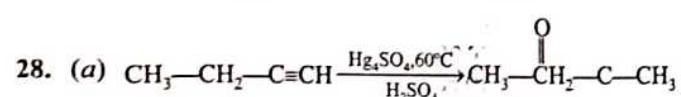
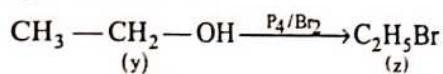
With acetylene it gives dichloroacetaldehyde.



The combustion of acetylene is highly exothermic and the heat produced during the combustion can be used for welding purposes in the form of oxy acetylene flame.



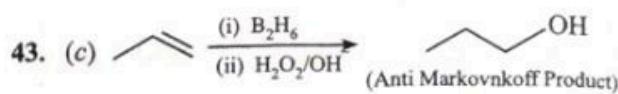
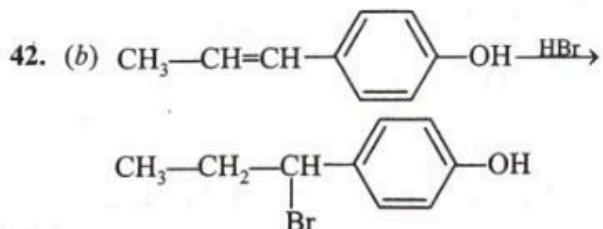
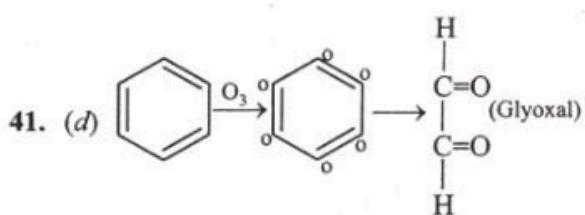
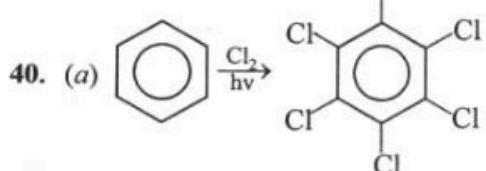
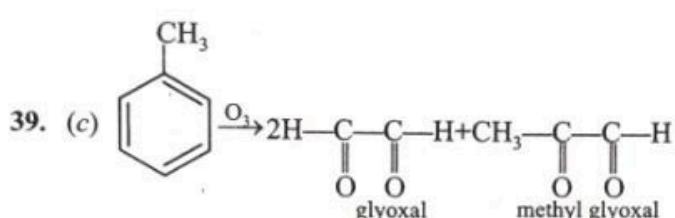
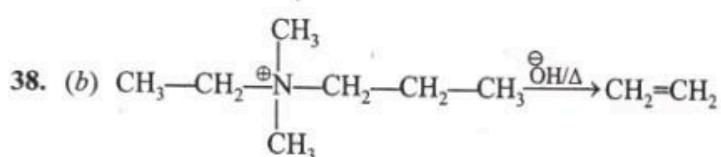
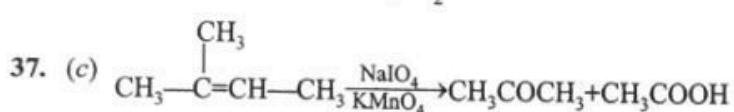
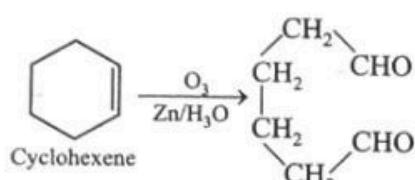
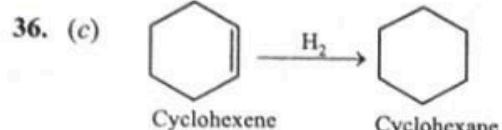
Cyclo octatetraene



$\text{CH}_2=\text{CH}_2$  less acidic.

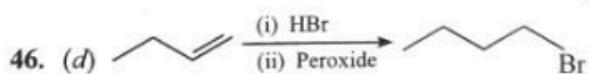
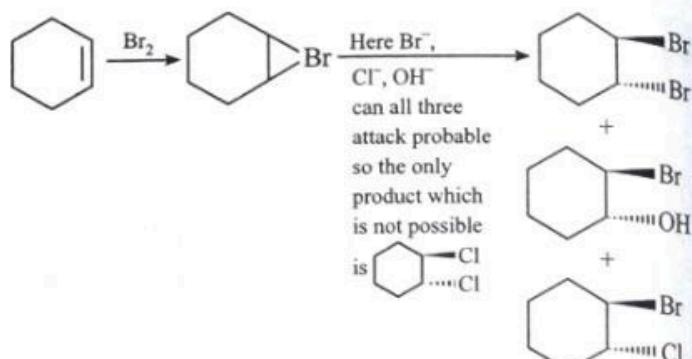
So order will be  $\text{CH}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{CH}_3$ .

35. (d) All kinds of unsaturated hydrocarbons will give chlorination.



44. (a) Since H—Cl and H—I do not break in radicals. Hence they don't give Anti Markovnikov's product.

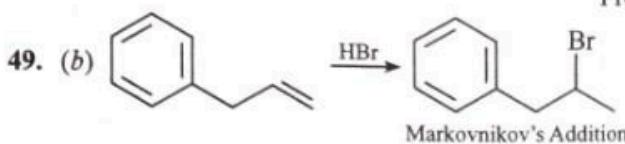
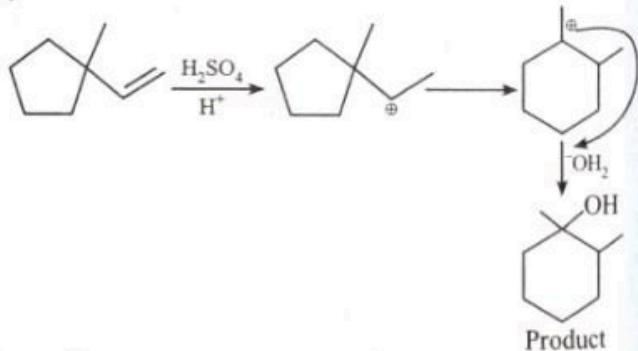
45. (d)



Anti Markovnikov's Product proceed through free radical mechanism.

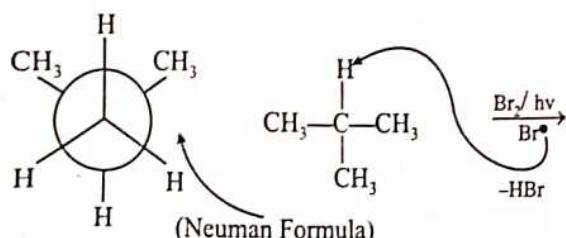
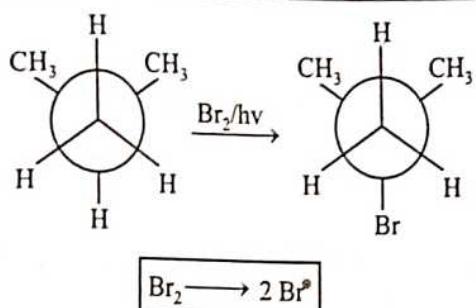
47. (a) Acid catalyzed Hydration is  $\text{SN}^+$  mechanism. Hence Reactivity order follow the stability of formed carbocation during the course of reaction. Hence  $(\text{CH}_3)_2\text{CH}=\text{CH}_2 > \text{H}_3\text{C}-\text{CH}=\text{CH}_2 > \text{H}_2\text{C}=\text{CH}_2$

48. (c)

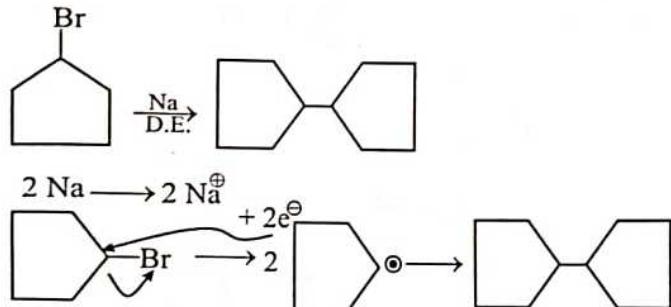


## O Exercise-2 (Learning Plus)

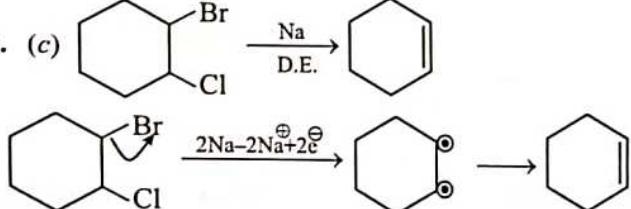
1. (b)



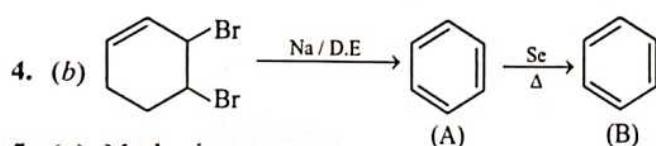
2. (a) Mechanism



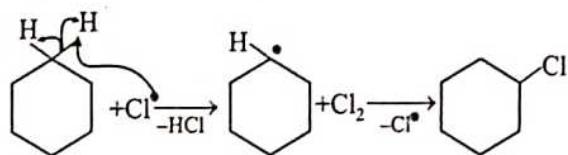
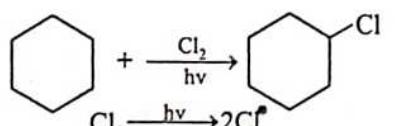
3. (c)



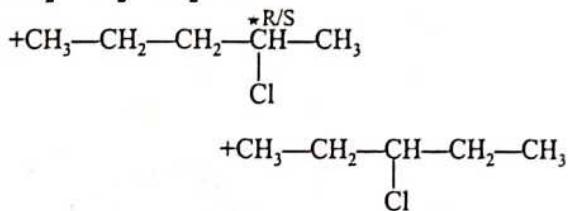
4. (b)



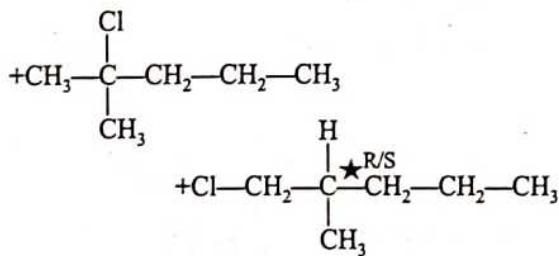
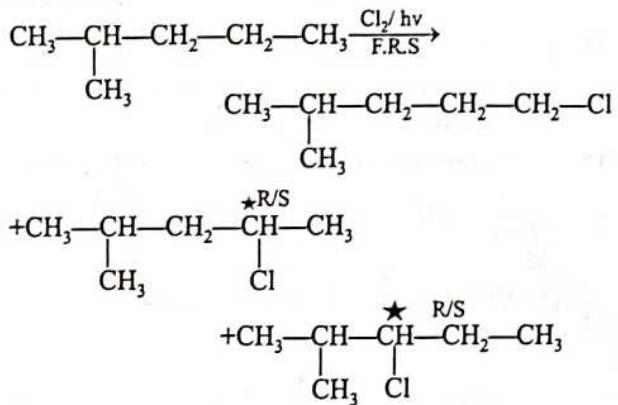
5. (a) Mechanism



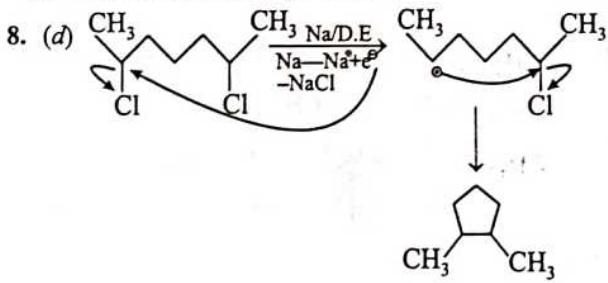
6. (c)



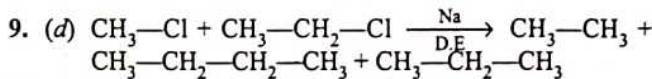
7. (c)



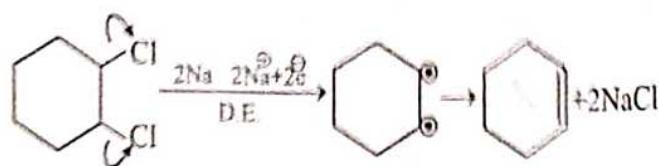
Total no. of monochloro product = 7



9. (d)



10. (c)



11. (a) Stability depends on hyperconjugation which further depends on total number of  $\alpha$ H.

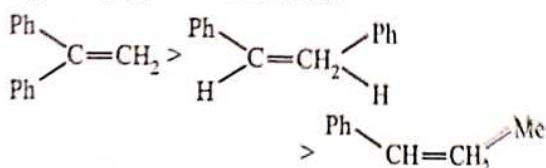
12. (c) Dipole moment is a vector quantity. In trans 1, 2-Dichloroethene, all the vector cancel each other

13. (d) Heat of hydrogenation =

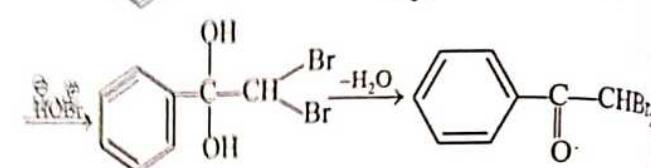
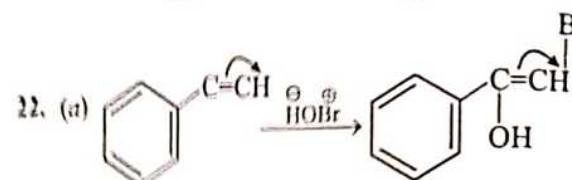
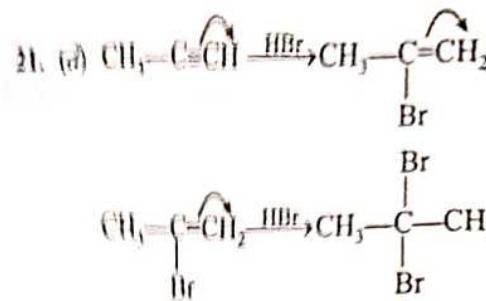
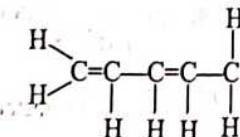
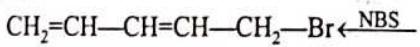
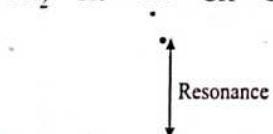
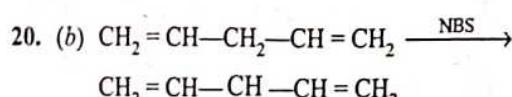
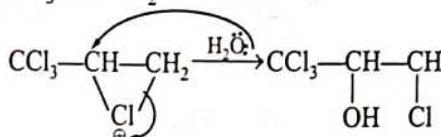
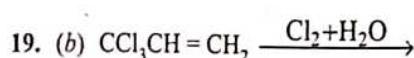
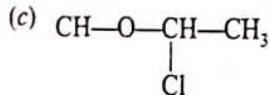
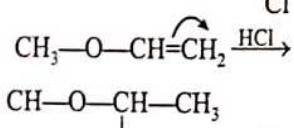
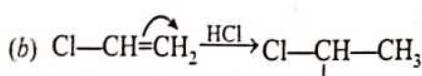
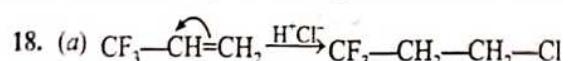
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### Stability of alkene or crowding across $\pi$ bond

