GRB BOOKS

Dr. P. BAHADUR

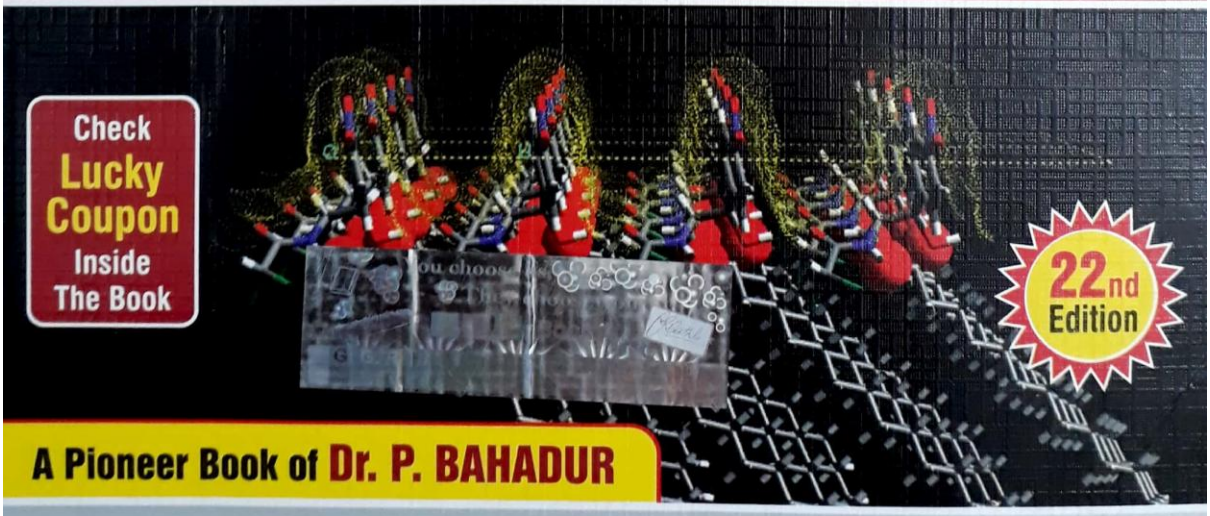
GRB

NUMERICAL CHEMISTRY

A New Pattern Book for

JEE (Main & Advanced)

& All Other Engineering Entrance Examinations

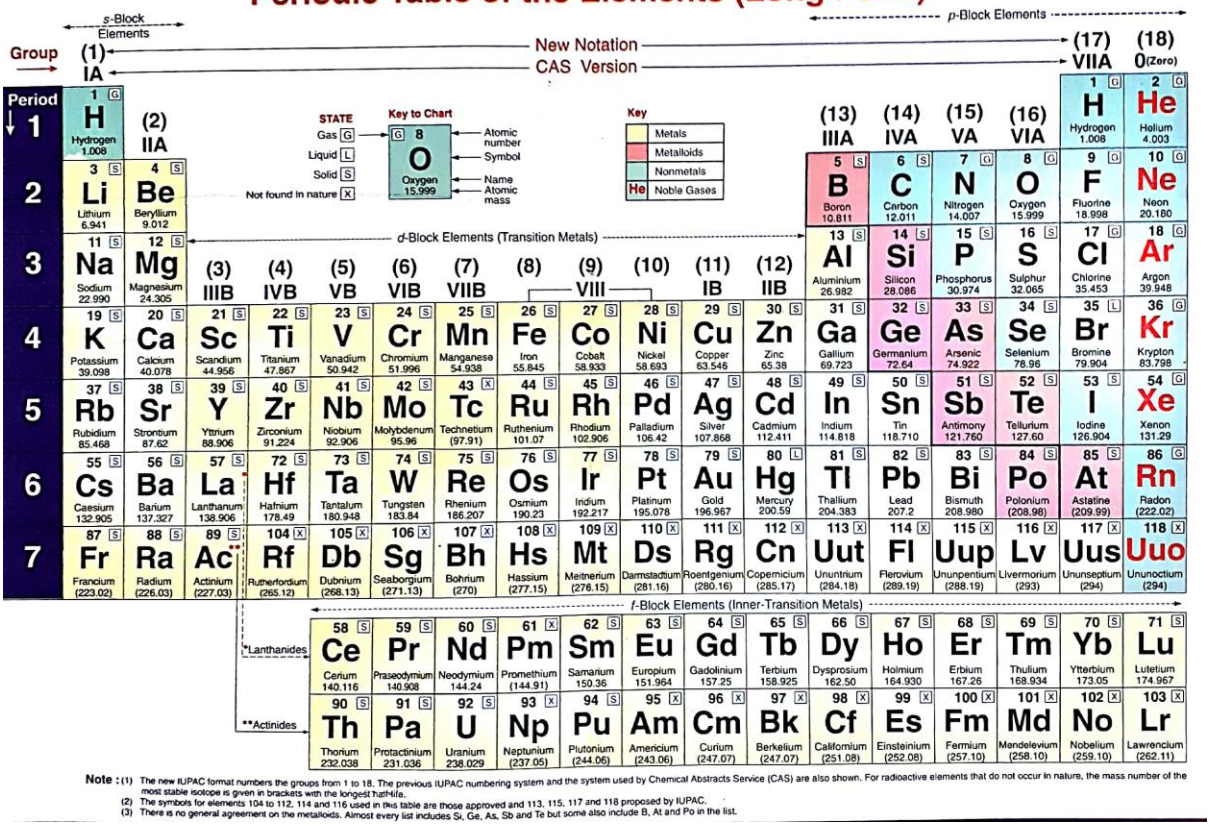


A Pioneer Book of Dr. P. BAHADUR

G. R. BATHLA PUBLICATIONS PVT. LTD.

DELHI

Periodic Table of the Elements (Long Form)



Period	(1) IA	(2) IIA	(3) IIIB	(4) IVB	(5) VB	(6) VIB	(7) VIIB	(8)	(9) VIII	(10)	(11) IB	(12) IIB	(13) IIIA	(14) IVA	(15) VA	(16) VIA	(17) VIIA	(18) 0(Zero)
1	1 G H Hydrogen 1.008																	2 G He Helium 4.003
2	3 S Li Lithium 6.941	4 S Be Beryllium 9.012											5 S B Boron 10.811	6 S C Carbon 12.011	7 G N Nitrogen 14.007	8 G O Oxygen 15.999	9 G F Fluorine 18.998	10 G Ne Neon 20.180
3	11 S Na Sodium 22.990	12 S Mg Magnesium 24.305											13 S Al Aluminium 26.982	14 S Si Silicon 28.086	15 S P Phosphorus 30.974	16 S S Sulphur 32.065	17 G Cl Chlorine 35.453	18 G Ar Argon 39.948
4	19 S K Potassium 39.098	20 S Ca Calcium 40.078	21 S Sc Scandium 44.956	22 S Ti Titanium 47.867	23 S V Vanadium 50.942	24 S Cr Chromium 51.996	25 S Mn Manganese 54.938	26 S Fe Iron 55.845	27 S Co Cobalt 58.933	28 S Ni Nickel 58.693	29 S Cu Copper 63.546	30 S Zn Zinc 65.38	31 S Ga Gallium 69.723	32 S Ge Germanium 72.64	33 S As Arsenic 74.922	34 S Se Selenium 78.96	35 L Br Bromine 79.904	36 G Kr Krypton 83.798
5	37 S Rb Rubidium 85.468	38 S Sr Strontium 87.62	39 S Y Yttrium 88.906	40 S Zr Zirconium 91.224	41 S Nb Niobium 92.906	42 S Mo Molybdenum 95.96	43 X Tc Technetium (97.91)	44 S Ru Ruthenium 101.07	45 S Rh Rhodium 102.906	46 S Pd Palladium 106.42	47 S Ag Silver 107.868	48 S Cd Cadmium 112.411	49 S In Indium 114.818	50 S Sn Tin 118.710	51 S Sb Antimony 121.760	52 S Te Tellurium 127.60	53 S I Iodine 126.904	54 G Xe Xenon 131.29
6	55 S Cs Caesium 132.905	56 S Ba Barium 137.327	57 S La Lanthanum 138.906	72 S Hf Hafnium 178.49	73 S Ta Tantalum 180.948	74 S W Tungsten 183.84	75 S Re Rhenium 186.207	76 S Os Osmium 190.23	77 S Ir Iridium 192.217	78 S Pt Platinum 195.078	79 S Au Gold 196.967	80 L Hg Mercury 200.59	81 S Tl Thallium 204.383	82 S Pb Lead 207.2	83 S Bi Bismuth 208.980	84 S Po Polonium (208.98)	85 S At Astatine (209.99)	86 G Rn Radon (222.02)
7	87 S Fr Francium (223.02)	88 S Ra Radium (226.03)	89 S Ac Actinium (227.03)	104 X Rf Rutherfordium (265.12)	105 X Db Dubnium (268.13)	106 X Sg Seaborgium (271.13)	107 X Bh Bohrium (270)	108 X Hs Hassium (277.15)	109 X Mt Meitnerium (276.15)	110 X Ds Darmstadtium (281.16)	111 X Rg Roentgenium (280.16)	112 X Cn Copernicium (285.17)	113 X Uut Ununtrium (284.18)	114 X Fl Flerovium (289.19)	115 X Uup Ununpentium (288.19)	116 X Lv Livermorium (293)	117 X Uus Ununseptium (294)	118 X Uuo Ununoctium (294)

*Lanthanides	58 S Ce Cerium 140.116	59 S Pr Praseodymium 140.908	60 S Nd Neodymium 144.24	61 X Pm Promethium (144.91)	62 S Sm Samarium 150.36	63 S Eu Europium 151.964	64 S Gd Gadolinium 157.25	65 S Tb Terbium 158.925	66 S Dy Dysprosium 162.50	67 S Ho Holmium 164.930	68 S Er Erbium 167.26	69 S Tm Thulium 168.934	70 S Yb Ytterbium 173.05	71 S Lu Lutetium 174.967
**Actinides	90 S Th Thorium 232.038	91 S Pa Protactinium 231.036	92 S U Uranium 238.029	93 X Np Neptunium (237.05)	94 S Pu Plutonium (244.06)	95 X Am Americium (243.06)	96 X Cm Curium (247.07)	97 X Bk Berkelium (247.07)	98 X Cf Californium (251.08)	99 X Es Einsteinium (252.08)	100 X Fm Fermium (257.10)	101 X Md Mendelevium (258.10)	102 X No Nobelium (259.10)	103 X Lr Lawrencium (262.11)

Note : (1) The new IUPAC format numbers the groups from 1 to 18. The previous IUPAC numbering system and the system used by Chemical Abstracts Service (CAS) are also shown. For radioactive elements that do not occur in nature, the mass number of the most stable isotope is given in brackets with the longest half-life.
(2) The symbols for elements 104 to 112, 114 and 116 used in this table are those approved and 113, 115, 117 and 118 proposed by IUPAC.
(3) There is no general agreement on the metalloids. Almost every list includes Si, Ge, As, Sb and Te but some also include B, At and Po in the list.

GRB

NUMERICAL CHEMISTRY

For JEE (Main & Advanced)
& All Other Engineering Entrance Examinations

By :

Dr. Prakash Bahadur

M.Sc., Ph.D.

Retd., Head of Chemistry Department,
D.A.V. (P.G.) College, Muzaffarnagar (U.P.)

Edited by :

Shalabh Saxena

B. Tech. (Chemical Engg.), Gold Medalist

CONTENTS

PART-A : GENERAL AND PHYSICAL CHEMISTRY

1. Gaseous State 1-53
2. Mole Concept and Equivalent Concept 54-94
3. Atomic Structure 95-138
4. Radioactivity 139-177
5. Periodic Properties, Chemical Bonding and Complexes 178-208
6. Oxidation-Reduction 209-228
7. Electrolysis and Electrochemical Cells 229-281
8. Redox Titrations 282-319
9. Colligative Properties and Solutions 320-362
10. Surface Chemistry 363-380
11. Chemical Kinetics 381-423
12. Chemical Equilibrium 424-477
13. Ionic Equilibria 478-534
14. Conductances of Solution 535-553
15. Thermodynamics 554-587
16. Thermochemistry 588-619
17. Crystallography 620-643

PART-B : ORGANIC CHEMISTRY

18. Quantitative Estimations 644-651
19. Structure and Reaction based Problems 652-823

PART-C : INORGANIC CHEMISTRY

20. Qualitative Estimations 824-911

PART-D : JEE(ADVANCED) MODEL TEST PAPER CHEMISTRY

§ **JEE (Advanced) Model Test Paper Chemistry 1-A** 912-914
Solutions (913)

§ **JEE (Advanced) Model Test Paper Chemistry 1-B** 915-917
Solutions (917)

§ **JEE (Advanced) Model Test Paper Chemistry 2-A** 918-920
Solutions (919)

§ **JEE (Advanced) Model Test Paper Chemistry 2-B** 921-923
Solutions (923)

§ **JEE (Advanced) Model Test Paper Chemistry 3-A** 924-926
Solutions (926)

§ **JEE (Advanced) Model Test Paper Chemistry 3-B** 927-929
Solutions (928)

§ **JEE (Advanced) Model Test Paper Chemistry 4-A** 930-932
Solutions (931)

§ **JEE (Advanced) Model Test Paper Chemistry 4-B** 933-935
Solutions (935)

- **Appendices** 936-945
- **Log Table & Antilog Table** 946-947

18 Quantitative Estimations

Determination of percentage analysis of elements in organic compounds or quantitative estimation of elements in organic compounds :

(1) Estimation of C and H : A known mass of organic compound is burnt in oxygen (Leibig method) and the products H_2O and CO_2 formed are absorbed in conc. H_2SO_4 and $KOH_{(aq.)}$ respectively. The percentage (%) are obtained using the formulae.

$$\% H = \frac{2}{18} \times \frac{\text{mass of } H_2O}{\text{mass of organic compound}} \times 100$$

$$\% C = \frac{12}{44} \times \frac{\text{mass of } CO_2}{\text{mass of organic compound}} \times 100$$

(2) Estimation of nitrogen :

(i) Duma's method :

$$\% N = \frac{28 \times \text{volume of } N_2 \text{ at NTP} \times 100}{22400 \times \text{mass of organic compound}}$$

(ii) Kjeldahl's method :

$$\% N = \frac{1.4\, N \times V}{\text{mass of organic compound}}$$

where $(N \times V)$, *i.e.*, Meq. of NH_3 given out during Kjeldahl's method measured in terms of Meq. of acid used for NH_3 neutralisation.

(3) Estimation of sulphur :

$$\% S = \frac{32 \times \text{mass of } BaSO_4 \times 100}{233 \times \text{mass of organic compound}}$$

(4) Estimation of halogens : Carius method

$$\% Cl = \frac{35.5 \times \text{mass of AgCl}}{143.5 \times \text{mass of organic compound}} \times 100$$

$$\% Br = \frac{80 \times \text{mass of AgBr}}{188 \times \text{mass of O.C.}} \times 100$$

$$\% I = \frac{127 \times \text{mass of AgI}}{235 \times \text{mass of O.C.}} \times 100$$

(5) Estimation of phosphorus :

$$\% P = \frac{62}{222} \times \frac{\text{mass of } Mg_2P_2O_7}{\text{mass of O.C.}} \times 100$$

(6) Estimation of oxygen : There is no direct method for estimation of oxygen in organic compounds. It is usually calculated by the difference.

$$\% O = 100 - [\% \text{ of all other elements in organic compound}]$$

Determination of empirical formula : The empirical formula of a molecule is determined using the % of elements present in it. Following method is adopted.

Element	%	Relative no. of atoms = % /atomic mass	Simplest ratio	Empirical formula

Relative no. of atoms : Divide the percentage of each element present in compound by its atomic mass. This gives the relative no. of atoms of element in molecule.

Simplest ratio : Find out lowest value of relative no. of atoms and divide each value of relative no. of atoms by this value to get simplest ratio of elements.

If the simplest ratio obtained are not complete integers, multiply them by a common factor to get integer values of simplest ratio.

Empirical formula : Write all constitutent atoms with their respective no. of atoms derived in simplest ratio. This gives empirical formula of compound.

Molecular formula : Molecular formula $= n \times$ empirical formula where 'n' is the whole no. obtained by

$$n = \frac{\text{molar mass of compound}}{\text{empirical formula mass of compound}}$$

molar mass of organic compound can be determined by any method for which data is given.

Some of the methods to determine molar mass are given below:

(1) Victor Meyer's method (See Problem 2)
(2) Duma's method (See Problem 3)
(3) Hofmann's method (See Problem 4)
(4) Ebullioscopic method and cryoscopic method (See Problem 13)
(5) Lowering in vapour pressure method (See Problem 10)

(6) Silver salt method (See Problem 6)
(7) Platinic chloride method (See Problem 7)
(8) Volumetric method for acid and base (See Problem 12)

Platinic chloride method : The method is based on the principle that organic bases combine with H_2PtCl_6 to form insoluble chloroplatinate which on ignition leaves metallic Pt as residue.

$$B_2 + H_2PtCl_6 \longrightarrow B_2H_2PtCl_6 \xrightarrow{\Delta} Pt$$

where B represents a monoacid base.

Let x g of $B_2H_2PtCl_6$ gives a g Pt as residue

$$\text{Mole of } B_2H_2PtCl_6 = \text{mole of Pt}$$

$$\frac{x}{\text{Molar mass of } B_2H_2PtCl_6} = \frac{a}{\text{Atomic mass of Pt}}$$

or $$\frac{x}{2 \times \text{Eq. mass of base} + \text{Molar mass of } H_2PtCl_6} = \frac{a}{195}$$

or $$\frac{x}{2 \times \text{Eq. mass of } B + 410} = \frac{a}{195}$$

$\therefore$ $$\text{Eq. mass of } B = \frac{1}{2}\left[\frac{x(195)}{a} - 410\right]$$

$\therefore$ Molar mass of base = Eq. mass of base × acidity

• NUMERICAL PROBLEMS •

1. An O.C. contains C = 40%, H = 6.6% and rest oxygen. Find out empirical formula of O.C.
2. A volatile organic compound on analysis following Victor Meyer's experiment gave as:
   Mass of organic compound = 0.1133 g
   Volume of air displaced = 22.8 mL
   Temperature = 15°C
   Pressure = 750 mm
   Vapour pressure of H_2O = 13 mm at 15°C
   Calculate vapour density and molar mass of compound.
3. A Duma's bulb full of air weighs 22.567 g at 20°C and 755 mm pressure. Full of vapours of a substance at 120°C and 755 mm pressure it weighs 22.8617 g. The capacity of bulb is 200 mL. Find the molar mass of substance. The density of air is 0.00129 g/mL.
4. During Hofmann's experiment 0.2g of an unknown compound is vaporized under reduced pressure 70 cm at 127°C and occupies 20 mL. Calculate molar mass of compound.
5. Combustion of 0.42 g of a compound gave 0.924 g CO_2 and 0.243 g H_2O. Due to distillation of 0.208 g of the compound with NaOH, ammonia evolved required 30 mL of $N/20$ H_2SO_4 for complete neutralization. Calculate the percentage composition of compound.
6. 0.607 g of silver salt of a tribasic acid on combustion gave 0.37 g pure Ag. Calculate the molar mass of acid.
7. An organic compound gave the following data : 0.236 g yielded 0.528 g CO_2 and 0.324 g H_2O on combustion. 0.295 g of the compound gave 56 mL N_2 at NTP. The compound is a monoacid base. It's platinic chloride salt contains 36.93% platinum. Calculate the molecular formula of compound.
8. 0.32g of organic compound containing sulphur on treatment with conc. HNO_3 in a Carius tube and then with excess of $BaCl_2$ produced 0.233 g of $BaSO_4$. Determine % of S in compound.
9. In Kjeldahl's method, the gas evolved from 1.325 g sample of a fertilizer is passed into 50.0 mL of 0.2030 N H_2SO_4. 25.32 mL of 0.1980 N NaOH are required for the titration of unused acid. Calculate the percentage of nitrogen in fertilizer. **(Roorkee 1991)**
10. A non-volatile hydrocarbon has 5.6% hydrogen. When 3.0 g of hydrocarbon is dissolved in 100 g of benzene, the relative lowering vapour pressure of benzene is 1.306×10^{-2} Nm^{-2}. Determine the molecular formula of non-volatile hydrocarbon. **(Punjab CET 1990)**
11. A sample of gaseous hydrocarbon occupying 1.12 litre at NTP, completely burnt in air and produced 2.2 g of CO_2 and 1.8 g H_2O. Calculate the mass of compound taken and volume of O_2 at NTP required for its burning. Also calculate molecular formula of hydrocarbon.
12. An aromatic monobasic acid contains 68.87% C and 4.9% H. 0.610 g of the acid required 25 mL of $M/10$ diacidic base for neutralization. What is molecular formula of acid?
13. The freezing point constant of C_6H_6 is 4.90 K mol^{-1} kg and its melting point is 5.51°C. A solution of 0.816 g of compound (A) when dissolved in 7.5 g of C_6H_6 freezes at 1.59°C. The compound (A) has C = 70.58% and H = 5.88%. Determine the molar mass and molecular formula of (A).
14. A monobasic organic acid gave on combustion the following % compositions : C = 39.9%; H = 6.69%. Also 0.2565 g of silver salt of acid gave on ignition 0.1659 g of Ag. Calculate molecular formula of acid.
15. A carbon compound containing only carbon and oxygen has an approximately molar mass of 290 g mol^{-1}. On analysis it is found to contain 50% by mass of each element. What is molecular formula of the compound?
16. Compound of C, H and N contains the three elements in the ratio 9 : 1 : 3.5, calculate empirical formula. If the molar mass is 108 g mol^{-1}, calculate molecular formula.
17. An organic compound contains 69.4% C, 5.8% H. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.05 M H_2SO_4. The excess acid required 25 mL of 0.1 M NaOH for neutralization. Determine molecular formula of the compound, if its molar mass is 121 g mol^{-1}. Draw possible structures of this compound.
18. An O.C., $C_xH_{2y}O_y$ was burnt with twice the oxygen needed for complete combustion to produce CO_2 and H_2O. The hot gases when cooled at 0°C and 1 atm pressure measured 2.24 litre. The water collected during cooling was 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm of Hg and it reduces by 0.104 mm when 50 g of organic compound is dissolved in 1000 g of water. What is organic compound?
19. A monoacid organic base gave the following data on analysis:
   (a) 0.2790 g of the base gave 0.7920 g CO_2 and 0.1890 g H_2O.
   (b) 0.1163 g of the base gave 14 mL of dry N_2 at NTP.
   (c) 0.2980 g of platinic chloride left 0.0975 g Pt.
   Calculate the molecular formula of base.
20. 0.2060 g of an organic compound on combustion gave 18.8 mL of moist nitrogen at 17°C and 756 mm pressure. If the vapour tension at 17°C is 14.5 mm, find the percentage of nitrogen in compound.

21. The analysis of an organic compound gave the following data:
   (a) 0.4020 g gave 0.6098 g and 0.2080 g of CO_2 and H_2O respectively.
   (b) 1.01 g by Kjeldahl's method produced ammonia which was neutralized by 23.2 mL of *N*/2 HCl.
   (c) 0.1033 g of compound gave 0.2772 g $BaSO_4$.
   (d) 0.1015 g when vaporized in Victor Meyer's apparatus displaced 27.96 mL of air at 15°C and 766 mm pressure. Calculate molecular formula (P'_{H_2O} at 15°C = 16 mm).