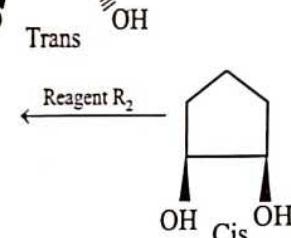
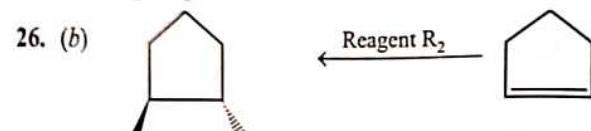
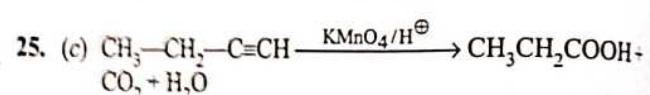
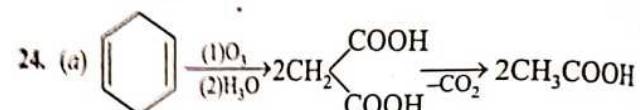
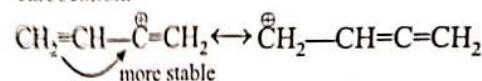
14. (c) Stability of Alkene depends upon substituents and Hyperconjugation effects. Hence



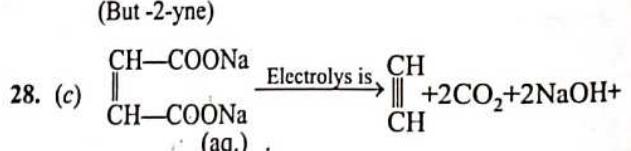
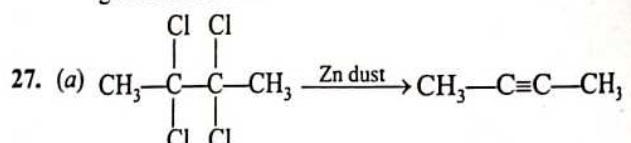
15. (c) Stability  $\alpha$  No. of  $\alpha$ -Hydorgen for hyperconjugation.  
 16. (a) Electrophilicity of Double Bond  $\alpha$  Stability of formed Carbocation  $\alpha$  no. of  $\alpha$ -H atom.  
 17. (d) No rearrangement in oxymercuration Demercuration.



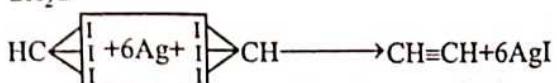
23. (A) When double bond and triple bond is in the conjugation then triple bond is more reactive due to more stable carbocation.



Syn addition with Baeyer's Reagent, So cis will form meso compound however peroxy acid in anti addition gives enantiomer.



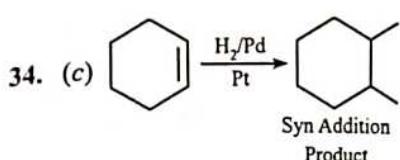
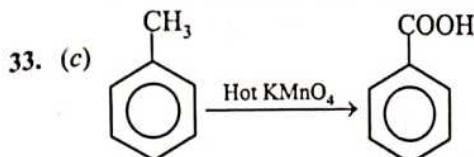
29. (d)  $2\text{H}_2\text{O}$



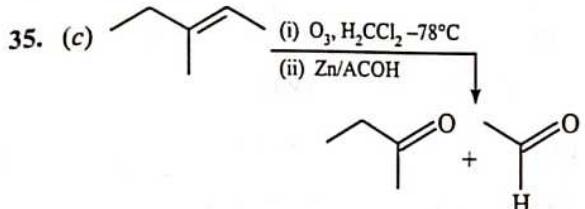
30. (c) sp Hybridisation of alkyne and also intermediate form is less stable.

31. (a)  $\text{CaC}_2 + \text{H}_3\text{O}^+ \rightarrow \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$  (Acetylene)

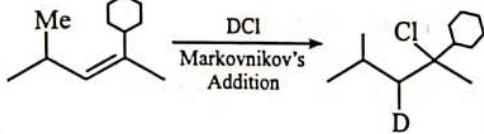
32. (b) Due to relatively compact  $e^-$  cloud of alkynyl, there are less reactive to electrophilic addition than alkenes.



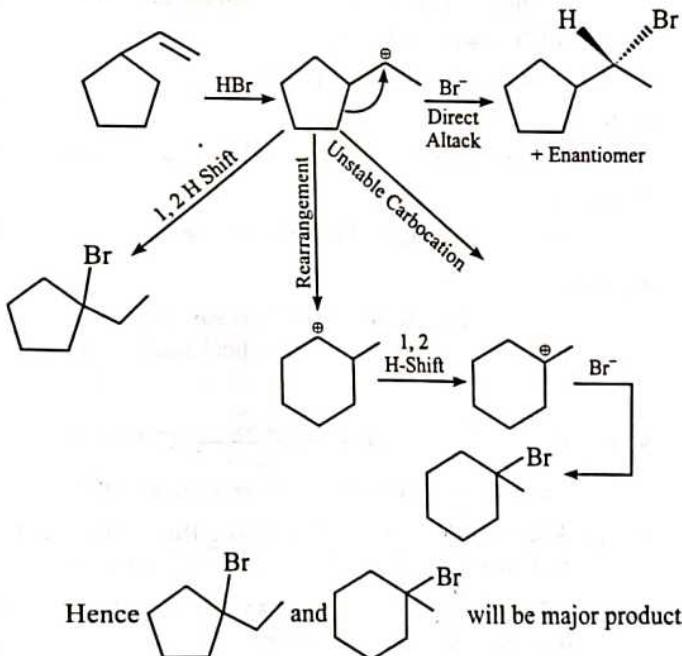
Hydrogenation of Alkene in presence of Metal is a syn addition.



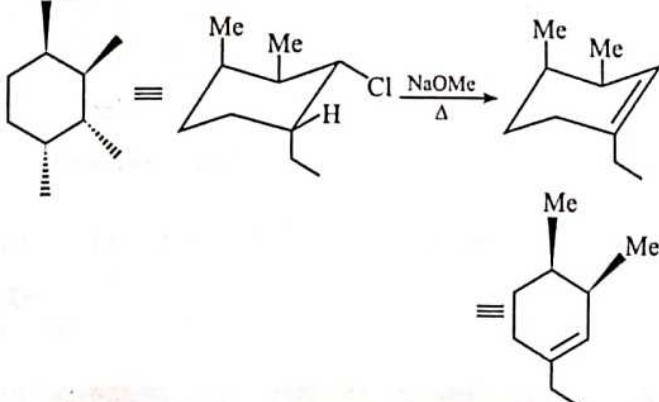
36. (b) 2-Cyclohexyl-4-methyl-2-pentene



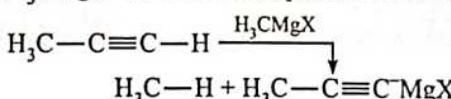
37. (d)



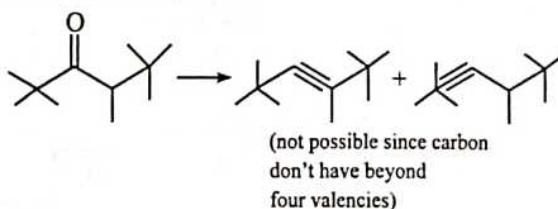
38. (a)



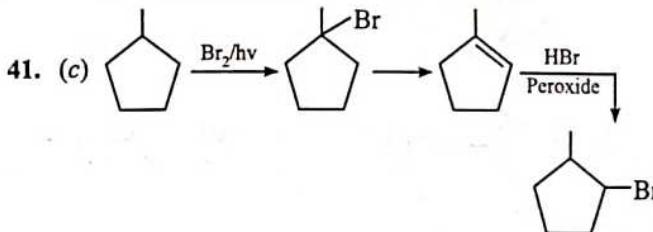
39. (d)  $\text{H}_3\text{CMgX}$  will take acidic proton from alkyne



40. (c) If we do retro synthesis



Hence correct answer will be four.

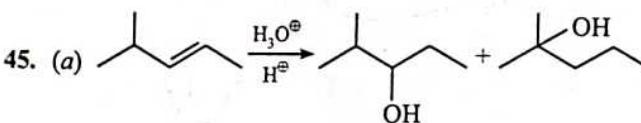
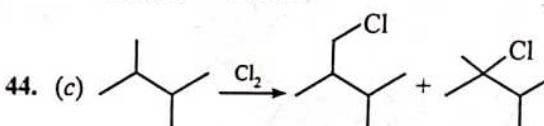


42. (d) All of the given reaction give the elimination product of Alkyne.

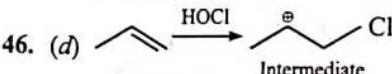
43. (c) Activating groups accelerate the electrophilic substitution reaction.

Hence order of rate I > III > IV > II

TM of F > +M of Cl

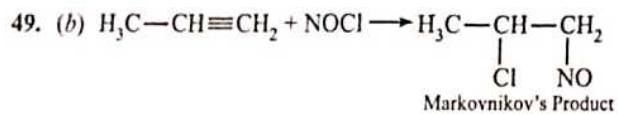
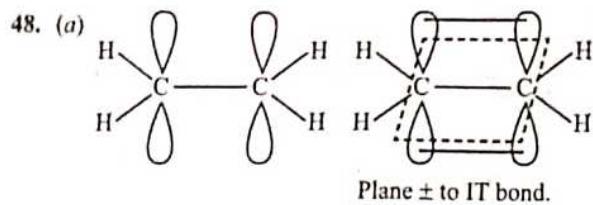


Alkene other than ethene can rearrange to given 2° & 3° alcohols.



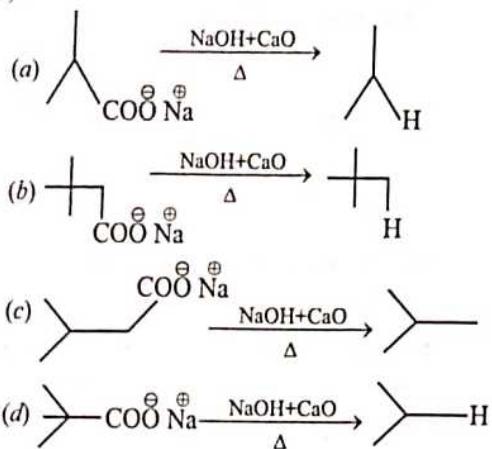
47. (a) Most unstable alkene will go for hydrogenation first,

hence correct answer will be  $\text{R}-\text{CH}=\text{CH}-\text{R}$

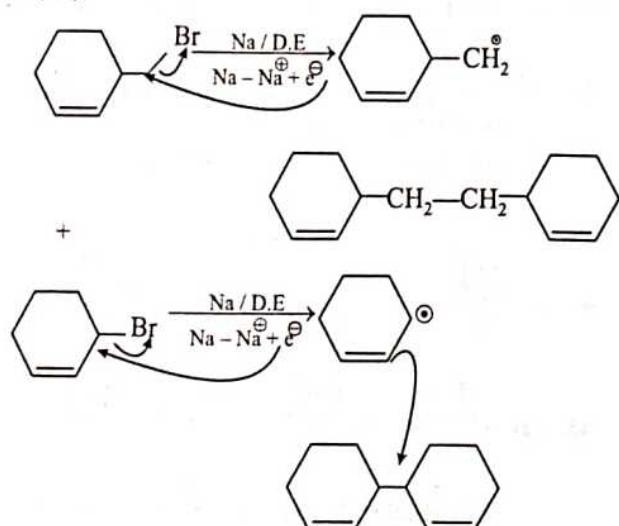


### Exercise-3 (JEE Advanced Level)

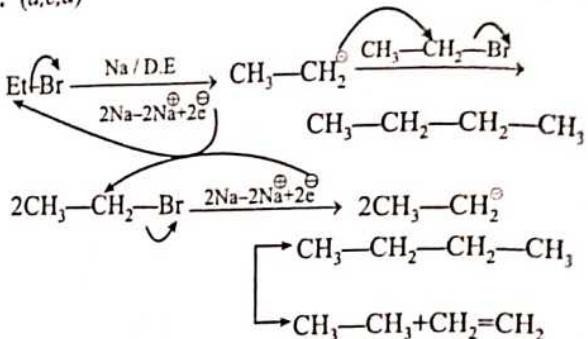
1. (c,d)



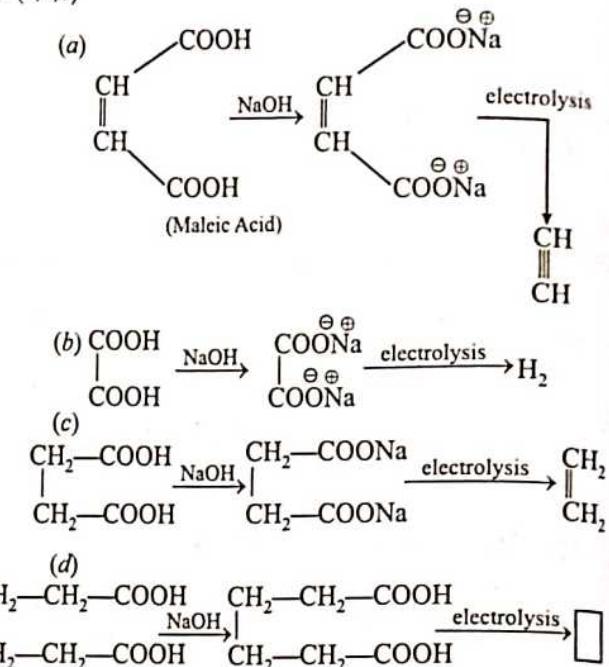
2. (a,b)



3. (a,c,d)



4. (a,b,c)



5. (a,b,c,d)

(a) and (b) Product of dehydrohalogenation.

(c) Product of dehalogenation.

(d) Kolbe's Electrolysis process.

6. (a,b,c)

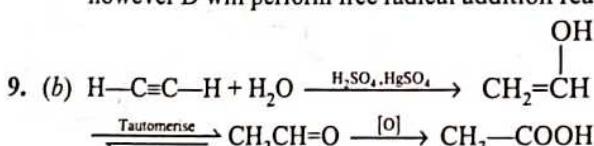
X is Birch Reducing agent and Y is Lindlar's catalyst.

7. (a,c,d)

(a,c,d) gives alkenes by cyclic T.S. on heating.

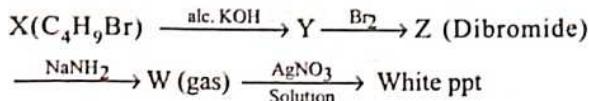
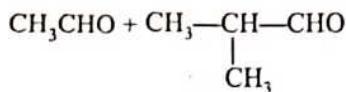
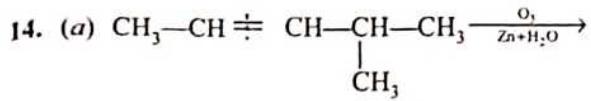
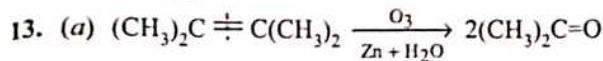
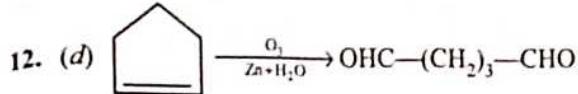
8. (a,b,c)

(a,b,c) will undergo free radical substitution reaction however D will perform free radical addition reaction.



10. (c) Addition of  $\text{H}_2\text{O}$  by Markovnikov's Rule and by anti-Markovnikov's Rule. (Hydroboration oxidation).

11. (c) Addition of  $\text{H}_2\text{O}$  by Markovnikov's Rule (By oxymercurcation demercurcation).



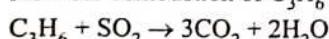
15. (d) 15 ml Hydrocarbon required 357 ml air (21% O<sub>2</sub>)

$$357 \text{ ml air contains} = \frac{357 \times 21}{100} = 75 \text{ ml O}_2$$

Ratio of Hydrocarbon and oxygen

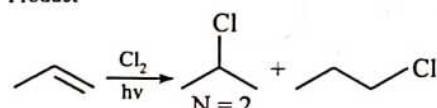
$$15 : 75 = 1 : 5$$

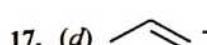
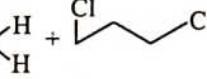
Now for combustion of C<sub>3</sub>H<sub>6</sub> (A)



Hence correct option will be (d).

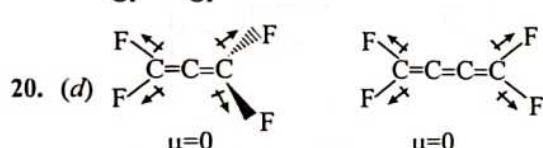
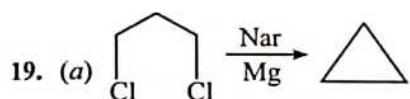
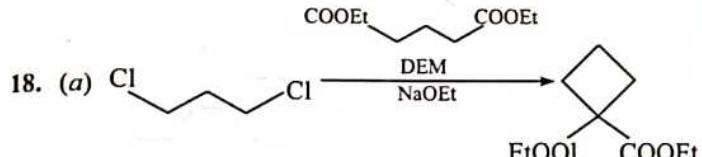
16. (a) C<sub>3</sub>H<sub>6</sub> ≡  will have 2 monochloro Product



17. (d)   $\xrightarrow{\text{Cl}_2}$   + 

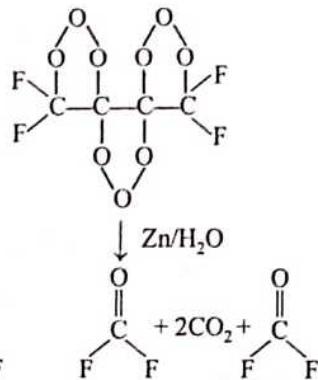
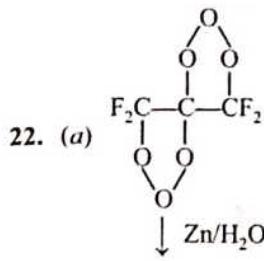
Optically active

Hence M = 2



Hence neither of them will show dipole moment.

21. (d) Both are optically inactive hence neither of them will be resolvable.



Hence both of them will give same product on reductive ozonolysis.

23. (a)

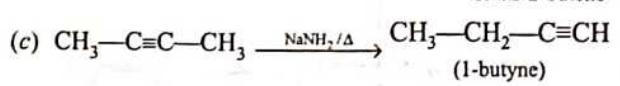
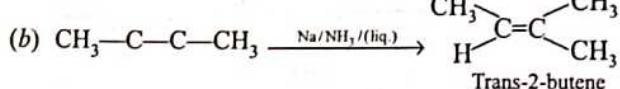
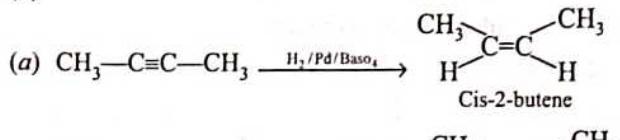
**Regioselectivity** : → Out of two positional isomers, one isomer is preferred.

**Stereoselectivity** : → When one stereoisomer of the reactant has selected one stereoisomer of the products

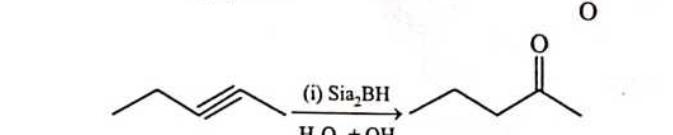
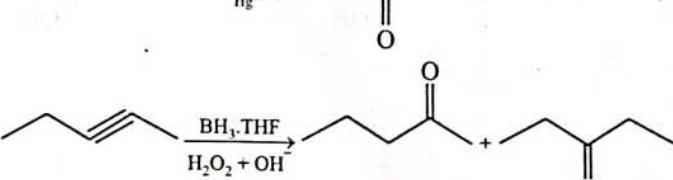
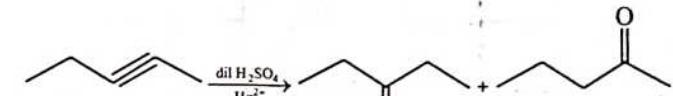
**Chemoselectivity** : → The reagent selects only one functional group /multiple bond/ substituents

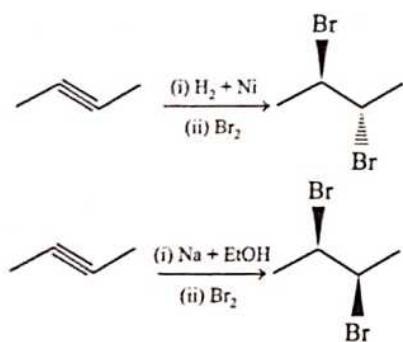
**Rearrangement** : → For increasing the stability carbocation undergo for rearrangement.

24. (a)

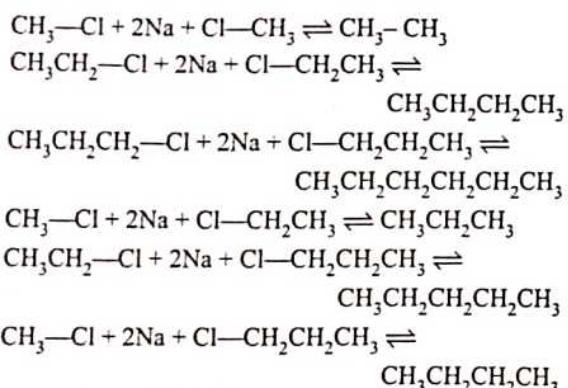


25. (c)



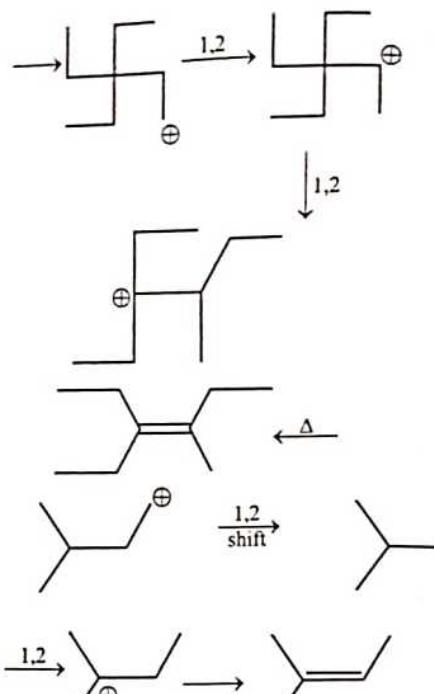
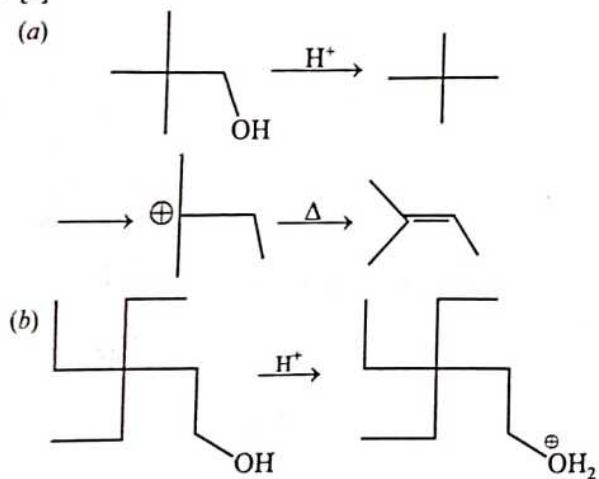


26. [6]

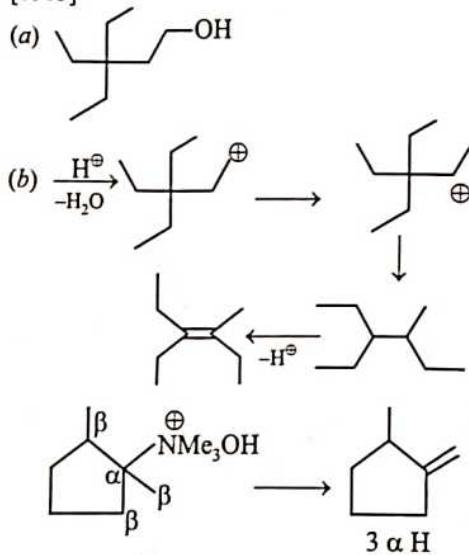


27. [4] On reaction with 2-chloro 3-methyl pentane gives non-identical four products.

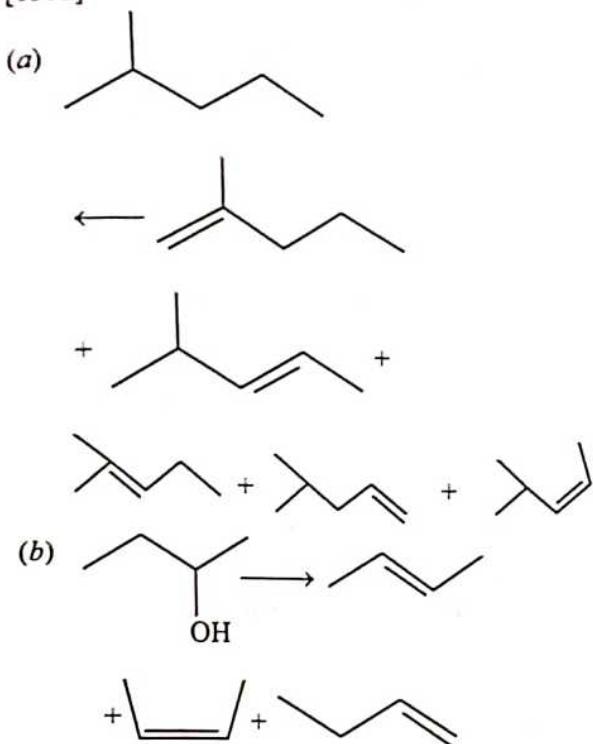
28. [4]



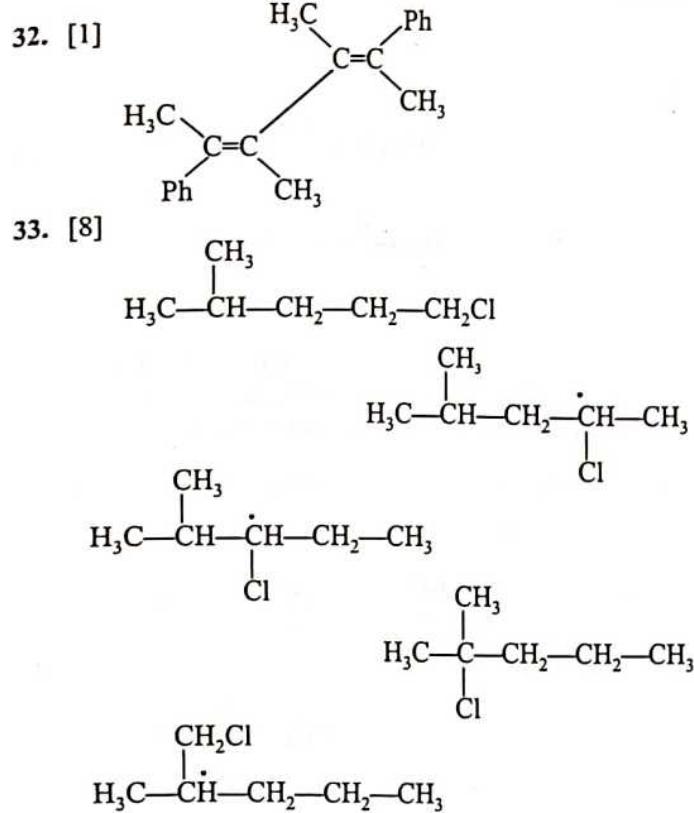
29. [0303]



30. [0503]

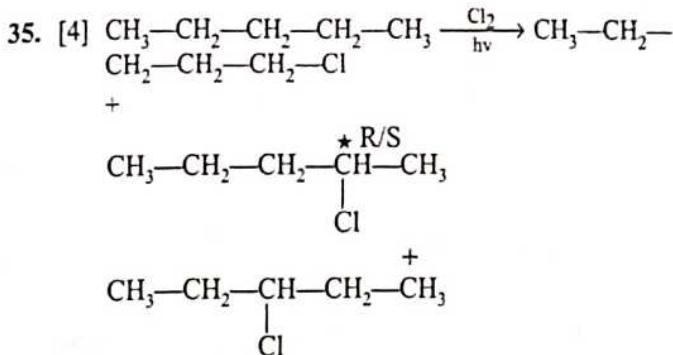


31. [3] More will be stability of carbocation more will be reactivity of substrate from which carbocation formed.

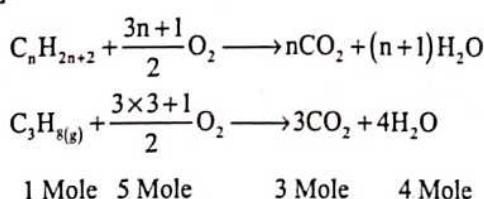


Compounds which have chiral carbon here exist in two forms: d and l.