22. An organic monoacid base has empirical formula C_3H_3NO. 0.0563 g of platinum was left from 0.1982 g of its platinate. Find the molecular formula and molar mass of base.

23. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67%, and oxygen : 38.07%. (i) Calculate the empirical formula of the minor product. (ii) When 5.5 g of minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula.
(Molal elevation constant of benzene is 2.53 K kg mol^{-1}). **(IIT 1999)**

24. 0.15 g of an organic compound on estimation by Carius method gave 0.12 g of AgBr. What is the percentage of bromine in organic compound?

25. 0.147 g of an organic compound on estimation by Carius method gave 0.287 g of AgCl. What is the percentage of chlorine in organic compound?

26. A sample of 0.50 g of an organic compound was estimated by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5 *M* H_2SO_4. The residual acid required 60 mL of 0.5 *M* NaOH for neutralisation. Find out the % of nitrogen in organic compound.

27. An organic compound contains 69% carbon and 4.8% hydrogen. If the remainder is oxygen calculate the mass of CO_2 and H_2O produced on complete combustion of its 0.2 g. Also calculate the mole of oxygen for complete combustion of one mole of this compound. Molar mass of organic compound is 122 g mol^{-1}.

SOLUTIONS (Numerical Problems)

1.

Element	%	%/Atomic mass	Relative no. of atoms	Simplest ratio
C	40	40/12	3.33	$\frac{3.33}{3.33}=1$
H	6.6	6.6/1	6.6	$\frac{6.6}{3.33}=2$
O	100−[40+6.6] = 53.4	53.4/16	3.33	$\frac{3.33}{3.33}=1$

$\therefore$ Empirical formula is $\mathbf{CH_2O}$.

2. Pressure of dry air displaced = 750 − 13 = 737 mm

Organic compound occupies the same volume in gaseous phase as air displaced.

Now, $$PV=\frac{w}{M}RT$$

$$\frac{737}{760}\times\frac{22.8}{1000}=\frac{0.1133}{M}\times0.0821\times288$$

$\therefore$ $$M=\mathbf{121.16\ g\ mol^{-1}}$$

Now, Vapour density $=\frac{\text{molar mass}}{2}=\frac{121.16}{2}=\mathbf{60.58}$

3. Assume mass of bulb = w'

$\therefore$ Mass of air in bulb = $(22.567-w')$ g

$$\text{Pressure of air}=\frac{755}{760}\text{ atm}$$

$$\text{Volume of air}=\frac{200}{1000}\text{ litre}$$

$$T=293\text{ K}$$

$$\text{Molar mass of air}=0.00129\times22400=28.90$$

using $PV=\frac{w}{M}RT$ for air

$$\frac{755}{760}\times\frac{200}{1000}=\frac{(22.567-w')}{28.90}\times0.0821\times293$$

$\therefore$ $$w'=22.3282\text{ g}$$

For vapours :

$$\text{Mass of vapours}=22.8617-22.3282=0.5335\text{g}$$

$$P_{\text{vapour}}=\frac{755}{760}\text{ atm}$$

$$\text{Volume of vapours}=200\text{ mL}$$

$$T=393\text{ K}$$

Again by $PV=\frac{w}{M}RT$

$$\frac{755}{760}\times\frac{200}{1000}=\frac{0.5335}{M}\times0.0821\times393$$

$\therefore$ $$M=\mathbf{86.64\ g\ mol^{-1}}$$

4. $P=\frac{70}{76}$ atm, $V=\frac{20}{1000}$ litre, $T=400$ K, $w=0.2$ g

$\because$ $$PV=\frac{w}{M}RT$$

$$\frac{70}{76}\times\frac{20}{1000}=\frac{0.2}{M}\times0.0821\times400$$

$\therefore$ $$M=\mathbf{356.55\ g\ mol^{-1}}$$

5. We have, $$\%\text{ of C}=\frac{12}{44}\times\frac{\text{mass of }CO_2}{\text{mass of compound}}\times100$$

$$=\frac{12}{44}\times\frac{0.924}{0.42}\times100=60\%$$

$$\%\text{ H}=\frac{2}{18}\times\frac{\text{mass of }H_2O}{\text{mass of compound}}\times100$$

$$=\frac{2}{18}\times\frac{0.243}{0.42}\times100=6.43\%$$

$$\%\text{ N}=\frac{1.4\,NV}{W}=\frac{1.4\times\frac{1}{20}\times30}{0.208}=10.09\%$$

$$\%\text{ O}=100-[\%\text{ C}+\%\text{ H}+\%\text{ N}]$$

$$=100-[60+6.43+10.09]=23.48\%$$

$\therefore$ C = **60%**, H = **6.43%**, N = **10.09%**, O = **23.48%**

6. Meq. of silver salt = Meq. of silver

$$\frac{0.607}{E}\times1000=\frac{0.37}{108}\times1000$$

$\therefore$ Eq. mass of silver salt = 177.2

$\because$ Tribasic acid and thus, valence = 3

$\therefore$ Molar mass of silver salt = $177.2\times3=531.6$

$\therefore$ Molar mass of acid = 531.6 − 3 × atomic mass of Ag + 3 × atomic mass of H

$$=531.6-3\times108+3=\mathbf{210.6}$$

7. $$\%\text{ of C}=\frac{12}{44}\times\frac{\text{mass. of }CO_2}{\text{mass of O.C.}}\times100$$

$$=\frac{12}{44}\times\frac{0.528}{0.236}\times100=61.07\%$$

$$\%\text{ of H}=\frac{2}{18}\times\frac{\text{mass of }H_2O}{\text{mass of O.C.}}\times100$$

$$=\frac{2}{18}\times\frac{0.324}{0.236}\times100=15.25\%$$

$$\%\text{ of N}=\frac{28\times\text{volume of }N_2\text{ at NTP}\times100}{22400\times\text{mass of compound}}$$

$$=\frac{28\times56\times100}{22400\times0.295}=23.73\%$$

$\because$ Empirical formula can be derived as;

Element	Percentage	Relative no. of atoms	Simplest ratio
C	61.07	5.09	3
H	15.25	15.25	9
N	23.73	1.695	1

$\therefore$ Empirical formula is C_3H_9N and

Empirical formula mass = 59

Now, Equivalent mass of base $=\frac{1}{2}\left[\frac{x}{a}\times195-410\right]$

where, x = mass of $PtCl_4$ salt, a = mass of Pt residue

$$=\frac{1}{2}\left[\frac{100\times195}{36.93}-410\right]=59$$

$\therefore$ Molar mass of base = 59 × acidity = 59 × 1 = 59 ($\because$ monoacid base)

$\therefore$ Molecular formula = $\mathbf{C_3H_9N}$

8. $\%\text{ of S} = \dfrac{32\times\text{mass of } BaSO_4}{233\times\text{mass of O.C.}}\times 100$

$= \dfrac{32\times 0.233}{0.32\times 233}\times 100 = \mathbf{10\%}$

9. Meq. of H_2SO_4 taken to absorb $NH_3 = 50\times 0.2030$

Meq. of H_2SO_4 left after NH_3 absorption

= Meq. of NaOH used for $H_2SO_4 = 25.32\times 0.1980$

$\therefore$ Meq. of H_2SO_4 used for NH_3

$= 50\times 0.2030 - (25.32\times 0.1980)$

or (NV) used for $NH_3 = 5.137$

$\therefore \quad \%\text{ N} = \dfrac{1.4\times NV}{\text{mass of substance}} = \dfrac{1.4\times 5.137}{1.325} = \mathbf{5.43\%}$

10. (i) Molar mass of hydrocarbon can be derived by Raoult's law

$$\frac{P^\circ - P_s}{P^\circ} = \frac{w/m}{w/m + W/M}$$

$$1.306\times 10^{-2} = \frac{3/m}{3/m + \dfrac{100}{78}} \quad \therefore m = 176.83$$

(ii) For empirical formula :

Element	Percentage	Relative no. of atoms	Simplest ratio
C	94.5	7.88	1.40 or 7
H	5.6	5.60	1.0 or 5

$\therefore$ Empirical formula is C_7H_5 and molecular formula is $(C_7H_5)_n$

Empirical formula mass = 89

$\because \quad n = \dfrac{\text{molar mass}}{\text{empirical formula mass}} = \dfrac{176.83}{89} \simeq 2$

$\therefore$ Molecular formula $= (C_7H_5)_2 = \mathbf{C_{14}H_{10}}$

11. 1.12 litre of hydrocarbon occupies mole $= \dfrac{1.12}{22.4} = 0.05$

Mole of CO_2 formed $= \dfrac{2.2}{44} = 0.05$

Mole of H_2O formed $= \dfrac{1.8}{18} = 0.10$

Let the hydrocarbon be C_aH_b

$$C_aH_b + \left(a + \frac{b}{4}\right)O_2 \longrightarrow a\,CO_2 + \frac{b}{2}H_2O$$

$\therefore$ 1 mole of C_aH_b gives = a mole CO_2

$\therefore$ 0.05 mole of C_aH_b will give = $0.05a$ mole of CO_2

$\therefore \quad 0.05a = 0.05 \quad \therefore a = 1$

$\therefore$ 1 mole of C_aH_b gives $= \dfrac{b}{2}$ mole H_2O

$\therefore$ 0.05 mole of C_aH_b will give $= 0.05\times\dfrac{b}{2}$ mole H_2O

$= 0.05\times\dfrac{b}{2} = 0.10 \quad \therefore b = 4$

$\therefore$ Hydrocarbon is $\mathbf{CH_4}$.

$\therefore$ Mass of 1.12 litre CH_4 at STP $= \dfrac{16\times 1.12}{22.4} = \mathbf{0.8\ g}$

Also, $\quad CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

1 mole CH_4 requires $= 2\times 32$ g O_2

$\therefore$ 0.05 mole CH_4 requires $= 2\times 32\times 0.05$

$= 3.2$ g $O_2 = \mathbf{2.24}$ litre $\mathbf{O_2}$

12.

Element	Percentage	Relative no. of atoms	Simplest ratio
C	68.87	5.74	3.5 or 7
H	4.9	4.9	3.0 or 6
O	26.23	1.64	1.0 or 2

$\therefore$ Empirical formula is $C_7H_6O_2$

Empirical formula mass = 122

Now molar mass of acid can be determined as :

Meq. of acid = Meq. of alkali used

$$\frac{0.610}{M/1}\times 1000 = 25\times\frac{1}{10}\times 2$$

$\therefore \quad M = 122$ g mol^{-1}

$\therefore \quad n = \dfrac{\text{molar mass of acid}}{\text{empirical formula mass}} = \dfrac{122}{122} = 1$

$\therefore$ Molecular formula of compound

$= (C_7H_6O_2)_n = (C_7H_6O_2)_1$

$= \mathbf{C_7H_6O_2}$

13. $\Delta T = 5.51 - 1.59 = 3.92^\circ$ C

(i) Molar mass of compound $(A) = \dfrac{1000K_f'\times w}{\Delta T\times W}$

$= \dfrac{1000\times 4.9\times 0.816}{7.5\times 3.92} = \mathbf{136}$

(ii) For empirical formula

Element	Percentage	Relative no. of atoms	Simplest ratio
C	70.58	$\dfrac{70.58}{12} = 5.88$	$\dfrac{5.88}{1.47} = 4$
H	5.88	$\dfrac{5.88}{1} = 5.88$	$\dfrac{5.88}{1.47} = 4$
O	$100 - (70.58 + 5.88) = 23.54$	$\dfrac{23.54}{16} = 1.47$	$\dfrac{1.47}{1.47} = 1$

$\therefore$ Empirical formula is C_4H_4O

Empirical formula mass = 68

Molar mass of $(A) = 136$

$\therefore$ Molecular formula of $(A) = (C_4H_4O)_n$

$\because \quad n = \dfrac{\text{molar mass}}{\text{empirical formula mass}} = \dfrac{136}{68} = 2$

$\therefore$ Molecular formula of $(A) = (C_4H_4O)_2 = \mathbf{C_8H_8O_2}$.

14.

Element	Percentage	Relative no. of atoms	Simplest ratio
C	39.9	3.32	1
H	6.69	6.69	2
O	$100 - (39.9 + 6.69) = 53.41$	3.34	1

$\therefore$ Empirical formula of compound = CH_2O

$\therefore \quad$ Empirical formula mass = 30

For molar mass of acid

Meq. of Ag salt of monobasic acid = Meq. of Ag

$$\frac{0.2565}{M/1}\times 1000=\frac{0.1659}{108}\times 1000$$

$\therefore$ Molar mass of Ag salt ($RCOOAg$) = 167

$\therefore$ Molar mass of acid ($RCOOH$) = 167 − 108 + 1 = 60

$\therefore$ Molecular formula of compound

$$=(CH_2O)_2=C_2H_4O_2=\mathbf{CH_3COOH}$$

15. (1) Molar mass of compound = 290

(2) It contains equal masses of C and H and thus,

Mass of C = 145

Mass of O = 145

$\therefore$ g-atoms of C $=\frac{145}{12}=12$

g-atoms of O $=\frac{145}{16}=9$

$\therefore$ Molecular formula = $\mathbf{C_{12}O_9}$

16. C : H : N :: 9 : 1 : 3.5 = 13.5

$\because$ 13.5 g contains $\frac{9}{12}$ g atom of C

$\therefore$ 108 g contains $\frac{9}{12}\times\frac{108}{13.5}$ g atom of C = 6

Similarly, g-atom of H in 1 mole $=\frac{1}{1}\times\frac{108}{13.5}=8$

g-atom of N in 1 mole $=\frac{3.5}{14}\times\frac{108}{13.5}=2$

$\therefore$ Molecular formula of compound is $\mathbf{C_6H_8N_2}$.

17. (i) Meq. of NH_3 evolved (NV) = Meq. of acid used for NH_3

$$=50\times 0.05\times 2-25\times 0.1=2.5$$

$\because$ % of N $=\frac{1.4\times NV}{\text{mass of O.C.}}=\frac{1.4\times 2.5}{0.303}=11.55$

(ii)

Element	Percentage	Relative no. of atoms	Simplest ratio
C	69.4	5.78	7
H	5.8	5.8	7
N	11.55	0.825	1
O	13.25	0.828	1

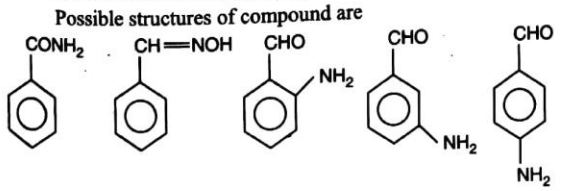
(iii) Empirical formula = C_7H_7NO

Empirical formula mass = 121

$\because$ Molar mass = 121 g mol^{-1}

$\therefore$ Molecular formula is $\mathbf{C_7H_7NO}$.

Possible structures of compound are



18. $C_xH_{2y}O_y+xO_2\longrightarrow xCO_2+yH_2O$

Since oxygen taken is $2x$ litre and thus x litre O_2 is left at STP after reaction. Also x litre of CO_2 is formed by 1 mole of O.C.

$\therefore$ $2x = 2.24$

$x = 1.12$ litre $CO_2=\frac{1.12}{22.4}$ mole CO_2 = 0.05 mole CO_2

Mole of H_2O formed (y) $=\frac{0.9}{18}=0.05$

$\therefore$ $x : y = 0.05 : 0.05$ $\therefore x = 1$

$y = 1$, *i.e.*, ratio of x and y

$\therefore$ Empirical formula of O.C. = CH_2O

and Empirical formula mass of O.C. = 30

Now Molar mass of compound is derived by Raoult's law

$\because$ $\frac{P°-P_s}{P_s}=\frac{w}{m}\times\frac{M}{W}$

$\because$ $P°-P_s = 0.104$ mm and $P° = 17.5$ mm

$\frac{0.104}{17.396}=\frac{50}{m}\times\frac{18}{1000}$ $\therefore$ $m = 150.5$ g mol^{-1}

$\therefore$ Molecular formula = $(CH_2O)_5$ $\because$ $n=\frac{150.5}{30}=5$

$$=\mathbf{C_5H_{10}O_5}$$

19. % of C $=\frac{12\times 0.7920\times 100}{44\times 0.2790}=77.42$

% of H $=\frac{2\times 0.1890\times 100}{18\times 0.2790}=7.53$

% of N $=\frac{28\times 14\times 100}{22400\times 0.1163}=15.05$

Element	Percentage	Relative no. of atoms	Simplest ratio
C	77.42	$\frac{77.42}{12}=6.45$	$\frac{6.45}{1.075}=6$
H	7.53	$\frac{7.53}{1}=7.53$	$\frac{7.53}{1.075}=7$
N	15.05	$\frac{15.05}{14}=1.075$	$\frac{1.075}{1.075}=1$

$\therefore$ Empirical formula = C_6H_7N

For molar mass by Platinic chloride method

Equivalent mass of base $=\frac{1}{2}\left[\frac{x}{a}\times 195-410\right]$

$$=\frac{1}{2}\left[\frac{0.2980\times 195}{0.0975}-410\right]=93$$

$\therefore$ Molar mass = Eq. mass × acidity = 93 × 1 = 93

$\therefore$ $n=\frac{\text{molar mass}}{\text{empirical formula mass}}=\frac{93}{93}=1$

$\therefore$ Molecular formula = $\mathbf{C_6H_7N}$

20. $V_{N_2} = 18.8$ mL

$P_{N_2} = 756 - 14.5 = 741.5$ mm, $T = 273 + 17 = 290$ K

By $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$ (at NTP)

$$\frac{741.5\times 18.8}{290}=\frac{760\times V}{273}$$

$\therefore$ V_{N_2} at STP = 17.27

$\therefore$ % of N $=\frac{28\times 17.27\times 100}{22400\times 0.2060}=\mathbf{10.5}$

21. % of C $=\frac{12\times 0.6098\times 100}{44\times 0.4020}=41.37$

$$\% \text{ of H} = \frac{2\times 0.2080\times 100}{18\times 0.4020} = 5.75$$

$$\% \text{ of S} = \frac{32\times 0.2772\times 100}{233\times 0.1033} = 36.85$$

$$\% \text{ of N} = \frac{1.4\times 23.2\times 1}{1.01\times 2} = 16.08$$

Element	Percentage	Relative no. of atoms	Simplest ratio
C	41.37	$\frac{41.37}{12} = 3.45$	$\frac{3.45}{1.15} = 3$
H	5.75	$\frac{5.75}{1} = 5.75$	$\frac{5.75}{1.15} = 5$
S	36.85	$\frac{36.85}{32} = 1{:}15$	$\frac{1.15}{1.15} = 1$
N	16.08	$\frac{16.08}{14} = 1.15$	$\frac{1.15}{1.15} = 1$

$\therefore$ Empirical formula is C_3H_5NS

Empirical formula mass = 87

Molar mass $(M) = \frac{wRT}{PV}$

$$M = \frac{0.1015\times 0.0821\times 288\times 1000\times 760}{750\times 27.96}$$

$$= 87 \text{ g mol}^{-1}$$

$\therefore$ $n = \frac{87}{87} = 1$

$\therefore$ Molecular formula = $\mathbf{C_3H_5NS}$

22. Equivalent mass of base $= \frac{1}{2}\left[\frac{x}{a}\times 195 - 410\right]$

where x is mass of $PtCl_4$ salt and a is mass of Pt residue

Thus, $E = \frac{1}{2}\left[\frac{0.1982}{0.0563}\times 195 - 410\right] = 138.24$

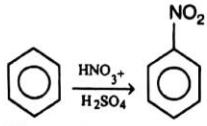
The base in monoacid, thus

molar mass $= E\times 1 = \mathbf{138.24}$

Empirical formula mass (C_3H_3NO)

$= 36+3+14+16 = 69$

$\therefore$ Molecular formula $= (C_3H_3NO)_2 = \mathbf{C_6H_6N_2O_2}$

23. 

+ a minor product

For empirical formula of minor product

C	$\frac{42.86}{12} = 3.57$	$\frac{3.57}{1.19} = 3$
H	$\frac{2.40}{1} = 2.40$	$\frac{2.40}{1.19} = 2$
N	$\frac{16.67}{14} = 1.19$	$\frac{1.19}{1.19} = 1$
O	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{1.19} = 2$

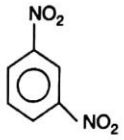
$\therefore$ Empirical formula is $C_3H_2NO_2$

Empirical formula mass = 84

Also Molar mass $= \frac{1000\times K\times w}{\Delta T\times W}$

$$= \frac{1000\times 2.53\times 5.5}{1.84\times 45} = \mathbf{168 \text{ g mol}^{-1}}$$

$\therefore$ Molecular formula $= (C_3H_2NO_2)_2 = \mathbf{C_6H_4N_2O_4}$,

i.e., 

24. $\therefore$ $\%\text{ Br} = \frac{\text{Atomic mass of Br} \times \text{mass of AgBr}}{\text{Molar mass of AgBr} \times \text{mass of organic compound}}\times 100$

$$= \frac{80\times 0.12\times 100}{188\times 0.15} = \mathbf{34.04\%}$$

25. Percentage of Cl

$$= \frac{\text{Atomic mass of Cl} \times \text{mass of AgCl}}{\text{Molar mass of AgCl} \times \text{mass of organic compound}}\times 100$$

$$= \frac{35.5\times 0.287\times 100}{143.5\times 0.147} = \mathbf{48.30\%}$$

26. Meq. of H_2SO_4 taken $= 50\times 0.5\times 2 = 50$

Meq. of NaOH used after passing $NH_3 = 60\times 0.5 = 30$

$\therefore$ Meq. of H_2SO_4 used for $NH_3 = 50 - 30 = 20 = (NV)$

$\therefore$ $\%\text{ of N} = \frac{1.4\times NV}{\text{mass of organic compound}}$

$$= \frac{1.4\times 20}{0.5} = \mathbf{56\%}$$

27. $\%\text{ of Carbon} = \frac{12}{44}\times\frac{\text{mass of } CO_2 \text{ produced}}{\text{mass of organic compound}}\times 100$

$\therefore$ $69 = \frac{12}{44}\times\frac{\text{mass of } CO_2 \text{ formed}}{0.2}\times 100$

$\therefore$ Mass of CO_2 formed $= \frac{69\times 44\times 0.2}{12\times 100} = 0.506$ g

Now,

$\%\text{ of hydrogen} = \frac{2}{18}\times\frac{\text{mass of } H_2O \text{ formed}}{\text{mass of organic compound}}\times 100$

or $4.8 = \frac{2}{18}\times\frac{\text{mass of } H_2O \text{ formed}}{0.2}\times 100$

$\therefore$ Mass of H_2O formed $= \frac{4.8\times 18\times 0.2}{2\times 100} = 0.0864$ g

Percentage analysis (C = 69%, H = 4.8%, O = 26.2) suggest the empirical formula and molecular formula of organic compound is $C_7H_6O_2$.

$$C_7H_6O_2 + \frac{15}{2}O_2 \longrightarrow 7CO_2 + 3H_2O$$

Thus, 1 mole of $C_7H_6O_2$ requires **7.5 mole** of oxygen for complete combustion.