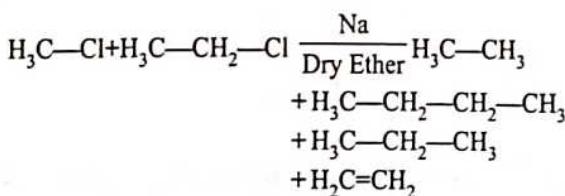
34. [4] Number of monochloro products are 6(P)  
And distillation fractions are 4 (Q)



36. [5]

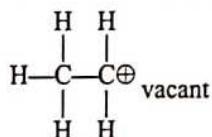


37. [4]



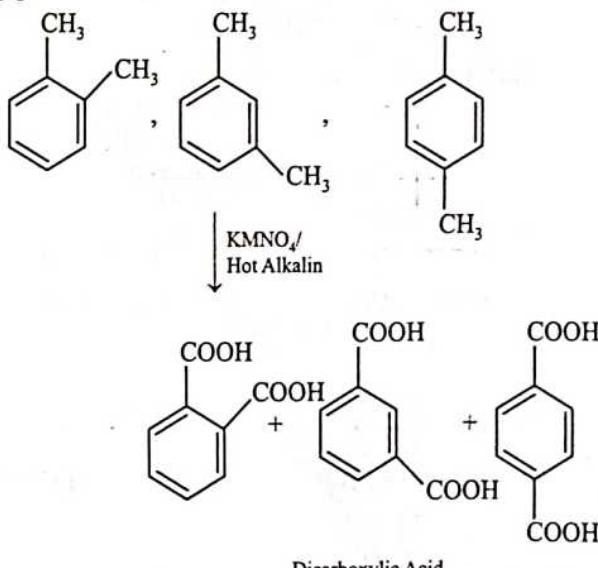
Hence total product will be (4).

38. [3]



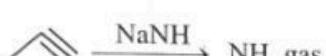
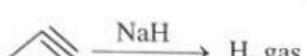
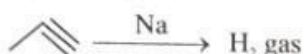
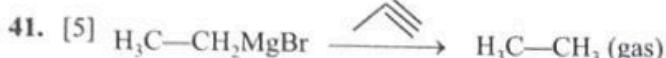
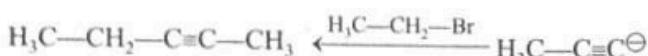
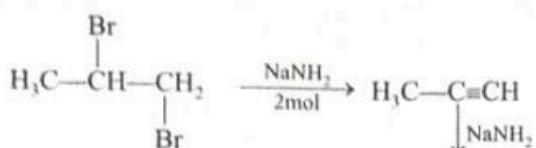
$\alpha\text{-H}=3$  available for hyperconjugation

39. [3]



Hence correct answer will be 3.

40. [3]



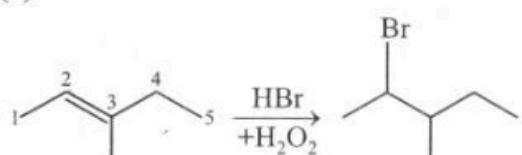
Hence correct answer will be 5.



## Exercise-4 (Past Year Questions)

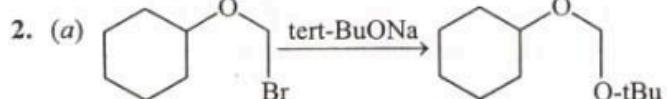
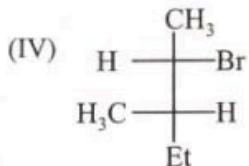
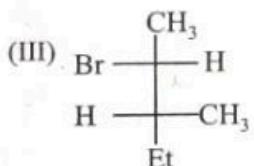
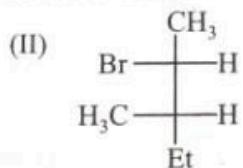
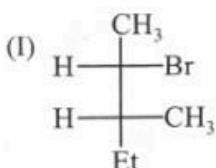
### JEE MAIN

1. (d)

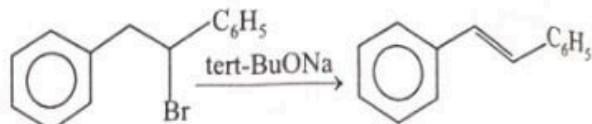


3-methyl pent-2-ene

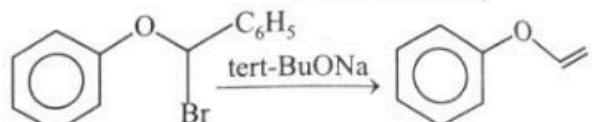
Anti markovnikov product  
(4 stereo isomers possible  
due to 2 chiral centre as  
molecule is nonsymmetric)



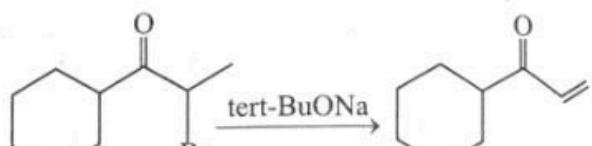
(Fails to decolorise the colour of bromine)



(It decolorises bromine solution)

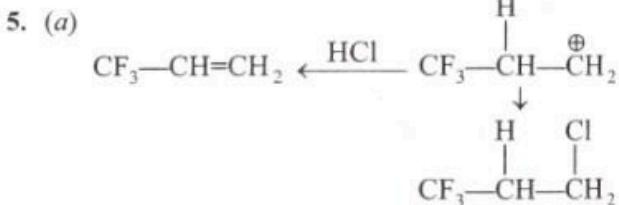
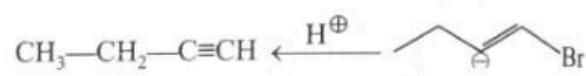
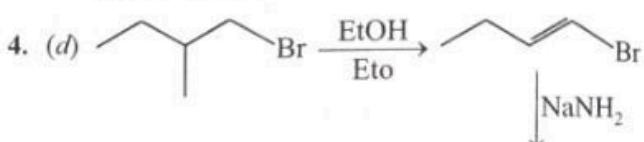


(It decolorises bromine solution due to unsaturation)

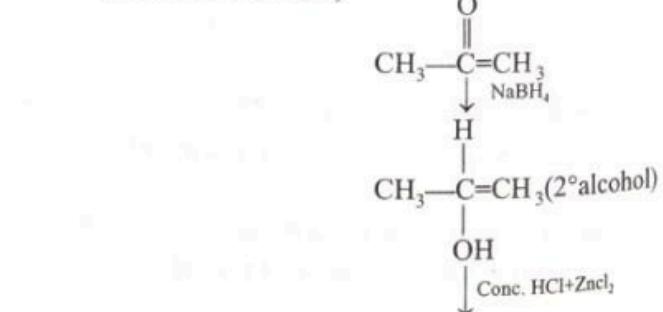
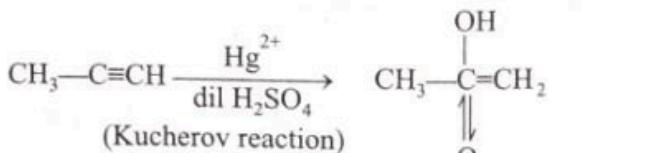
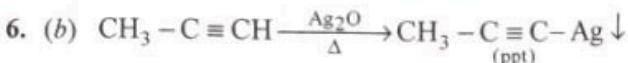


(It decolorises bromine solution due to unsaturation)

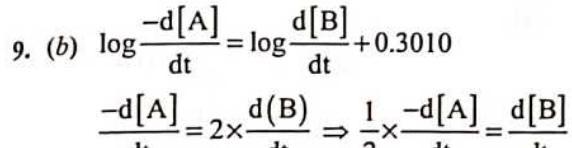
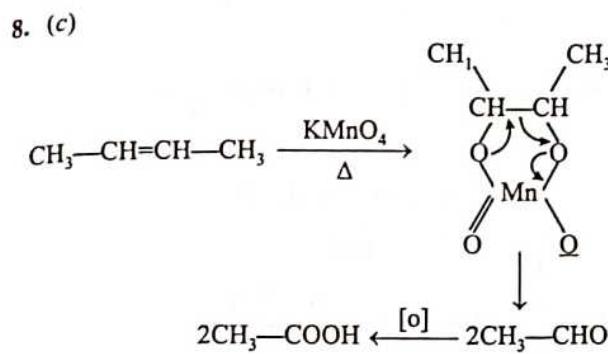
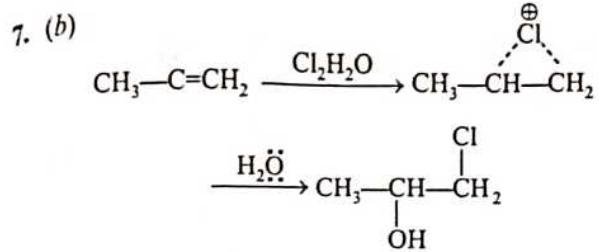
3. (d) Formation of allyl radical will promote a hydrogen to replace easily.



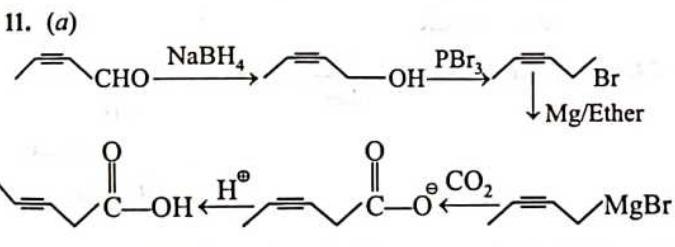
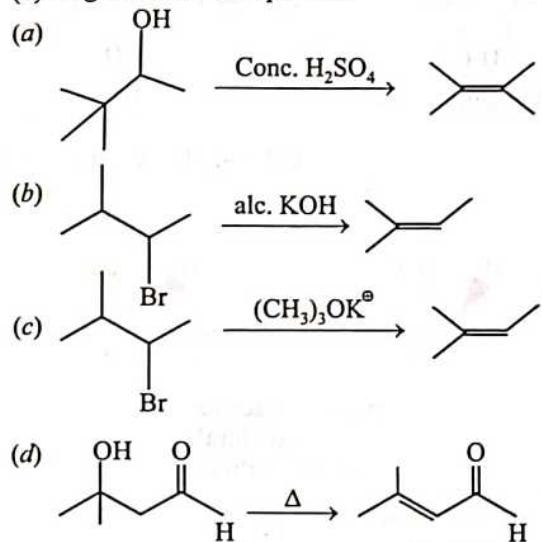
Due to higher  $e^-$  withdrawing nature of  $\text{CF}_3$  group. It follows anti markovnikov's product.



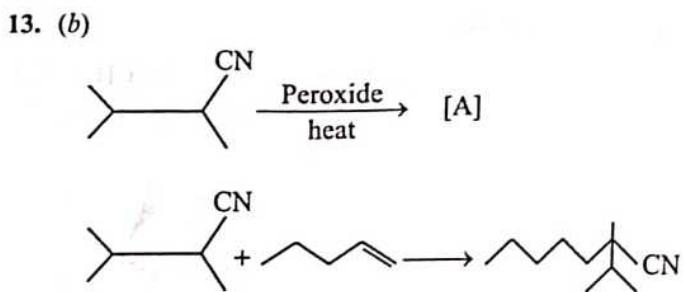
Turbidity within 5 min.  
(Lucas Reagent Test)



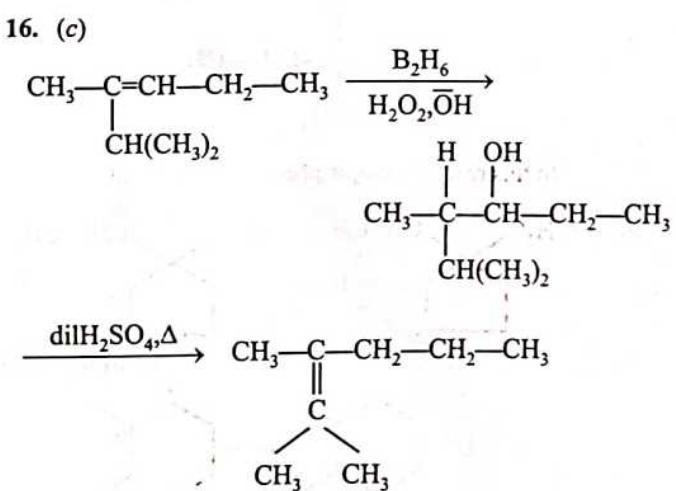
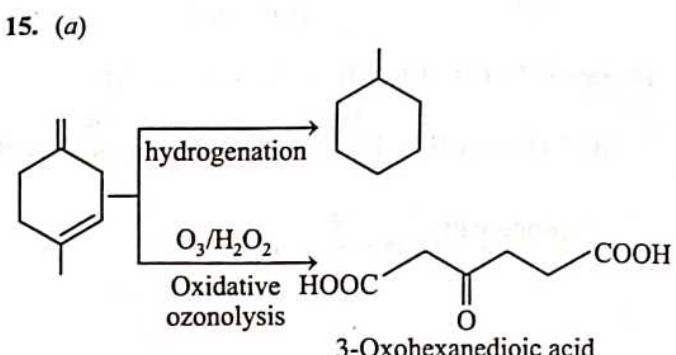
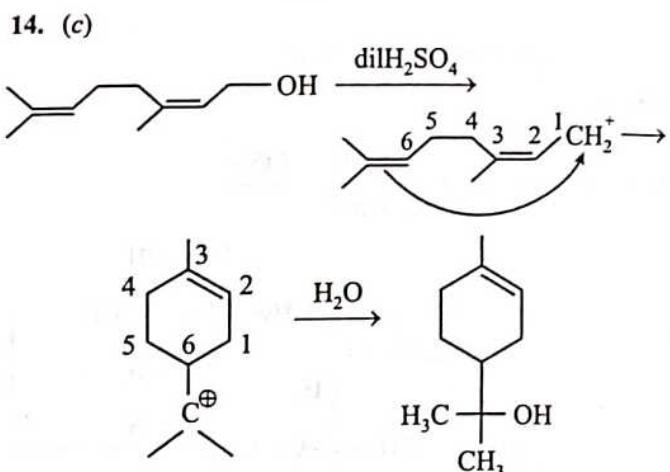
10. (d) C gives Hoffmann product.



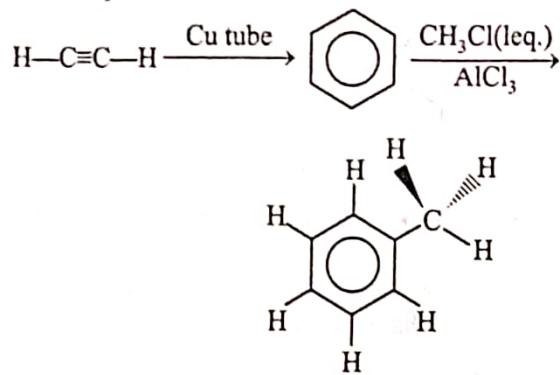
12. (c) Vinyl halides and aryl halides do not give Friedel craft's reaction.



[A] Would be more stable radical and undergoes radical addition to form [B].