19 Structure and Reactions Based Problems

Problems based on reactions and structures of organic compounds:

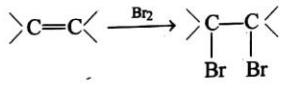
In order to solve the problems based upon reaction and assign the structure of organic compounds, one must be familiar with characteristic reactions, mechanism of reaction of the functional groups present in organic compound. It has, therefore, been advised to students to go through a deep insight of reactions, their mechanism, conditions under which reaction will proceed for a given organic compound.

However, a few reactions, on which generally the problems are based, are given below :

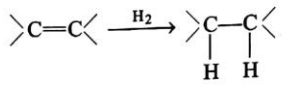
1. Unsaturation in molecule :

A compound is unsaturated (*i.e.*, has **double** or **triple**) bonds if it is confirmed by the following **addition reactions.**

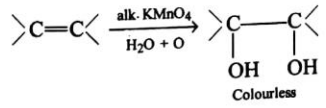
(a) Discharges or decolourizes Br_2 in CCl_4 or Br_2 water :



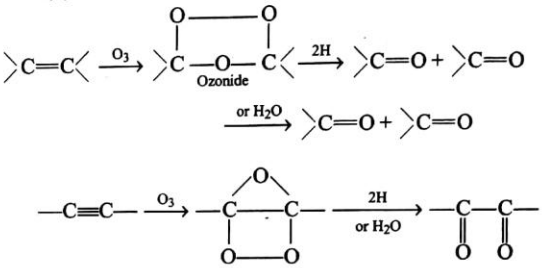
(b) Shows addition of H_2 :



(c) Decolourizes Baeyer's reagent, *i.e.*, 1% cold alk. $KMnO_4$:



(d) Undergoes ozonolysis :



NOTE : (i) Ozonolysis of symmetrical alkene produces two mole of same carbonyl compounds.

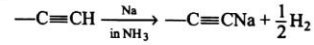
(ii) Ozonolysis of cycloalkenes gives one product having two carbonyl groups.

(iii) Ozonolysis of alkynes gives one product having two carbonylic groups.

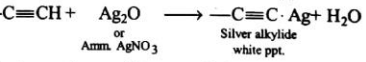
(iv) The products formed during ozonolysis also help in deciding the nature and position of unsaturation in molecule.

(v) If organic compound is terminal alkyne, it

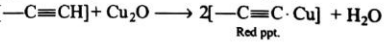
(a) gives H_2 with Na.



(b) reduces amm. $AgNO_3$ to give white ppt.

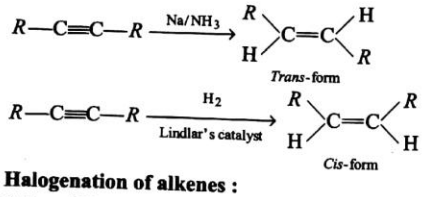


(c) gives red ppt. with ammonical Cu_2Cl_2.



(e) Hydrogenation of alkynes :

Non-terminal alkynes are hydrogenated to give *trans*-isomers if Na/NH_3 is used whereas *cis*-isomer is formed if Lindlar's catalyst is used.



(f) Halogenation of alkenes :

Addition of Br_2 on *cis*-2-butene forms a racemic mixture of 2,3-dibromobutane whereas *trans*-2-butene forms *meso* derivative of 2,3-dibromobutane. Both follow anti addition.

2. Halides :

(i) Monohalides on treating with KOH(*aq.*) give alcohol.

$$R—X \xrightarrow{KOH\ (aq.)} ROH$$

(ii) Monohalides on treating with alc. KOH give alkene. (Also, read Saytzeff rule for elimination).

$$R \cdot CH_2 \cdot CH_2X \xrightarrow{(alc.)\ KOH} R \cdot CH{=}CH_2$$

(iii) Dihalides on treating with KOH(*aq.*), give—

(a) Diol—It is dihalide with halogens on different carbon atoms.

$$CH_2X—CH_2X \xrightarrow{KOH\ (aq.)} CH_2OH \cdot CH_2OH$$

(b) Aldehyde—It is gem dihalide with terminal position to halogens.

$$CH_3 \cdot CH_2 \cdot CHX_2 \xrightarrow{KOH\ (aq.)} CH_3 \cdot CH_2 \cdot CHO$$

(c) Ketone—It is gem dihalide with non-terminal position to halogens.

$$CH_3 \cdot CX_2 \cdot CH_3 \xrightarrow{KOH\ (aq.)} CH_3 \cdot CO \cdot CH_3$$

(iv) Trihalides on treating with KOH(*aq.*) give acid, then all the three halogens are on terminal carbon atoms.

$$CH_3CX_3 \xrightarrow{KOH\ (aq.)} CH_3COOH$$

(v) Carbylamine reaction of haloform.

$$\underset{\text{Alcoholic}}{CHCl_3 + RNH_2 + 3KOH} \longrightarrow \underset{\text{Unpleasant odour}}{RNC} + 3KCl + 3H_2O$$

This is a distinction test in between $CHCl_3$ and CCl_4; primary amines with other amines.

3. Alcohols :

(i) Give effervescences of H_2 gas with Na or K.

$$R—OH + Na \longrightarrow RONa + \frac{1}{2}H_2$$

(ii) Give red colour with ceric ammonium nitrate.

(iii) Form esters with acids, acid chlorides and acid anhydrides.

$$\underset{\text{Alcohol}}{R—OH} + \underset{\text{Acid}}{HOOCR'} \longrightarrow \underset{\text{Ester}}{R'COOR} + H_2O$$

(iv) Distinction in primary, secondary and tertiary alcohols.

(a) Primary alcohols on oxidation give aldehydes and then acid. (Both contain the same number of carbon atoms as the parent alcohol.

$$R—CH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH$$

(b) Secondary alcohols on oxidation give ketone with same number of carbon atoms and then acids on prolong oxidation containing lesser number of carbon atom than the parent alcohol.

$$R \cdot CHOH \cdot R' \xrightarrow{[O]} R \cdot COR'$$

(c) Tertiary alcohols on vigorous oxidation form ketones and then acids. (Each with lesser number of carbon atoms then the parent alcohol.)

$$(CH_3)_3 \cdot COH \longrightarrow CH_3 \cdot CO \cdot CH_3$$

(d) **Lucas reagent test :** Primary alcohol react with Lucas reagent [$ZnCl_2$ (anhy.) + HCl(conc.)] only on heating. Secondary alcohols give white turbidity only after 5–10 minutes of reaction. Tertiary alcohols give white turbidity immediately.

(v) Alcohols on dehydration at relatively :

(a) lower temperature give ether.

$$2R—OH \xrightarrow[\text{agent}]{\text{Dehydrating}} ROR$$

(b) higher temperature give alkene. The order of ease of dehydration of alcohol is tertiary alcohol > secondary alcohol > primary alcohol

$$CH_3 \cdot CH_2OH \xrightarrow[\text{agent}]{\text{Dehydrating}} CH_2{=}CH_2$$

4. Ethers :

(i) Inert and neutral in nature.

(ii) An ether with conc. HI—

(a) In cold gives an alcohol and alkyl iodide.

$$R—O—R + HI \longrightarrow RI + ROH$$

In case of mixed ethers, the iodide attaches to the smaller alkyl group.

$$CH_3 \cdot OC_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

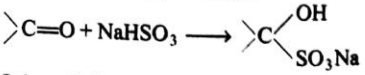
(b) In hot it gives two mole of alkyl iodide.

$$ROR + 2HI \longrightarrow 2RI + H_2O$$

$$R—O—R' \xrightarrow{2HI} RI + R'I + H_2O$$

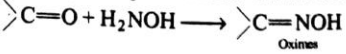
5. Aldehydes and ketones or carbonyl compounds :

(i) A carbonyl compound shows addition reaction with sodium bisulphite forming white ppt.



NOTE: Only methyl ketones and all aldehydes show this test.

(ii) Carbonyl compounds form oximes and hydrazones.



$$>C=O + H_2N\cdot NHC_6H_5 \longrightarrow \underset{\text{Phenyl hydrazones}}{>C=N\cdot NHC_6H_5}$$

(iii) A carbonyl compounds is aldehyde if it;

(a) Reduces Fehling solution (except benzaldehyde).

$R—CHO + 2CuO \longrightarrow RCOOH + Cu_2O$ (red ppt.)

(b) Reduces Tollens reagent.

$R—CHO + Ag_2O \longrightarrow RCOOH + 2Ag$ (silver mirror)

(c) Reduces Schiffs reagent and gives pink colour.

(d) Gives red ppt. with Benedict's reagent.

(e) On reduction gives primary alcohol.

$$R—CHO \xrightarrow{2H} RCH_2OH$$

(iv) A carbonyl compound, if does not show above tests for aldehyde, is ketone.

(v) Some other characteristic tests are :

(a) Iodoform test : Organic compounds having $CH_3—\underset{\underset{O}{\|}}{C}—$ unit attached to carbon or hydrogen give yellow ppt. (iodoform) with $I_2 + NaOH$

$$CH_3\cdot CO\cdot CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

only acetaldehyde and all methyl ketones respond this test.

(b) With 2,4-dinitrophenylhydrazine : Both aldehydes and ketones give orange yellow solid with 2,4-dinitrophenylhydrazine.

6. Acids :

(i) An acid turns blue litmus red.

(ii) An acid gives effervescences with $NaHCO_3$.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$$

(iii) An acid forms ester with alcohols in presence of concentrated H_2SO_4.

$$RCOOH + R'OH \xrightarrow{\text{Conc. } H_2SO_4} RCOOR' + H_2O$$

(iv) An acid on decarboxylation (on heating with soda lime) loses CO_2 and forms hydrocarbon.

$$RCOOH \xrightarrow{NaOH + CaO} R—H + CO_2\uparrow$$

(v) Dry distillation of Ca salt of an acid gives aldehydes and ketones.

$$2(HCOO)_2Ca \longrightarrow 2HCHO + 2CaCO_3$$

$$2(CH_3COO)_2Ca \longrightarrow 2CH_3COCH_3 + 2CaCO_3$$

$$(HCOO)_2Ca + (CH_3COO)_2Ca \longrightarrow 2CH_3CHO + 2CaCO_3$$

NOTE: (a) Aldehydes are formed only when at least one of the component is $Ca(HCOO)_2$.

(b) In case of dry distillation of mixed Ca salts of acids all possible products are formed.

$$(HCOO)_2Ca + (CH_3COO)_2Ca \longrightarrow CH_3CHO + HCHO + CH_3COCH_3$$

(vi) Acids form amides on heating with NH_3 which on further heating with P_2O_5 give cyanides.

$$RCOOH + NH_3 \longrightarrow \underset{\text{Amm. salt}}{RCOONH_4} \xrightarrow{\Delta} \underset{\text{Amide}}{RCONH_2} \xrightarrow{P_2O_5} RCN$$

7. Acid derivatives :

(a) Esters :

(i) all the esters possess fruity smell.

(ii) Esters on hydrolysis give acid and alcohol.

$$RCOOR' \xrightarrow{HOH} RCOOH + R'OH$$

(iii)Esters on reduction produce two molecules of alcohol.

$$RCOOR' \xrightarrow{Red} RCH_2OH + R'OH$$

(iv) Phenolphthalein test.

(v) Feigl test.

(b) Acid chlorides :

(i) On hydrolysis give HCl and carboxylic acid.

$$RCOCl \xrightarrow{HOH} RCOOH + HCl$$

(ii) On reduction give alcohols.

$$RCOCl \xrightarrow{\text{Reduction}} RCH_2OH$$

(c) Acid amides :

(i) On boiling with alkali give ammonia.

$$RCONH_2 + NaOH \longrightarrow RCOONa + NH_3\uparrow$$

(ii) On heating with HNO_2 give acids and N_2 gas.

$$RCONH_2 + HONO \longrightarrow RCOOH + N_2 + H_2O$$

(iii) On heating with P_2O_5, yield nitriles.

$$RCONH_2 \xrightarrow[-H_2O]{P_2O_5,\ \Delta} RCN$$

(iv) Amides, on heating with Br_2 and $KOH(aq.)$, undergo Hofmann's bromamide reaction to give primary amines.

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

(d) Acid anhydrides :

(i) On hydrolysis give acid.

$$(RCO)_2O \xrightarrow{HOH} 2RCOOH$$

(ii) On reacting with alcohols give acid and ester.

$$(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$$

8. Amines :

(i) Primary amines undergo carbylamine reaction. (See trihalides)

(ii) Action of HNO_2 on amines are given below.

(a) Primary amine :

$$R\cdot CH_2NH_2 \xrightarrow{HNO_2} RCH_2OH + N_2 + H_2O$$

(b) Secondary amine :

$$R_2NH \xrightarrow{HNO_2} \underset{\text{Yellow oil, nitroso compound}}{R_2N{-}N{=}O}$$

(c) Tertiary amine :

$$(R)_3N \xrightarrow{HNO_2} R_3N \cdot HNO_2 \xrightarrow{\Delta} R_2N \cdot NO + ROH$$

(iii) Action of $C_6H_5SO_2Cl$ (Hinsberg test).

(a) Primary amines : Give sulphonamide, soluble in alkali.

$$C_6H_5SO_2Cl + RNH_2 \longrightarrow RNHSO_2C_6H_5 \xrightarrow{NaOH} RNNaSO_2C_6H_5$$

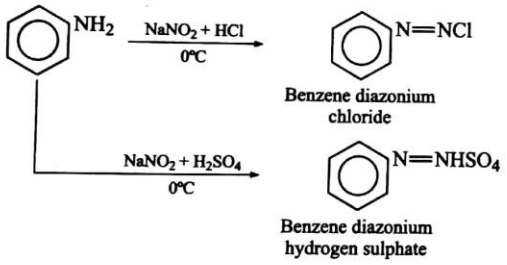
(b) Secondary amines : Give sulphonamide, insoluble in alkali.

$$C_6H_5SO_2Cl + R_2NH \longrightarrow R_2NSO_2C_6H_5$$

(c) Tertiary amines : Do not react.

(iv) Some other characteristics of aromatic amines having $-NH_2$ gp. in nucleus.

(a) Undergo diazotization with $NaNO_2$ + HCl or $NaNO_2$ + H_2SO_4 at 0°C.



(b) Undergo coupling reaction.

(c) Easily oxidised even by air.

9. Cyanides and Isocyanides :

(i) On reduction give primary amines and secondary amines respectively.

$$\underset{\text{Cyanides}}{RCN} \xrightarrow{\text{Reduction}} RCH_2NH_2$$

$$\underset{\text{Isocyanide}}{RNC} \xrightarrow{\text{Reduction}} RNHCH_3$$

(ii) On hydrolysis give acid and primary amine respectively.

$$RCN \xrightarrow{HOH} RCOOH$$

$$RNC \xrightarrow{HOH} RNH_2 + HCOOH$$

10. Nitro compounds :

(i) Give yellow colour with NaOH solution.

(ii) On reduction in acid medium (Sn + HCl), give primary amines.

$$R{-}NO_2 \xrightarrow{Sn/HCl} RNH_2$$

11. Aromatic compounds :

(a) An aromatic compound is one which obey Huckel rule, *i.e.*, aromaticity is due to extensive delocalisations of π-electrons (*i.e.*, $(4n+2)$ π-electron where n is any integer or 0, 1, 2 ...) in planar ring system.

(b) A host group already present in benzene nucleus directs the incoming (guest) substituent to occupy ortho, meta or para position.

(c) Some groups are *o*- and *p*-directing, *e.g.*, $-NH_2$ —OH—O*R*, —$NHCOCH_3$, —SH, —CH_3, —*X*, $-NH_3^+$, —NC, etc., whereas some are *m*-directing, *e.g.*, —CN, —SO_3H, —NO_2, —CHO, —COOH, —CCl_3, etc.

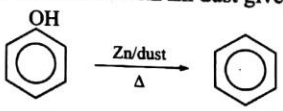
12. Phenols :

(i) Soluble in alkali.

(ii) Turn blue litmus to red.

(iii) Give no effervescences with $NaHCO_3$, although acidic in nature.

(iv) On distillation with Zn dust give benzene.



(v) Show characteristic colour with $FeCl_3(aq.)$.

13. Carbohydrates :

(i) Molish's test : A drop or two of alcoholic solution of α-naphthol is added to 2 mL of aqueous solution of compound. 1 mL of conc. H_2SO_4 is added carefully along the sides of test tube. The formation of a violet ring at the junction of two liquids confirm the presence of carbohydrate.

(ii) Osazone formation : Glucose and fructose on heating with excess of phenylhydrazine in acetic acid gives a yellow crystalline compound osazone having m.pt. 205°C.

• NUMERICAL PROBLEMS •

1. Select the chiral objects from the following list.
Nail, screw, scissor, knife, spool of thread, empty spool or thread less spool, glove, shoe, a pair of shoe, sock, pullover sweter, rubber ball, pyramid of cheeps, helix, double helix, tennis racket, hand, foot, ear, rifle, letters (*M, O, A*), letters (*P, J, F*).

2. Write down the structure of stereoisomers of the following:
(a) 2,3-Dihydroxybutane.
(b) 3-Phenyl-2-propenoic acid.

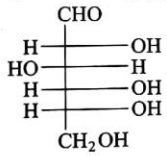
3. Write down the no. of asymmetric carbon in each optically active compound and report the no. of isomers.
(a) $CH_3 \cdot (CHOH)_2\, COOH$
(b) $COOH \cdot (CHOH)_2\, COOH$

4. Write down the structures of stereoisomers formed when *cis*-2-butene is reacted with Br_2. **(IIT 1995)**

5. A racemic mixture of (±) 2-phenyl propanoic acid on esterification with (+) 2-butanol gives two esters. Mention the stereochemistry of two esters formed. **(IIT 2003)**

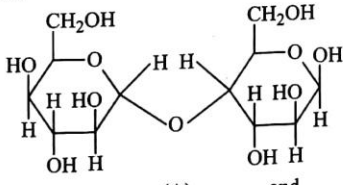
6. Draw Newmann projection of relatively less stable staggered form of *n*-butane. The reason of low stability of this form is due to (a) torsional strain (b) van der Waals' repulsion, (c) both of them. **(IIT 2004)**

7. The Fischer projection of *D*-(+) glucose is given as:

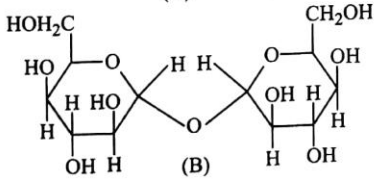


Write the Fischer projection of (a) L-(–) glucose and (b) the products formed after its reaction with Tollen's reagent. **(IIT 2004)**

8. Which of the following disaccharide will not reduce Tollens reagent? **(IIT 2005)**

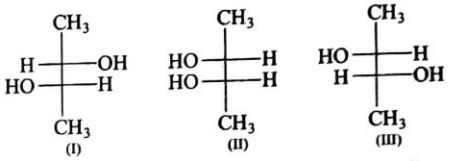


(A) and



(B)

9. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III. **(IIT 2000)**

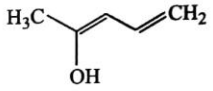


(I) (II) (III)

10. How many asymmetric carbon atoms are created during the complete reduction of benzil (PbCOCOPh) with $LiAlH_4$? Also, write the number of possible stereoisomers in the product. **(IIT May 1997)**

11. Optically active 2-iodobutane on treatement with NaI in acetone gives a product which does not show optical activity. Explain why? **(IIT 1995)**

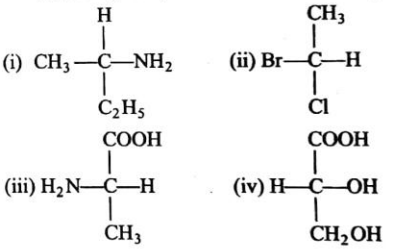
12. Write resonance structure of the given compound. **(IIT 2003)**



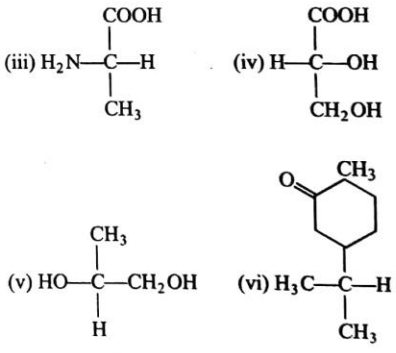
13. Write the stereoisomers formed when trans-2-butene reacts with (i) Bromine (ii) Baeyer's reagent.

14. Write the stereoisomers formed when *cis*-2-butene reacts with (i) Bromine (ii) Baeyer's reagent.

15. (a) Predict the nature of *R* or *S* configuration for the following compounds.



(i) (ii)



(iii) (iv)

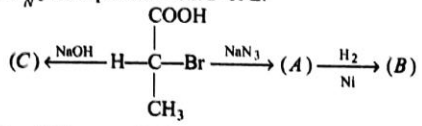
(v) (vi)

(b) Draw the *R* or *S* configuration for the following predicting precedence order of groups.
(i) 3-bromohexane (ii) 1,3-dichloro pentane (iii) 3-chloro, 3-methyl pentane (iv) 1,2-dibromo-2-methyl butane
(v) 3-chloro, 2,2,5-tri methyl heptane (vi) lactic acid

(vii) $CH_3CH_2CH_2CH\begin{matrix} D \\ \diagdown \\ Cl \end{matrix}$

16. Optically active sec-butyl alcohol retains its activity indefinitely in contact with aqueous base, but it rapidly converted into optically inactive (racemic) sec-butyl alcohol by dil. H_2SO_4. Explain.

17. Complete the equation and assuming all but one of the steps are $S_{N}2$ each product with *D* or *L*.



18. (*W*) and (*X*) are optically active isomers of C_5H_9Cl. (*W*) on treatment with one mole of H_2 is converted to an optically inactive compound (*Y*), but (*X*) gives an optically active compound (*Z*) under the same conditions. Give structure of (*Y*) and configuration of (*W*), (*X*) an (*Z*) in Fischer projections. **(Roorkee 2000)**

19. 0.90 g of an organic compound $C_4H_{10}O_2$ (*A*) when treated with sodium, 224 mL of hydrogen were evolved at NTP. Compound (*A*) could be separated into fractions (*B*) and (*C*) by crystallization of which, fraction (*B*) could only be resolved into optical isomers (*D*) and (*E*). Write down the structure formulae of (*A*) to (*E*) with proper reasoning.

20. Write down the structures of close homologues of heptane having in their molecule one quaternary C-atom and the other having two tertiary carbon atoms.

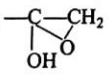
21. A hydrocarbon (*A*) was found to have vapour density 36. It forms only single monochloro substitution product. Suggest (*A*).

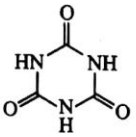
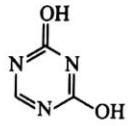
22. Which alkane having a molar mass of 86, will form only two monobromo alkanes?

23. How will you distinguish 1-chloro-2-butene and 2-chloro-2-butene?

24. C_6H_{12} is an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound C_6H_{14}. What are these?

25. Point out the isomerism shown by each pair :

(i) CH_3COCH_2OH and 

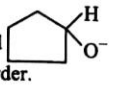
(ii)  and 

(iii) Propylamine and isopropylamine.

(iv) Methyl propylamine and diethylamine.

26. Pentan-2-one forms two oximes whereas pentan-3-one forms two oximes. Explain.

27. List the following alkoxide nucleophiles in order of decreasing $S_{N}2$ reactivity :

Me_3CO^-, MeO^-, $MeCH_2O^-$, Me_2CHO^- and 

How does $S_{N}2$ mechanism account for this order.