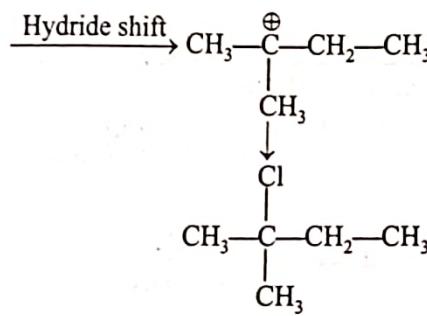
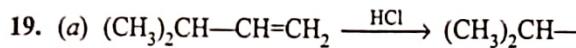
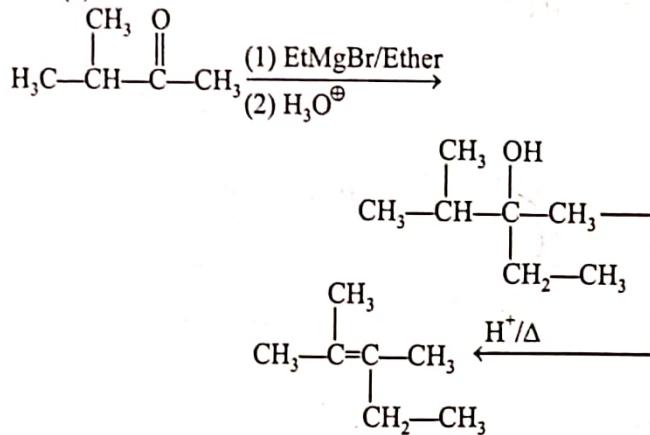


17. [13.00 to 13.00]

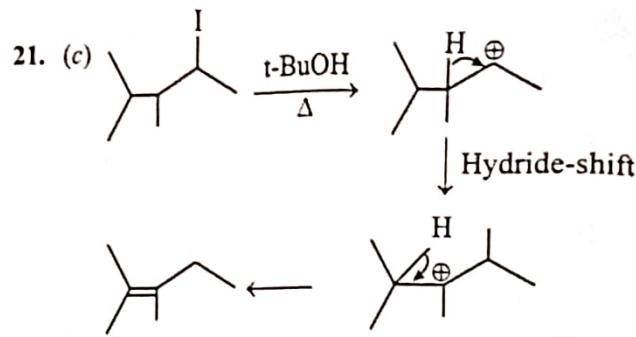
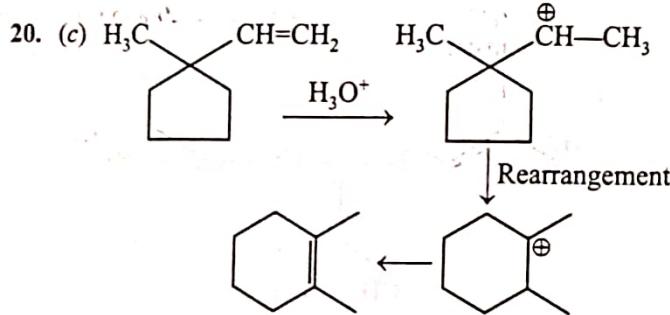


Number of atoms in one plane = 13.

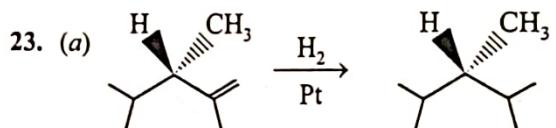
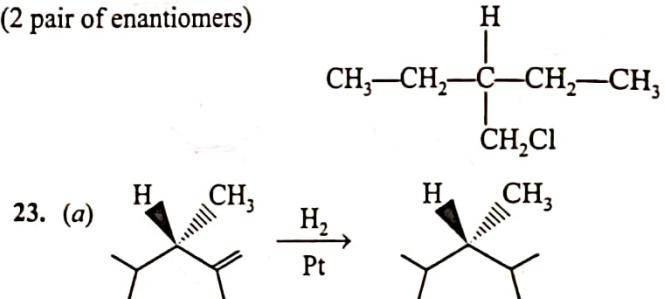
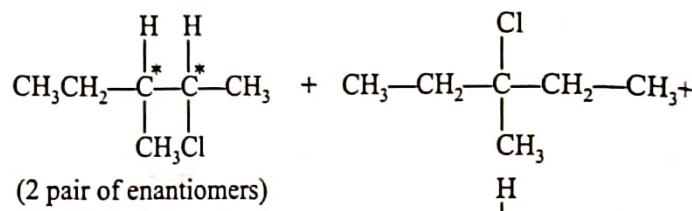
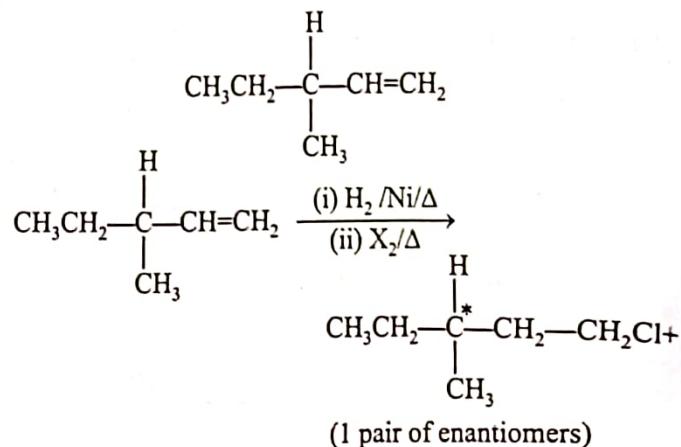
18. (b)



In this reaction, major product is not chiral.

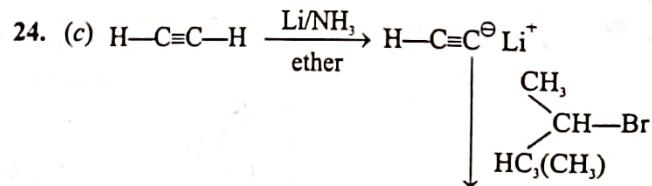


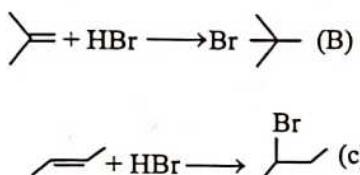
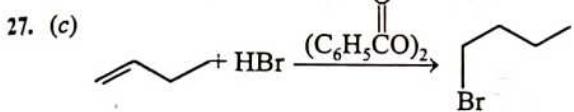
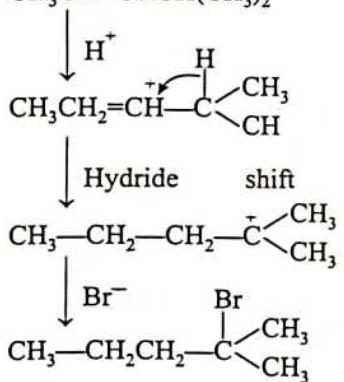
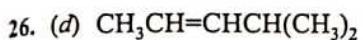
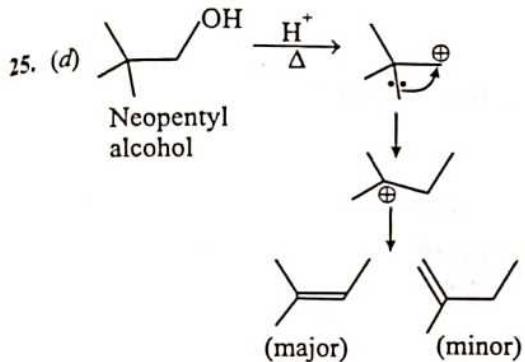
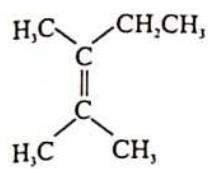
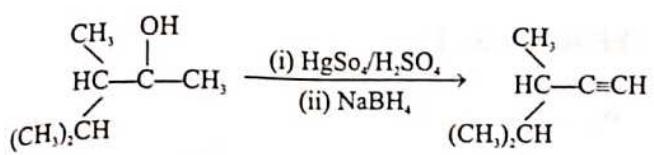
22. [8] The simplest optically active alkene is



Optically inactive  
as no chiral  
centre is there

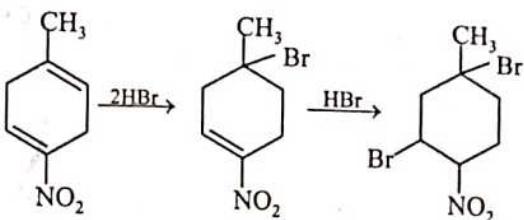
Optically inactive  
as no chiral  
centre is there



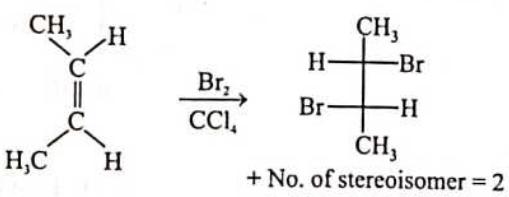


Boiling point decreases with branching  
 $\therefore$  order of B.P. is A > C > B

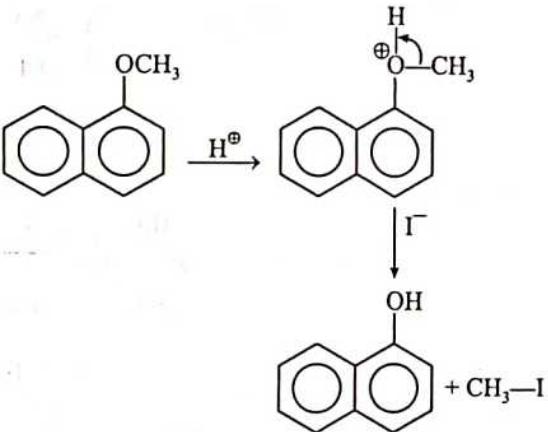
28. (a)



29. [2]



30. (d)



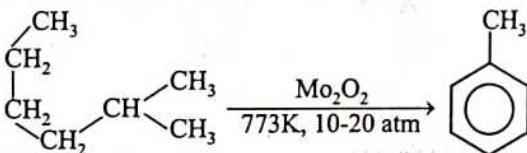
31. (b) Alc. KOH causes elimination

$\text{Pd/BaSO}_4$  - Lindlar's catalyst

BHC is obtained by the addition reaction of  $\text{Cl}_2$  with benzene in presence of U.V.

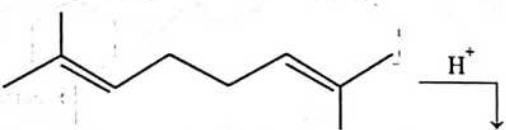
Thin film of polyacetylene can be used as electrode in batteries.

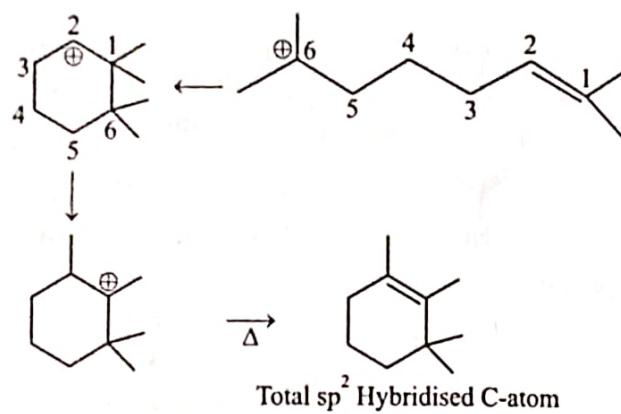
32. (d)



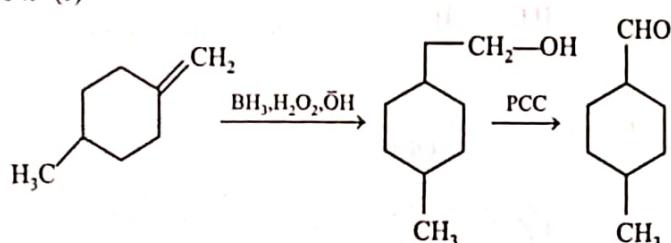
$\text{Mo}_2\text{O}_3$  at 773K temperature and 10-20-atm pressure is aromatising agent.

33. [2]

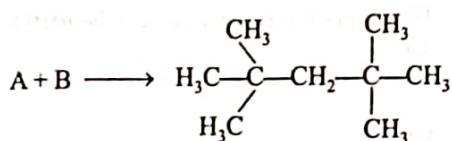
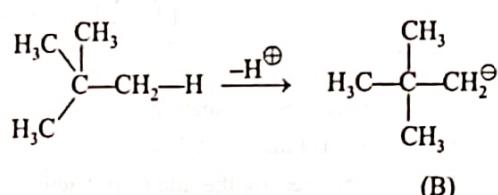
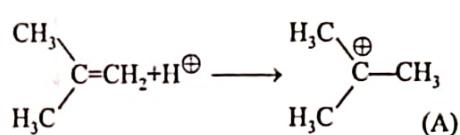




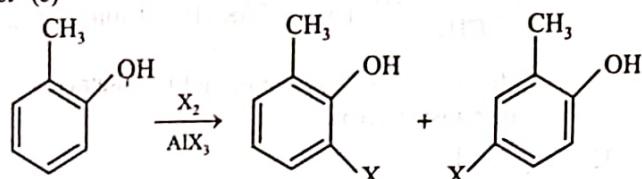
34. (c)



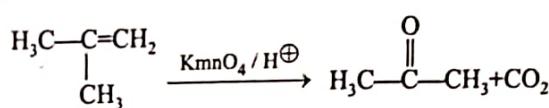
35. (b)



36. (c)

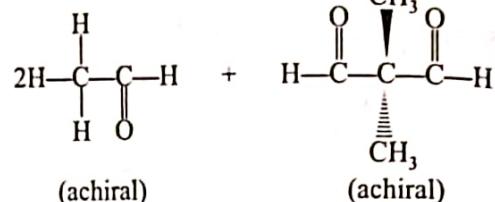
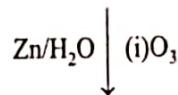
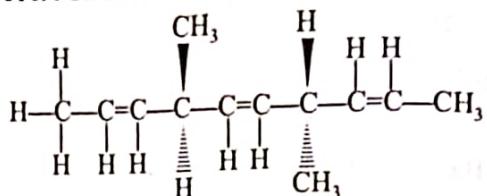


37. (d)



JEE ADVANCED

38. (a)



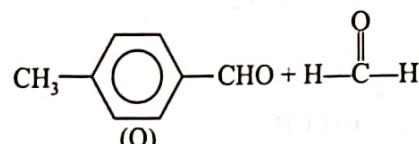
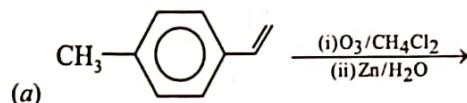
39. (b) Boiling point  $\propto$  Van Der Waals forces  
                           Van Der Waals forces  $\propto$  surface area

$$\text{Surface Area} \propto \frac{1}{\text{Branching}}$$

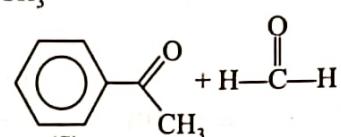
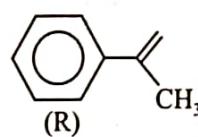
Hence branching leads to lesser surface area which results less boiling point.

Hence B.P. order will be III > II > I.