28. Discuss the nature of products formed and the mechanism for the addition of HCl on 3-methyl-1-butene.

29. Predict the major product of dehydrohalogenation of 4-bromo-1-hexene.

30. Account for the fact that addition of $CBrCl_3$ in the presence of peroxide takes place faster to 2-ethyl-1-hexene than to 1-octene.

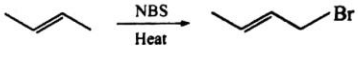
31. Suggest the intermediate and mechanism for the reaction :

32. On treatment with HCl, 1,3-butadiene yields a mixture of 3-chloro-1-butene and 1-chloro-2-butene. How do you account for the formation of these two products?

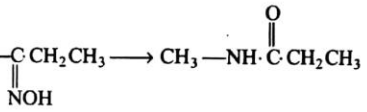
33. Write down the two products (major and minor) obtained on dehydration of neopentyl alcohol.

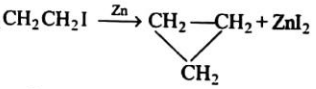
34. Which acts as an acid in aqueous solution of HBr and in dry HBr? Which is the stronger one? Which can better transfer a hydrogen ion to an alkene?

35. Write down the type of chemical changes :

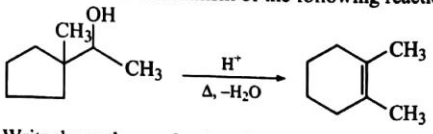
(i) 

(ii) $CHCl_3 + OH^- \longrightarrow :CCl_2 + H_2O + Cl^-$

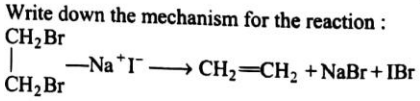
(iii) 

(iv) 

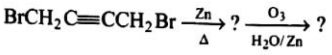
36. Write down the mechanism of the following reaction :

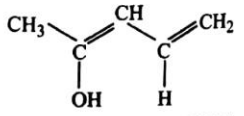


37. Write down the mechanism for the reaction :



38. Complete the following reaction :



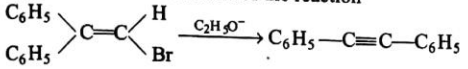
39. Write resonance structure for 

(IIT 2003)

40. 3,3-dimethyl butan-2-ol loses a molecule of water in the presence of conc. H_2SO_4 to give tetramethyl ethylene as a major product. Suggest a suitable mechanism. **(IIT 1996)**

41. Ethyl acetoacetate has two form keto and enol but phenol (enol) do not show keto form.

42. Write down the mechanism of the reaction



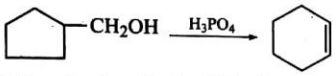
43. Write down the mechanism for the reduction of alkyne in ethanol by Na.

44. Write the mechanism of the reaction,

45. Write down the mechanism of oxidation of isopropyl alcohol by $K_2Cr_2O_7/H_2SO_4$.

46. Write the mechanism for the acid dehydration of cyclobutyl carbinol.

47. Write the mechanism for



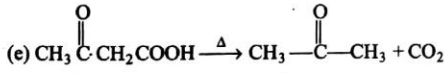
48. Suggest mechanisms for the following reactions :

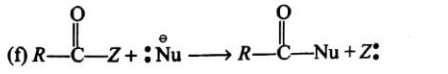
(a) $RH + SO_2 + Cl_2 \xrightarrow{h\nu} RSO_2Cl + HCl$

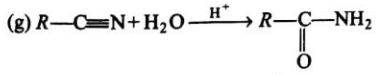
(b) $RCONH_2 \xrightarrow{NaOH + Br_2} RNH_2$

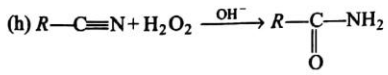
(c) $n\text{-}C_4H_9OH \xrightarrow{HBr} nC_4H_9Br$

(d) $(CH_3)_3C\cdot OH \xrightarrow{HBr} (CH_3)_3C\cdot Br$

(e) 

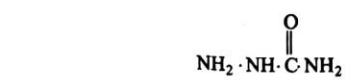
(f) 

(g) 

(h) 

49. Write down the mechanism for the cleavage of 2,2-dimethyl oxirane by acid (H^+). **(IIT 1997)**

50. Write down the mechanism for the addition of $NaHSO_3$ on carbonyl gp.

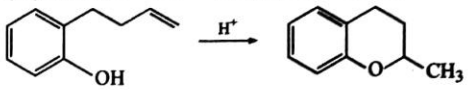
51. There are two $-NH_2$ gps. in semicarbazide that might react with a carbonyl gp. Why the $-NH_2$ gp. adjacent to in  does not react with carbonyl compound ?

52. Peroxy acetic acid (CH_3CO_3H) is a weaker acid than acetic acid, Why ?

53. 3,3-Dimethyl-butan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. **(IIT 1996)**

54. (a) Write the intermediate steps for each of the following reaction. **(IIT 1998)**

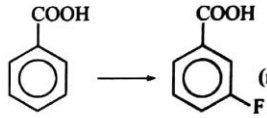
(i) $C_6H_5CH(OH)C{\equiv}CH \longrightarrow C_6H_5CH{=}CHCHO$

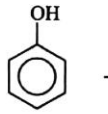
(ii) 

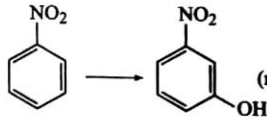
(b) Show the steps to carry out the following transformations.

(i) Ethylbenzene ⟶ benzene **(IIT 1998)**

(ii) Ethylbenzene ⟶ 2-phenylpropionic acid **(IIT 1998)**

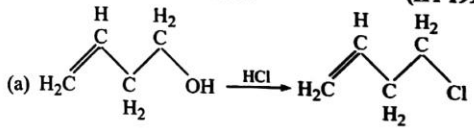
(iii)  (not more than 3 steps) **(IIT 2003)**

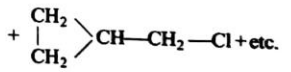
(iv)  Aspirin **(IIT 2003)**

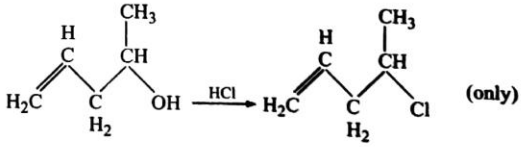
(v)  (not more than 4 steps) **(IIT 2004)**

(vi) Aniline ⟶ Benzylamine not more than three steps **(IIT 2000)**

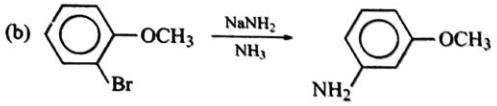
55. Explain briefly the formation of the products giving the structures of the intermediates. **(IIT 1999)**

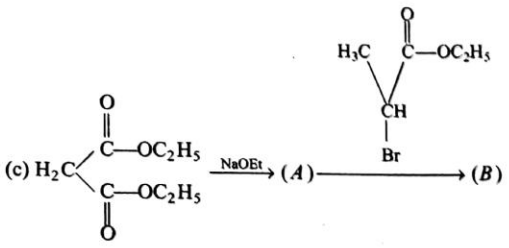
(a) 

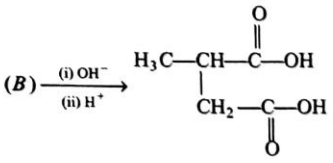




(only)

(b) 

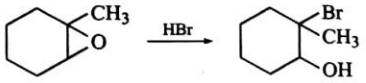
(c) 



56. Write down the mechanism of the reaction :

$$C_6H_5CH_2CH{=}CH_2 \xrightarrow[\Delta]{KOH} C_6H_5CH{=}CHCH_3$$

57. Write mechanism for the reaction :



58. Isobutylene, a gas an dissolution in 63% H_2SO_4 yields a deliquescent white solid (*A*). On heating solid (*A*) with water liquid (*B*) is obtained. What are (*A*) and (*B*).

59. Sulphanilic acid is insoluble in water and acid but soluble in alkali, why?

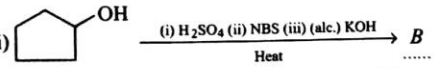
60. Which one is the stronger acid : 3-butenoic acid or 3-butynoic acid and why?

61. Discuss action of heat on α-, β- and γ-hydroxy carboxylic acids.

62. $CHCl_3$ is more acidic than CHF_3. Explain.

63. Complete the following giving the structures of the major organic products :

(i) $2F_2C{=}CCl_2 \xrightarrow{Heat} A$ .....

(ii)  .....

64. Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of $FeBr_3$ it gives *p*-bromotoluene. Give explanation for the above observations.

65. Give reasons for the following :

(i) Tert-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$. **(IIT 2000)**

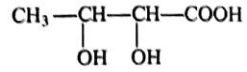
(ii) $CH_2{=}CH^-$ is more basic than $HC{\equiv}C^-$. **(IIT 2000)**

(iii) Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. **(IIT 2000)**

(iv) Which one is more soluble in diethyl ether, anhydrous $AlCl_3$ or hydrous $AlCl_3$? **(IIT 2003)**

66. Read the statements given below and write 'true' against correct statement(s). If any of the statements is wrong, rectify the mistake/mistakes and give a correct statement in its place. **(Roorkee 2001)**

(a) Tollens reagent converts $CH_3{-}CH{=}CH{-}CHO$ to



(b) Total number of optical isomers of 3,4-dichlorohexane is 3.

(c) When heated with dilute H_2SO_4, $C_6H_5SO_3H$ undergoes further sulphonation to give $C_6H_4(SO_3H)_2$.

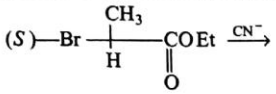
(d) Addition of HI to 3,3-dimethyl-1-butene not only gives 1-iodo-3,3-dimethylbutane, but also 2-iodo-2,3-dimethyl butane.

67. 7-bromo-1,3,5-cycloheptatriene remains in ionic form but 5-bromo-1,3-cyclopentadiene does not ionise even in presence of Ag^+ ion. Explain. **(IIT 2004)**

68. Write the structures of but-2-ene and 2-methylpropene and show addition of HBr on both of them in presence and absence of peroxide.

69. 2,3-dimethyl but-2-ene does not decolorise Br_2/CCl_4 but decolorises Br_2/H_2O. Explain.

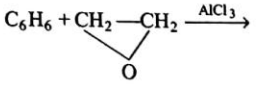
70. Give the product of the following displacement reaction :



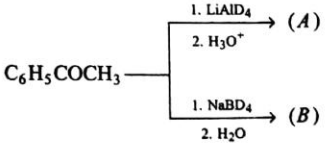
71. Give the product of the following reaction :

$$CH_3CH_2CH_2CH_2CHBr_2 \xrightarrow[200°C]{KOH(s)}$$

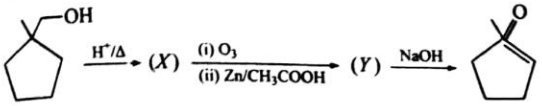
72. Give the product of the following reaction :



73. Give the products of the following reactions :



74. Identify X and Y in the given reaction.



(IIT 2005)

75. Give the structure of the major organic products formed 3-ethyl-2-pentene under each of the following reaction conditions.

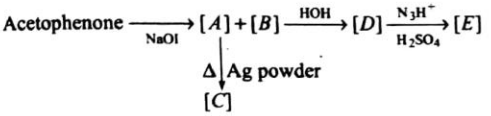
(a) HBr in the presence of peroxide

(b) Br_2/H_2O

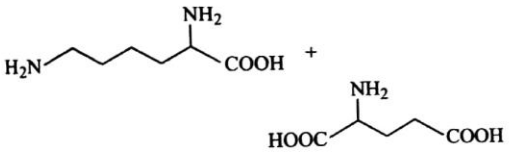
(c) $Hg(OAc)_2/H_2O$; $NaBH_4$. **(IIT 1996)**

76. Acetophenone on reaction with hydroxylamine-hydrochloride can produce two isomeric oximes. Write structures of the oximes. **(IIT July 1997)**

77. Complete the following :



78. Following two amino acids liosine and glutamine form dipeptide linkage. What are two possible dipeptides? **(IIT 2003)**



79. Identify X and Y in the following change :

$C_5H_{13}N \xrightarrow[-N_2]{NaNO_2 + HCl} Y$ (Tertiary alcohol) + other products (X) optically active.