40. (a,c)

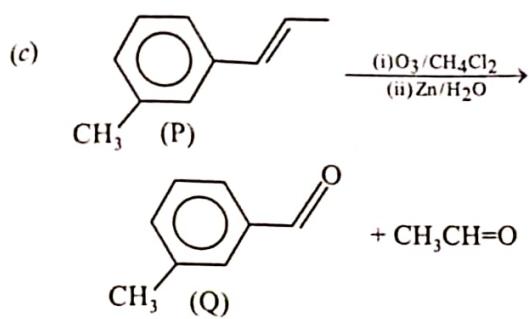


given Cannizzaro reaction  
but no haloform

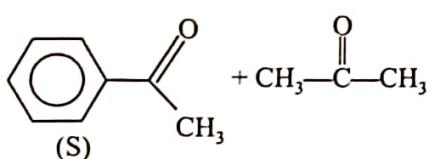
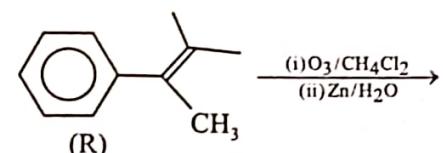


(S)  
No Cannizzaro  
but give haloform

(b) Product of ozonolysis of R is having 9 carbon



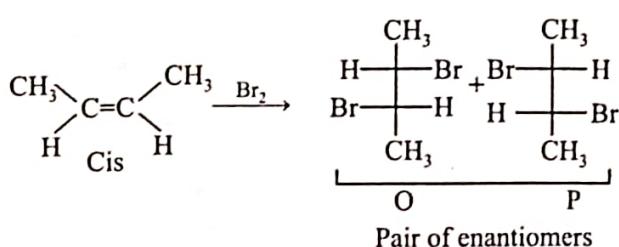
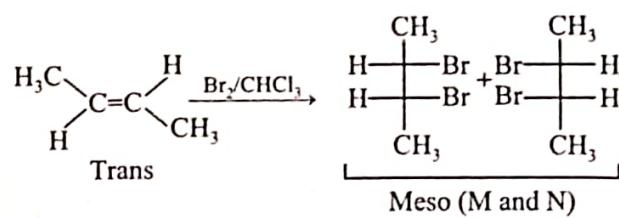
Given Cannizzaro reaction  
but no haloform



No Cannizzaro  
but give haloform

(d) Product of ozonolysis of R is having 9 carbon

41. (b,c)



C is anti Racemic

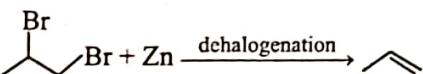
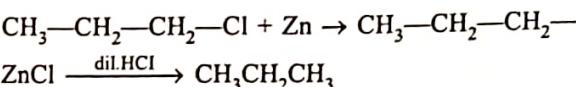
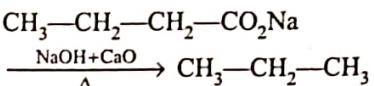
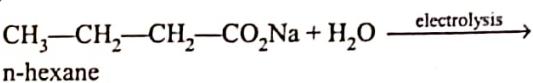
M and N are meso (identical)

O and P are pair of enantiomers

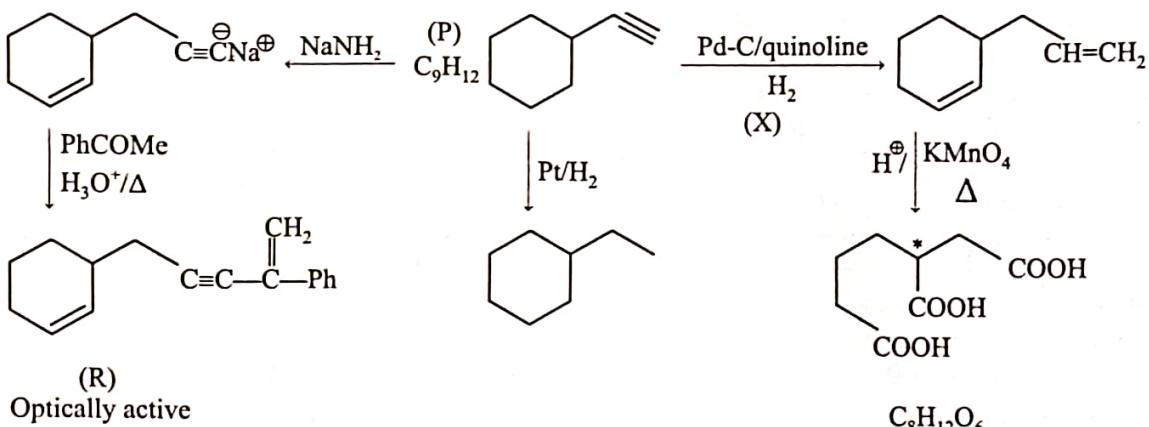
(b) Bromination proceeds through anti addition.

(c) (M and O) and (N and P) are two pairs of diastereomer.

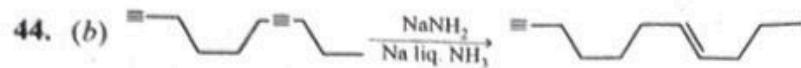
42. (b,c)



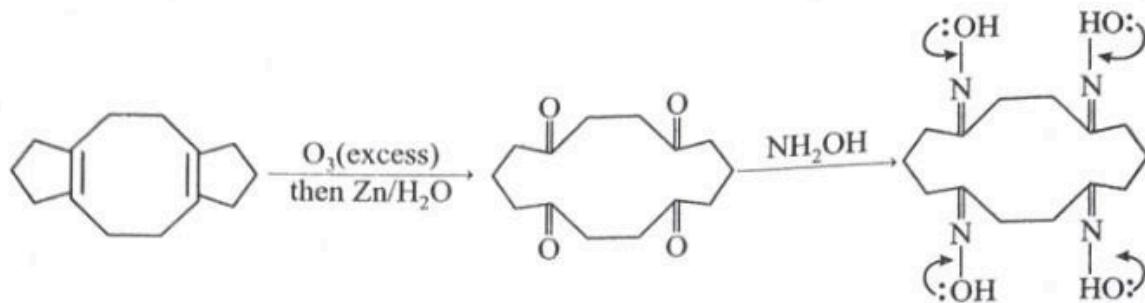
43. (b,c)



$\text{C}_8\text{H}_{12}\text{O}_6$   
Optically active acid  
(Q)



45. [12]



Total 12 atoms are sp<sup>2</sup> hybridized.

## CHAPTER

# 16

# Environmental Chemistry



## Exercise-1 (Topicwise)

1. (c) Domestic waste contains biodegradable pollutants.
2. (a) Tocoferol / Vit E → It has high concentration of antioxidants thus it produces resistance against carcinogens.
3. (b) DDT is an organochlorine compound used as an insecticide in agricultural fields. The major disadvantage of DDT is bioaccumulation or not easily degrading nature, due to fat solubility it is accumulated in living tissues.
4. (c) World environment day is celebrated on 5<sup>th</sup> June.
5. (c) Photo chemical oxidants are the secondary pollutants that are formed when primary pollutants like hydrocarbons, oxides of sulphur, oxides of nitrogen react with sunlight. Nitrous oxide, PAN and acrolein contribute to the formation of the photochemical smog.
6. (c) Freon typically contain hydrocarbon, chlorine or bromine. Thus freons are types of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and connected compounds.
7. (b) Burning of fossil fuels is the main source of pollution of SO<sub>2</sub>.
8. (c) CO<sub>2</sub> is not a kind of pollutant. It is produced naturally by humans and animals as a product of metabolic activities. It is accountable for sustaining the temperature of the atmosphere and plants use CO<sub>2</sub> as an essential element at the time of photosynthesis.
9. (d) Secondary air pollutants are produced photochemically from primary pollutants and are called photochemical oxidants. These occur in photochemical smog. PAN is a major constituent of photochemical smog.
10. (c) H<sub>2</sub> does not have a direct effect on climate. Thus H<sub>2</sub> gas is not a greenhouse gas.
11. (c) The reaction of SO<sub>2</sub> with water molecules present in atmosphere form sulphuric acid which gets precipitated through acid rain. This precipitation can

cause decolouring, cracks and decomposition of the monument.

12. (a) Acid rain is a result of a chemical reaction occurring in a localized area where the concentration of the oxides of nitrogen and sulphur are high.
13. (c) The ozone layer protects us from harmful ultraviolet rays of the sun.
14. (d) The greenhouse effect can be defined as the capture and re-radiation of the infrared by the tropospheric gases like O<sub>3</sub>, CO<sub>2</sub>, water vapours and dust.
15. (b) UV radiations cause skin cancer.
16. (c) Greenhouse effect is related to the global warming caused by the accumulation of greenhouse gases like CO<sub>2</sub>, CH<sub>4</sub> etc.
17. (b) CFCs reach the stratosphere and break when exposed to the UV rays. This releases the reactive chlorine which further reacts with ozone to form simple oxygen.
18. (a) UV rays cause photochemical splitting of O<sub>2</sub> molecules in the stratosphere. The nascent oxygen (O) combines with molecular oxygen to form ozone.
19. (b) Hydroelectric power plants are powered by water. This is a clean fuel source, as it won't pollute the air like other power plants that burn fossil fuels such as coal or natural gas.
20. (a) CO is harmful to human beings. This is because the haemoglobin found in the human blood has a very great affinity for CO as compared to O<sub>2</sub>. Thus it competes with O<sub>2</sub> for haemoglobin.
21. (d) Abundance of the nutrients like phosphate, nitrates results in the enrichment of an ecosystem like pond, lake and cause algal bloom.
22. (a) Intake of water contaminated with nitrates can cause the blue baby syndrome, (the O<sub>2</sub> carrying capacity of the blood decreases gradually).
23. (b) Minimata disease is caused by mercury poisoning in water. It affects the patient's brain, causing, impairment of functions like speech, thoughts, vision etc.

24. (d) Methaemoglobinemia caused by the decreased ability of blood to carry vital  $O_2$  around the body. One of the most common causes is nitrate in drinking water.
25. (a) BOD is biochemical oxygen demand.
26. (d) DDT is an insecticide used in agriculture. It is non-biodegradable in nature. It cannot degrade with the help of microbes. So, it starts accumulation and accumulated in the form of ultimate consumer of food chain.
27. (a) Chlorinated hydrocarbon is synthetic chemicals used as insecticides. They are stored in the body as fat reserves and hence remain in the environment for long period of time after application.
28. (b) Noise pollution is measured in decibels.
29. (a) Biodegradable pollutant is sewage.
30. (c) CO is present in highest concentration in exhaust emission.
31. (a) The best method to determine the quantity of organic pollutants in water is by measuring BOD (the amount of  $O_2$  dissolved by aerobic bacteria growing on the organic material present in a water sample at a specific temperature over a specific time period).
32. (a) Dental fluorosis (also termed mottled enamel) is an extremely common disorder, characterized by hypomineralization of tooth enamel caused by ingestion of excessive fluoride during enamel formation.
33. (a) Chlorine treatment of water is a process of adding chlorine to drinking water and to kill parasites, bacteria and viruses.
34. (a) Pollution is rising due to due to automobiles and industries.
35. (a) The sudden mass death of water animals mainly fishes occurs due to the depletion of oxygen in the water body. Thus more likely in case of Eutrophic lake.
36. (d) Discharge of untreated sewage into streams which contains high quantity of nutrients induce the disproportionate growth of algae causing eutrophication which results into depletion of dissolved oxygen in the water.
37. (a) Jaundice is caused by the intake of contaminated water.
38. (b) The pollutants chlorofluorocarbons are the major source of air pollution contributed by aerosols.
39. (d) Acid rain is caused by large-scale emission of acidic gases into the atmosphere from thermal power plants, industries, and automobiles. The most common ones are  $SO_2$ ,  $NO_2$  etc.
40. (a) The basic component of smog is  $O_3$  and PAN.
41. (a) Discharge of untreated sewage, surface run-off water from agricultural fields, and industrial wastes leads to eutrophication and explosive growth of plankton and blue green alga. This increases turbidity and reduces levels of dissolved oxygen.
42. (b) Waste which cannot be decayed as well as decomposed by the environment acts as a source of pollution. Thus non biodegradable chemicals are the most harmful type of environment pollutants.
43. (d) Freons contains chlorine atoms, these chlorine atoms makes chemical bonding with ozone and thus results in ozone destroy and generates ozone-hole in space.
44. (c) The  $CO_2$  content in atmospheric air is about 0.034%.
45. (c) In coming year, skin related disorder will become very common due to depletion of ozone layer, thinning of the ozone layer increases the number of UV radiations reaching the earth's surface.
46. (c) The term biomagnification refers to the increase in the concentration of nondegradable pollutants as they pass through food chain.
47. (a) CO exerts a harmful effect because it is respiratory inhibitor.
48. (d)  $CO_2$  and water vapours are not direct atmospheric pollutant.  $CO_2$  is required by plants to carry on photosynthesis.
49. (c) The concentration of DDT increases, as it moves or travels along the food chains. Its concentration is maximum in top trophic level. This process is called biomagnification.
50. (a) Lead (Pb) is the most hazardous metal pollutants of automobile exhausts. It affects central nervous system and distorts the red blood corpuscles.

## O Exercise-2 (Learning Plus)

- (a)  $CO_2$  absorbs and stores the energy near the earth's surface when incoming solar radiation is reflected back to the space. If there is no  $CO_2$  then there would be no absorption of solar energy and hence the temperature of earth's surface would be less than the present level.
- (b) Gas responsible for bhopal tragedy of 1984 was Methyl isocyanate.
- (a) Greenhouse affect refers to warming of earth's surface.
- (a) The main source of aerosols is the emission of jet planes, where fluorocarbon ( $CF_2Cl_2$ ) are used.
- (c) The minimata disease in Japan was caused through the pollution of water by mercury.
- (b) Excess amounts of fluoride ions in drinking water can cause dental fluorosis, skeletal fluorosis, bone damage etc.
- (b) The greater an organism's trophic level in a food chain, the higher the level of concentration of DDT in its body. Thus higher concentration is it to be seen in top carnivores.
- (c) Biomagnification happens because a toxic substance accumulated by an organism cannot be metabolized or

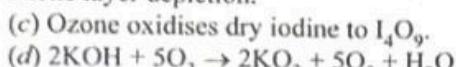
- excreted, and it is passed on to the next higher trophic level. In an aquatic ecosystem, birds are at the highest trophic level.
9. (c) Lichens are very good pollution indicators as they do not grow in  $\text{SO}_2$  polluted environments.
  10. (a) Eutrophication is caused by increase nutrient concentration leading to plentiful growth of simple plant life.
  11. (a) Increase asthmatic attacks in certain seasons are related to inhalation of seasonal pollen.
  12. (d)  $\text{SO}_2$  pollution is indicated by usnea (lichens) as lichens do not grow in  $\text{SO}_2$  environment.
  13. (c) The food chain with the organism given in question is phytoplankton  $\rightarrow$  Crab  $\rightarrow$  Eel  $\rightarrow$  sea gull.  
where the top carnivore of the fourth trophic level will have the highest concentration of DDT.
  14. (b) Dissolved  $\text{O}_2$  is also needed for the decomposition of organic matter. That is why fish die in water bodies polluted by sewage due to reduction in dissolved  $\text{O}_2$ .
  15. (c) When huge amount of sewage is dumped into a river the BOD will increase.
  16. (b) Fluorine water pollutant causes brittleness of teeth.
  17. (c) Measurement of the rate of  $\text{O}_2$  in unit volume of water over a period of time is done to find out Biochemical Oxygen demand.
  18. (a) Sewage discharge in water bodies leads to organic loading or occurrence of excess organic matter inside water body. Its putrefaction decreases dissolved oxygen leading to competition for oxygen among fishes.
  19. (b) Eutrophication causes reduction in dissolved oxygen.
  20. (c) Photochemical smog occurs in day time whereas the classical smog occurs in early morning hours.
  21. (c) Chlorine nitrate which is found in the stratosphere causes break down of the ozone layer.
  22. (a) Main cause of ozone decay is CFCs.
  23. (c) It is beneficial because ozone cuts out the ultraviolet radiation of the sun.
  24. (d) In Antarctica ozone depletion is caused due to the formation of chlorine nitrate.
  25. (b) Ozone layer protects human beings on earth from the harmful effect of ultraviolet radiations coming from sun.
  26. (d) CFCs are called freon.
  27. (a) CFCs are chemically most stable, colourless, odourless and harmless gases.
  28. (b)  $\text{Cl}^\bullet$  obtained from CFCs reacts with  $\text{O}_3$  present in stratosphere.
  29. (b) During the Antarctic winter, when polar stratospheric clouds become widespread, chemical reactions convert less reactive forms of chlorine into large amounts of highly reactive forms.
  30. (b) Eutrophication is a source of water pollution. It occurs when water is high in nutrients.
  31. (c) The global warming of the earth's surface is mainly due to deforestation rather than reforestation.
  32. (a) Hydrocarbon are primary precursors while  $\text{O}_3$ , PAN are secondary precursors of photochemical smog.
  33. (c) Photochemical smog can be reduced by using catalytic converter in the automobiles and plantation of certain plants like pinus, juniperus, vitis etc.
  34. (c) CFCs gets broken by the action of UV radiation coming from the sun and produce  $\text{Cl}^\bullet$  radicals  

$$\text{CF}_2\text{Cl}_2 \xrightarrow{\text{UV}} \text{CF}_2\text{Cl}^\bullet + \text{Cl}^\bullet$$
  35. (a) Photochemical smog has high concentration of oxidising agents rather than reducing agents and is, therefore, called as reducing smog.
  36. (d) Soot particles have diameter of about 5nm,  $\text{H}_2\text{SO}_4$  fog particles have size of 500-1000 nm, fly ash particles have diameter of  $5 \times 10^5$  nm  
So, (a), (b) and (c) are correct.

### Exercise-3 (JEE Advanced Level)

1. (a,c,d) Photochemical smog causes headache, corrosion of painted surface, extensive damage to plant life.
2. (c,d)  $\text{NO}_2$  is more harmful as compared to NO. Acid rain contains mainly dissolved carbon dioxide, sulphur dioxide and nitrogen oxides.
3. (a,b,c) Particles have a diameter of about 5mm.  $\text{H}_2\text{SO}_4$  fog particles have size of 500 – 1000 nm.
4. (a,c) Sodium chlorate and sodium arsenite are weedicides while DDT and BHC are pesticides.
5. (a,d) The main cause of ozone depletion is the presence of chlorine containing gases and oxides of nitrogen.
6. (a,b,c) Incineration, dumping and anaerobic digestion by microbes are three important methods used for the disposal of sludge.
7. (a,b,c) Cadmium, lead and mercury are toxic metals.
8. (a,b,c,d) Carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), Nitrous oxide ( $\text{N}_2\text{O}$ ), ozone ( $\text{O}_3$ ) and water vapours are greenhouse gases present in earth's atmosphere.
9. (d) Gaseous CFCs slowly rise into the stratosphere, are broken down by strong ultraviolet radiation, release chlorine atoms and then react with ozone molecules.
10. (d) Ozone is preferred over chlorine gas because it avoids the unpleasant smell and taste of chlorine gas.
11. (a) The dark colour of ozone is due to intense absorption of red light.

ozone layer depletion.



12. (d) DDT, aldrin and dieldrin are non-biodegradable pesticides.  
 13. (d) Sodium arsenite, sodium chlorate and triazine all are herbicides.  
 14. (d) BHC, malathion and chlorinated hydrocarbon are insecticides.  
 15. (a)

Acid rain	Oxides of nitrogen, oxides of sulphur
Green house effect	Carbon dioxide
Ozone hole	Oxides of nitrogen, CFCs
Eutrophication	Phosphate fertilizer i.e. plant nutrient (excess).

16. (c)

Classical smog	$SO_2$
Photochemical smog	$NO_2$
Particulate Pollutants	Bacteria, Smoke, $Fe_3O_4$
Gaseous pollutants	$SO_2, NO_2$

17. (d)

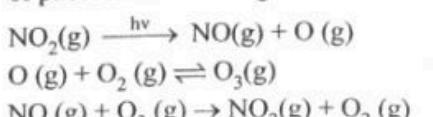
Peroxy acetyl	Photochemical smog
Polycyclic	Carcinogens Molecules
Hg compounds	Minamata disease nitrate
IR active	Global warming aromatic hydrocarbons

## Exercise-4 (Past Year Questions)

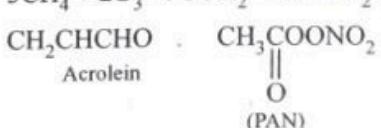
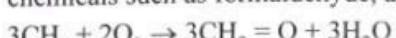
### JEE MAIN

1. (c) Concentration of nitrate is maximum.  
 2. (b)  $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2] + 2F^- \xrightarrow{(drinking water upto 1 ppm)}$   
 $[3Ca_3(PO_4)_2 \cdot CaF_2] + 2OH^-$   
 (Harder teeth enamel)  
 3. (c)  $CH_4$  is not present in stratosphere.  
 4. (a)  $N_2$  Molecule has minimum role in the formation of photochemical smog. While  $CH_2 = O$ ,  $O_3$  and  $NO$  has major role. When fossil fuels are burnt, a variety of pollutants are emitted. Two of them are hydrocarbons

(unburnt) and  $NO$ . When these pollutants build upto high levels, a chain reaction occurs from their interaction with sunlight. The reactions involved in the formation of photochemical smog are as follows:



$O_3$  reacts with unburnt hydrocarbons to produce chemicals such as formaldehyde, acrolein and PAN.

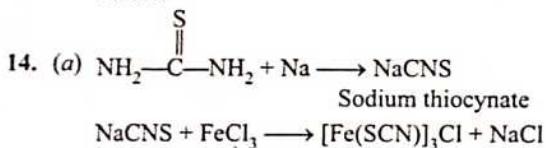


5. (c)  $SO_2$  gas causes stiffness of flower buds.  
 6. (a) In ozone layer the wavelength of U.V radiation is 300 – 340 nm.  
 7. (d) Freons (CFC's) are not common components of photochemical smog.  
 8. (b) Acid rain reacts with marble. Hence, the Taj Mahal which is made up of marble is discoloured.  
 9. (a) The upper stratosphere consists of ozone ( $O_3$ ), which protect us from harmful ultraviolet (UV) radiations coming from sun.  
 10. (c)  
 11. (d) Excessive release of  $CO_2$  into the atmosphere results in global warming.  
 12. (d) Nitrogen oxides and hydrocarbons (unburnt fuel) are primary pollutant that leads to photochemical smog.  
 13. (c) It's a fact, the layer of atmosphere between 10km to 50km above sea level is called as stratosphere.  
 14. (c) Troposphere is the lowest region of atmosphere bounded by Earth beneath and the stratosphere above where most of the clouds form and where life form exists.  
 15. (a) Photochemical smog occurs in warm (sunlight) and has high concentration of oxidising agent therefore it is called photochemical smog/oxidising smog.  
 16. (c) Fact based  
 17. (b) The permissible level in ppm unit is  
 $Fe = 0.2$   
 $Mn = 0.05$   
 $Cu = 3$   
 $Zn = 5$   
 $Mn$  is higher  
 18. (c) In cold water, dissolved oxygen can reach a concentration upto 10 ppm.  
 19. (a) More polluted water has high biological oxygen demand.  
 20. (b)  $CO_2$ ,  $H_2O$  vapours CFC'S and  $O_3$  are green house gases.  
 21. (c) The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical Oxygen Demand (BOD).



## **Exercise-1 (Topicwise)**

1. (d) In sublimation a solid substance changes into vapour form directly.
  2. (c) Boiling point of methanol & acetone is very close to each other.
  3. (c) Turpentine oil is a mixture of volatile & non volatile components so it is not mixed with water easily.
  4. (d) Chromatography is used for the purification of organic compound whose phase is either solid, liquid or gas.
  5. (b) Steam distillation is applied for separation of those compounds which are steam volatile & insoluble in water.
  6. (d) Distillation is not used in evaporation process.
  7. (b) Same for the purification, we use steam distillation.
  8. (d) Chromatography is used for the separation of small sample of mixture of plant pigments & dye stuffs.
  9. (d) Azeotropic mixture has constant or same boiling point.
  10. (c) It is placed between the flask containing the mixture & adapter in fractional distillation.
  11. (b) It can be purified by vacuum distillation.
  12. (d) It is purified by sublimation.
  13. (c) Hydrazine does not contain C so does not give blue colour.



15. (b) Thiourea will give red colour with  $\text{FeCl}_3$ .

16. (d) This test is used for presence of halogens, nitrogen & sulphur.

17. (c) It does not contain C.

18. (b) When covalently bonded  $\text{N}_2$  is fused with Na it transforms into  $\text{NaCN}$ .

19. (c) Sodium extract +  $\text{CH}_3\text{COOH} \rightarrow (\text{CH}_3\text{COO})_2\text{Pb}$   
 $\downarrow$   
 Black ppt  
 $(\text{PbS})$

It shows the presence of sulphur in organic compound.

It shows the presence of sulphur in organic compound.

20. (a)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  is responsible for the blue colour.

21. (d) The Beilstein test is a simple qualitative chemical test for organic halides.

22. (a) 0.233 g of  $\text{BaSO}_4$  contains  $\frac{32 \times 0.233}{23.3}$  g of S

$$\% \text{ S} = \frac{32 \times 0.233 \times 100}{233 \times 0.32} = 10\%$$

23. (a) In Duma's method  $\text{N}_2$  gas is collected over nitrometer.

24. (b)  $\text{CuSO}_4$  acts as catalytic agent.

25. (c) Nitrogen can be estimated by both kjeldahl's & duma's method.

26. (b) Nitrogen present in the organic compound is estimated as  $\text{NH}_3$  in kjeldahl's method.

27. (c)  $\text{X} + \text{NaOH} \longrightarrow \text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}$   
 Amount of  $\text{NH}_3$  generated =  $\frac{200 \times 1}{1000} \times 14 \text{ gm} = 2.8 \text{ gm}$   
 $\% \text{ N} = \frac{2.8}{6} \times 100 = 46.67\%$

28. (a)  $\text{Mg}(\text{ClO}_4)_2$  & anhydrous  $\text{CaCl}_2$  used as dessicant because they are distinct water absorbents.

29. (c) 0.17 g of  $\text{NH}_3$  has =  $\frac{14}{17} \times 0.17 = 0.14 \text{ g of N}$

$$\begin{aligned} \% \text{ N} &= \frac{\text{mass of N}}{\text{mass of compound}} \times 100 \\ &= \frac{0.14}{28} \times 100 = 50\% \end{aligned}$$

## **Exercise-2 (Learning Plus)**

- (b) 
$$\% \text{ C} = \frac{\text{molar mass of C} \times \text{mass of CO}_2 \text{ (given)}}{\text{mass of compound} \times \text{mass of CO}_2}$$
  - (a) Benzoic acid reacts with base & become benzoate which is soluble in water & other polar solvent.
  - (a) Differential extraction based upon different solubilities.

$$4. (b) \% \text{ H} = \frac{2 \times \text{mass of water}}{1.8 \times \text{mass of compound}} \times 100$$

5. (d) Column chromatography is used to isolate a single chemical compound from a mixture.

6. (b) Silical gel has high specific surface area which allows to adsorb water readily.

7. (b) Aniline can be purified by steam distillation since it boils at a temp. of 371.5K in the presence of steam.

8. (b) It is used for steam volatile compounds.

9. (b) In steam distillation, the vapour pressure of the volatile compound is less than the atmospheric pressure.

10. (b) It is used for separation of compound.

11. (a) Boiling point of a liquid increases with increase in pressure.

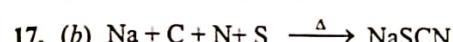
12. (d) P is estimated as  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$  &  $\text{Mg}_2\text{P}_2\text{O}_7$ .

13. (c) In vacuum distillation liquids are distilled by avoiding decomposition at low temp.

14. (b) Naphthalene is volatile and benzoic acid is non-volatile. Hence they can be separated by sublimation.

15. (c) The red colour is due to formation of  $\text{Fe}(\text{CNS})_3$ .

16. (a) In Carius method Cl is converted into  $\text{AgCl}$ .



18. (b) Fractional crystallization is the one where we can differentiate solids having different solubilities.

19. (b) Sulphanilic acid contains N, S & C which give  $\text{NaSCN}$ .  $\text{NaSCN}$  with  $\text{FeCl}_3$  gives red blood colour due to formation of  $\text{Fe}(\text{SCN})_3$ .

20. (d) Kjeldahl's method is not applicable for compounds containing N as nitro, azo & compounds having N are directly attached to the ring.

21. (a) Chromatography is the most useful & latest technique of separation & purification of organic compounds.

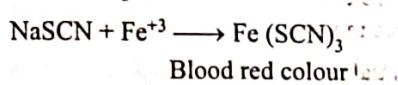
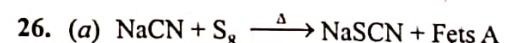
$$22. (a) \% \text{ C} = \frac{12}{44} \times \frac{\text{mass of CO}_2 (\text{gm})}{\text{mass of compound (gm)}} \times 100$$

$$\% \text{ H} = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O (gm)}}{\text{mass of compound (gm)}} \times 100$$

$$23. (b) \% \text{ P} = \frac{62}{222} \times \frac{\text{mass of Mg}_2\text{P}_2\text{O}_7 (\text{gm})}{\text{mass of compound}} \times 100$$

24. (a) This indicates presence of S.

25. (b) Yellow colour indicated the presence of P.



$$27. (d) \frac{\text{mass of organic compound}}{\text{mass of AgBr}} = \frac{\text{molar mass of organic compound}}{\text{molar mass of AgBr}}$$

$$\text{molar mass of organic compound} = \frac{0.15 \times 188}{0.12}$$

$$\% \text{ of bromine in organic compound} = \frac{\text{molar mass of Br}}{\text{molar mass of organic compound}} \times 100$$

$$= \frac{80 \times 0.12}{0.15 \times 188} \times 100$$

$$= 34.04\%$$

28. (b) Miscible mixture of  $\text{C}_6\text{H}_6 + \text{CHCl}_3$ , can be separated by distillation method due to the significant difference in their boiling points, boiling point of Benzene is  $80.1^\circ\text{C}$  while that of chloroform is  $61.2^\circ\text{C}$ .

29. (c) O-nitrophenol is a weaker acid than  $\text{H}_2\text{CO}_3$ .

30. (c) It is an example of partition chromatography.

31. (b) Substances are distributed between a stationary phase & a mobile phase.

32. (b) Addition of  $\text{K}_2\text{SO}_4$  increases the boiling point of  $\text{H}_2\text{SO}_4$ .

33. (d) Hydrogen of the organic compound ignites to form  $\text{H}_2\text{O}$ .

34. (c)

Element	%	Atomic ratio	Simplest ratio
C	64.3	$64.3/12 = 5.4$	3
H	7.2	$7.2/1 = 7.2$	4
O	28.5	$28.5/16 = 1.8$	1

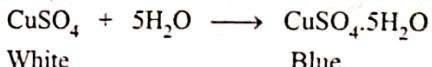
The empirical formula of compound is  $\text{C}_3\text{H}_4\text{O}$ .

35. (c) Amines are basic in nature. Therefore, aniline reacts with  $\text{HCl}$  to form a salt which dissolves in water. Hence, aniline can be separated from benzene by using  $\text{HCl}$ .

### Exercise-3 (JEE Advanced Level)

1. (a) Hair contains amino acids which upon fusion with soda-lime ( $\text{NaOH} + \text{CaO}$ ) evolve  $\text{NH}_3$ .

2. (d) Anhydrous  $\text{CuSO}_4$  turns blue in presence of water.



3. (b) The first distillation product of petroleum is petroleum ether. Note that natural gases comes out first during extraction of petroleum.

4. (c) Paper chromatography is a liquid-liquid partition chromatography.

5. (d) Aryl halides are not hydrolyzed by alcoholic silver nitrate.

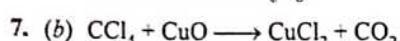
6. (d)  $C = \frac{92.3}{12} = \frac{7.69}{7.69} = 1$

$$H = \frac{7.69}{7.69} = 1$$

Empirical formula  $\rightarrow C_1H_1$

X is alkyne so it is  $C_2H_2$

Y is Benzene  $\rightarrow C_6H_6$



8. (d)  $C : H : O = \frac{24}{12} : \frac{4}{1} : \frac{32}{16} = 1 : 2 : 1$

9. (c) In kjeldahl's method all the nitrogen is converted into  $(NH_4)_2SO_4 \cdot K_2SO_4$ .

10. (a) In estimation of C, organic compound is heated with CuO.

11. (b,c,d)

Thiourea ( $NH_2CSNH_2$ ) contains both N and S. Hence depending upon the amount of Na used, all the three, that is  $Na_2S$ ,  $NaCN$  and  $NaCNS$  are formed but not  $Na_2SO_4$ .

12. (b) It gives red colour when it has both N & S.

13. (b)  $\%C = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of O.C.}} \times 100$

$$= \frac{12}{44} \times \frac{0.147}{0.2} \times 100 = 20$$

$$\%H = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of O.C.}} \times 100$$

$$= \frac{2}{18} \times \frac{0.12}{0.2} \times 100 = 6.7$$

$$\%O = 100 - (20 + 6.7) = 73.3$$

14. (a,b,d)

Fractional distillation is used for separating liquids that have difference in boiling point less than 25K.

15. (a,b,c)

Steam distillation is used to separate substance which are steam volatile and immiscible with water.

16. (a,b,d)

Urea, acetamide give this test.

17. (a,b,d)

As  $FeCl_3$  is added as a reagent and not formed during the reaction.

18. (b,c,d)

$CuCl_2$ ,  $C_6H_5N$  and thiourea give this test.

19. (a,b,d)

Kjeldahl's method is not applicable to nitro or diazo groups.

20. (b,c)

In crystallization solute should be more soluble in the hot solvent than in the cold.

21. (a,d)

Distillation is used when substance has non volatile impurities & boils without decomposition.

22. (a,b,c,d)

All are the correct for differential extraction.

23. (a,b,c)

Chromatography is used to separate compounds having similar boiling points.

24. (a,b)

N and S are confirmed

25. (c) Br can be identify by red. brown fumes.

26. (a,c,d)

In Lassaigne's test substance is not converted into soluble ionic compound.

27. (b)  $\%Cl = \frac{35.5}{108.5 + 35.5} \times \frac{0.287}{0.189} \times 100 = 37.56\%$

28. (c)  $\%S = \frac{32}{233} \times \frac{0.934}{0.243} \times 100 = 52.78\%$

29. (d) All of the above

30. (a) Fact based

31. (a) Fact based

32. (a) Fact based

33. [4] Kjeldahl's method is not used for nitro & diazo compounds.

34. [5] N, S, Cl, Br I can be detected.

35. [7]  $C : H : O = \frac{69.4}{12} : \frac{4.9}{1} : \frac{25.7}{16}$   
 $= 5.78 : 4.9 : 1.61$   
 $= 7 : 6 : 2$

$C_7H_6O_2 \rightarrow$  Empirical formula

36. [5] Empirical formula is  $C_6H_5NO_2$

37. [3] Naphthalene, benzoic acid and anthracene are purified by sublimation.

38. [6]  $\%Cl = \frac{35.5}{143.5} \times \frac{5}{2.561} \times 100 = 47.9$

Element	%	Atomic ratio	Simplest ratio
C	49	49/12=4.1	3
H	2.72	2.72/1 = 2.72	2
Cl	47.9	47.9/35.5 = 1.35	1

$C_3H_2Cl$  is the empirical formula.

$$n = 147/73.5 = 2$$

The molecular formula is  $C_6H_4Cl_2$ .

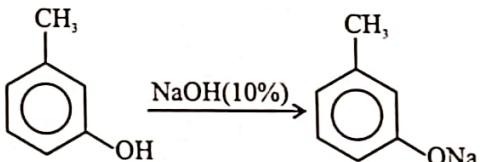


## Exercise-4

### (Past Year Questions)

#### JEE MAIN

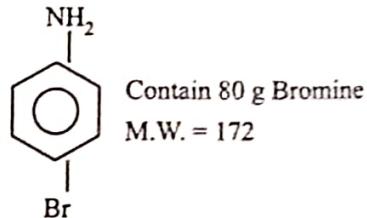
1. (d) Aq.  $\text{NaHCO}_3$  is used to distinguish between phenol & benzoic acid. It does not react with phenol.
2. (a) At atmospheric pressure the boiling point of glycerol is  $290^\circ\text{C}$  so it decomposes before it distills.
3. (d) Kjeldahl's method is not applicable for nitro, diazo & compounds containing N in the ring.
4. (b) Benzaldehyde is an absorbate, alumina is an adsorbent (stationary phase) and acetonitrile is mobile phase.
5. (a) Due to higher density of dichloromethane than water DCM would be the lower layer and water will form the upper layer in the separating funnel.
6. (b)  $\text{H}_2\text{O}$  : Sugar – Recrystallisation  
 $\text{H}_2\text{O}$  : Aniline - Separation by steam distillation  
 $\text{H}_2\text{O}$  : Toluene - Differential extraction
7. (c)  $[\text{C}_x\text{H}_y\text{N}_z] \xrightarrow[\text{method}]{\text{Dumas}} 6\text{CO}_2 + 4\text{H}_2\text{O} + \text{N}_2$   
Moles of  $\text{CO}_2 = 6$ , so moles of C = 6  
Moles of  $\text{H}_2\text{O} = 4$ , so moles of H = 8  
Moles of  $\text{N}_2 = 1$ , so moles of N = 2  
 $\therefore$  Formula is  $\text{C}_6\text{H}_8\text{N}_2$ .
8. (c) Phenols (e.g. m-cresol), being weak acid, are soluble in dil NaOH but insoluble in  $\text{NaHCO}_3$ .



9. (d) In column chromatograph; a solid adsorbent is packed on a column and a solution containing number of solute particles is allowed to flow down the column. The solute molecules get adsorbed on the surface of adsorbent and move through column at different rates based on differential adsorption of the substances on the solid phase.
10. (c) In chromatography,  $R_f$  represents retardation factor.  

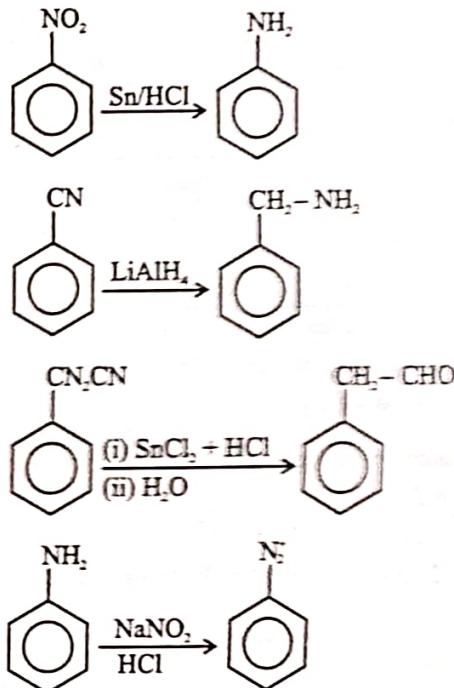
$$R_f = \frac{\text{Distance moved by the substance from baseline}}{\text{Distance moved by the solvent from baseline}}$$
  
 $\therefore$  Higher  $R_f$  value means lower adsorption.
11. (b) Phosphorus is detected in the form of yellow ppt of ammonium phosphate molybdate on reaction with ammonium molybdate.
12. (b) Liquid having lower boiling point comes out first in fractional distillation. Simple distillation can't be used as boiling point difference is very small.

13. (a) Kjeldahl method is not applicable for nitro or diazo groups present in the ring, as nitrogen atom can't be converted to ammonium sulfate under the reaction conditions.
14. (a) Given, 0.172g organic compound showed presence of 0.08g Bromine or 172g organic compound will show 80g Bromine which matches exactly with option (a).



15. (c) Distillation under reduced pressure is done for separating glycerol in soap industries.

16. (c)



Nitro and diazo compounds do not give Kjeldahl estimation of Nitrogen.

17. [50] Mass of organic compound = 1.6 gm

$$\text{Mass of AgBr} = 1.88 \text{ gm}$$

$$\text{Moles of Br} = \text{Moles of AgBr} = \frac{1.88}{188} = 0.01$$

$$\text{Mass of Br} = 0.01 \times 80 = 0.80 \text{ gm}$$

$$\% \text{ of Br} = \frac{0.80 \times 100}{1.60} = 50\%$$

18. (b) Lucas reagent - Conc.  $\text{HCl}/\text{ZnCl}_2$

Dumas method -  $\text{CuO}/\text{CO}_2$

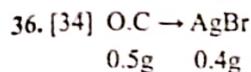
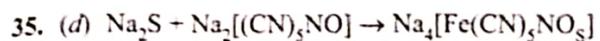
Kjeldahl's method -  $\text{H}_2\text{SO}_4$

Hinsberg test -  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}/\text{aq. KOH}$

19. (d) More polar compound will come out first. The order of polarity in the given compound is acetophenone > benzylidene > aniline.



34. (c) The function of mobile phase is to carry the components present on TLC.



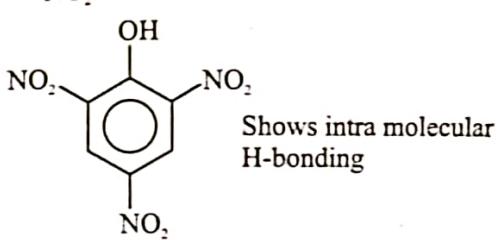
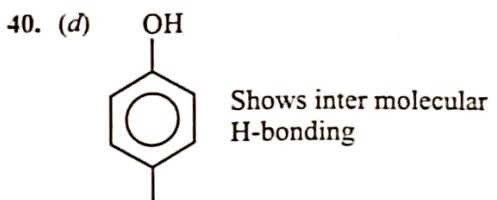
$$\text{moles of Br} = \text{moles of AgBr} = \frac{0.4}{188}$$

$$\% \text{Br} = \frac{\frac{0.4}{188} \times 80}{0.5} \times 100 \\ = 34.04\%$$

37. [64] meq of  $\text{H}_2\text{SO}_4$  used by  $\text{NH}_3 = 12.5 \times 1 \times 2 = 25\%$  of N in the compound  $= \frac{25 \times 10^{-3} \times 14 \times 100}{0.55} = 63.6$   
 $\approx 64\%$

38. [56]  $\% \text{N} = \frac{1.4(\text{N}_1 \text{V}_1)}{\text{mass of organic compound}}$   
 $\% \text{N} = \frac{1.4(2.5 \times 2 \times 2)}{0.25} = 56$

39. [2]  $\frac{R_{f_A}}{R_{f_B}} = \frac{\frac{2.08}{3.25}}{\frac{1.05}{3.25}} = \frac{2.08}{1.05} = 2$



Solvent polarity has been related to  $R_f$  value of nitro compounds.

100 mg p-nitrophenol and picric acid have different  $R_f$  value on silica gel plate.

$\therefore$  Preparative TLC is best to separate 100 mg of para nitrophenol and picric acid.

41. (a) Mass of organic compound = 0.45 gm

Mass of AgBr obtained = 0.36 gm

$$\therefore \text{Moles of AgBr} = \frac{0.36}{188}$$

$$\therefore \text{Mass of Bromine} = \frac{0.36}{188} \times 80 = 0.1532 \text{ gm}$$

$$\% \text{ Br in compound} = \frac{0.1532}{0.45} \times 100 = 34.04\%$$

42. (d) (A) Chloroform + Aniline  $\rightarrow$  Distillation

(B) Benzoic acid + Napthalene  $\rightarrow$  Crystallisation

(C) Water + Aniline  $\rightarrow$  Steam distillation

(D) Napthalene + Sodium chloride  $\rightarrow$  Sublimation

43. (a) Thin layer chromatoatography (TLC) is another type of adsorption chromatography which involves separation of substance of a mixture over a thin layer of an adsorbent coated on glass plate.

A thin layer (about 0.2 mm thick) of an adsorbent at (silica gel) or (Alumina) is spread over a glass plate of suitable size. Hence Assertion (A) is correct and Reason (R) is correct explanation of (A)

44. [22] V = 22.7 ml, T = 280 K

$$P_{\text{total}} = 759 \text{ mmHg}$$

$$P_{\text{N}_2} = 759 - 14.2 = 744.8 \text{ mmHg}$$

$$n_{\text{N}_2} = \frac{744.8 \times 22.78}{760 \times 1000 \times 0.082 \times 280} = 0.00097$$

$$W_{\text{Nitrogen}} = 0.02716$$

$$\% \text{ N} = \frac{0.02716}{0.125} \times 1000 = 21.728$$

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