Also, report whether Y is optically active or not. Report the structures of all the intermediates. **(IIT 2005)**

80. (a) Dehydration of,

gives a compound which exists in two isomeric forms. Give the structures of both the isomers.

(b) Explain in not more than 2,3 lines.

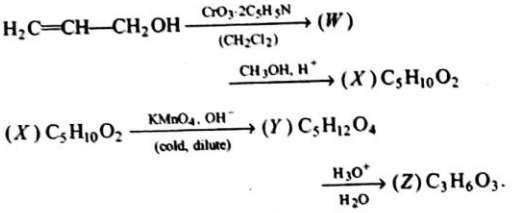
(i) Aniline does not undergo Friedel-Crafts reaction.

(ii) Mineral acid is added in excess in diazotization of arylamines.

(c) Complete the reaction,

$(CH_3)_2C{=}CH_2 + \text{isobutane} \xrightarrow[273\ K]{HF}$ **(Roorkee 1999)**

81. Give structures of (W), (X), (Y) and (Z) in the following reactions. **(Roorkee 2000)**

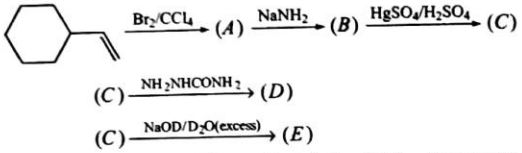


82. Write the products in the following reactions :

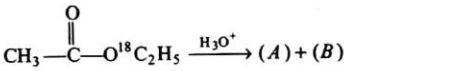
(i) $CH_3CH{=}CH_2 + Br{\cdot}CCl_3 \xrightarrow{Peroxide}$

(ii) $CH_3CH{=}C(CH_3)_2 + HCl \xrightarrow{Peroxide}$ **(Roorkee 1998)**

83. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures : **(IIT 2001)**

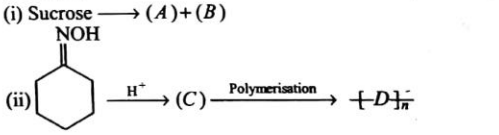


84. Write the structures of the products (A) and (B). **(IIT 2000)**

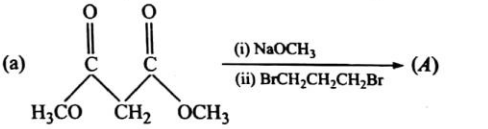


85. Give the structures of the products in each of the following reactions : **(IIT 2000)**

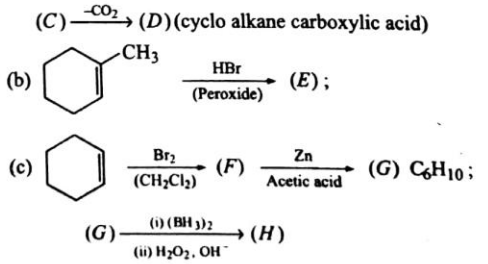
(i) Sucrose $\longrightarrow (A)+(B)$



86. What are (A) to (L) in the scheme of reactions given below ?



(Roorkee 2000)



(d) $(J) \xleftarrow[H_2O]{HCrO_4} (I) \xrightarrow[(Pyridine)]{CrO_3} CH_3CHO$

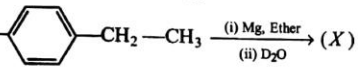
(e) Acetone (2 mol.) $\xrightarrow{OH^-} (K) \xrightarrow[Heat]{NaHSO_4} (L)$.

87. Give structures/configurations of the products (T) to (Z) of the following reactions: **(Roorkee 2001)**

(a) $H_3C-\underset{CH=CH_2}{\overset{C_2H_5}{C}}-H + D_2 \xrightarrow{Pd} (T)+(U)$

(b) $R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[(ii)\ H_2O]{(i)\ N_3H,\ Heat} (V)$

(c) $I^- + CH_3-CH_2-CH_2-\underset{H}{\overset{D}{C}}-I \longrightarrow (W)$

(d)  $\xrightarrow[(ii)\ D_2O]{(i)\ Mg,\ Ether} (X)$

(e) $H_2C=\underset{CH_3}{\overset{}{C}}-COOH \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ BH_3,\ THF} (Y)$

(f) $2HC\equiv C-H \xrightarrow[O_2]{Cu^{2+}} (Z)$

88. Identify (A) to (K) as reactant, reagent, product and name of the reaction in the following: **(Roorkee 1999)**

(i) $3(CH_3)_2C=O \xrightarrow{(A)} (B)$ Aldol condensation

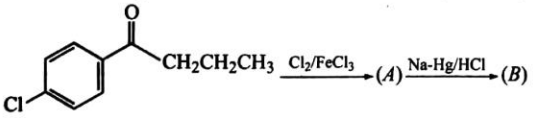
(ii) $CH_3COCl + H_2 \xrightarrow{(C)} (D)$ Rosenmund's reaction

(iii) $(E) \xrightarrow[C_2H_5ONa]{NH_2NH_2} CH_3CH_2CH_3\ (F)$

(iv) $C_6H_5OH \xrightarrow{(G)} (H_1)+(H_2)$ Elb's oxidation

(v) $C_6H_5N_2Cl \xrightarrow[HCl]{(J)} (K)$ Gattermann reaction

89. Write structures of the products (A), (B), (C), (D) and (E) in the following scheme: **(IIT 2002)**

 $\xrightarrow{Cl_2/FeCl_3} (A) \xrightarrow{Na\text{-}Hg/HCl} (B)$

$\xrightarrow{HNO_3/H_2SO_4} (C) \xrightarrow{CH_2=CHCH_2O^-Na^+} (D) \xrightarrow{H_2/Pd/c} (E)$

90. Identify (A) to (D) in the following sequence of reactions:

$\xrightarrow[DMF]{KCN} (A) \xrightarrow[EtOH,\ PhCHO]{NaOEt,\ \Delta} (B) \xrightarrow{H_3O^+,\ \Delta} (C)$

$\xrightarrow[2.\ CH_3NH_2]{1.\ SOCl_2} (D)$

(IIT 2004)

91. Predict the major products in the following reactions:

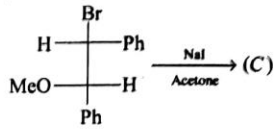
(i) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$

(ii) $C_6H_5CH_2COOCH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr\ (excess)}$

(iii) $C_6H_5C_2H_5 \xrightarrow[2.\ NaCN]{1.\ Br_2,\ Heat,\ Light}$ **(IIT 1994)**

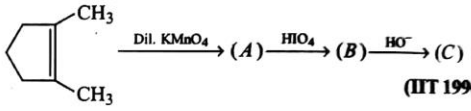
(iv) $\begin{matrix} CH_3CH_2 \\ H \end{matrix}\!\!>\!C=O \xrightarrow[2.\ LiAlH_4]{1.\ KCN/H_2SO_4} (D)$ **(IIT 1996)**

(v) Predict the structure of the product in the following reaction. **(IIT 1996)**



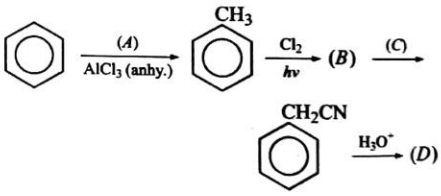
(vi) Suggest appropriate structure of the missing compounds.

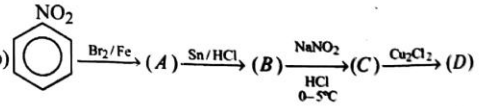
(The number of carbon atoms remains the same throughout the reactions.)



(IIT 1996)

92. Complete the following:

(a) 

(b) 

(IIT 1992)

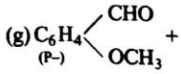
(c) $CH_3CH_2CH_2OH \xrightarrow{P + Br_2} (A) \xrightarrow{KOH\ alc.} (B)$

$\xrightarrow{HBr} (C) \xrightarrow[\Delta]{NH_3(g)} (D)$

(d) $C_6H_5COOC_6H_5 \xrightarrow{Mononitration} (A)$ **(IIT 1993)**

(e) $C_6H_5CONH_2 \xrightarrow{P_2O_5} (A) \xrightarrow[H_2O,\ \Delta]{H^+} (B)$ **(IIT 1992)**

(f) $+ (CH_3)_2CH\cdot CH_2Cl \xrightarrow{AlCl_3} (A)$

(g)  (IIT 1992)

(h) $CH_3—CH_2—COOH \xrightarrow[\text{Bromine}]{P \text{ and}} (A)$

$(A) \xrightarrow[2.\ H^+]{1.\ \text{Alcoholic KOH (excess)}} (B)$ (IIT 1995)

(i) 2,4 - Dinitroaniline $\xrightarrow[\text{anisole}]{NaNO_2 \text{ and HCl at } 5°C} (C)$ (IIT 1995)

(j) $C_6H_5—CHO + CH_3—COOC_2H_5$

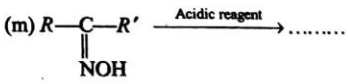
$\xrightarrow[C_2H_5OH \text{ and heat}]{NaOC_2H_5 \text{ in absolute}} (D)$ (IIT 1995)

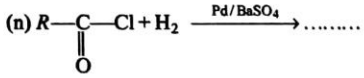
(k) o-$HOOC—C_6H_4—CH_2—C_6H_5 \xrightarrow{SOCl_2} (G)$

$(G) \xrightarrow[AlCl_3]{\text{Anhydrous}} (H); (H) \xrightarrow[HCl]{Zn\text{-}Hg} (I)$ (IIT 1995)

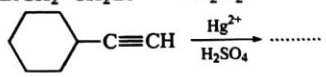
(l) $(A) \xrightarrow{PCl_5} (B) \xrightarrow{LiAlH_4} (C) \xrightarrow[H_2SO_4]{HBr} (D) \xrightarrow[\text{Ether}]{Na}$

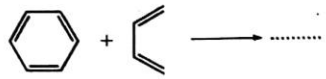
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$

(m) 

(n) 

(o) $BrCH_2 \cdot CH_2Br \xrightarrow{?} C_2H_2$

(p) 

(q) 

(r) $C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{Alcoholic KOH, heat}} (A) + (B)$

(IIT 1998)

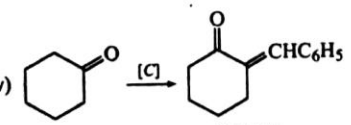
(s) $CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\ \text{Heat}} (A) + (B)$ (IIT 1998)

(t) $(CH_3)_2CHOCH_3 \xrightarrow{HI\ (\text{excess}),\ \text{Heat}} (A) + (B)$ (IIT 1998)

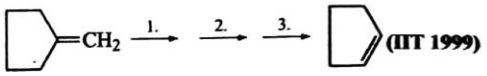
(u) $CH_3CONHC_6H_5 \xrightarrow{Br_2,\ Fe} (A) + (B)$ (IIT 1998)

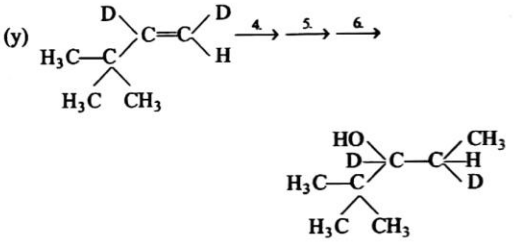
(v) $C_6H_5CH{=}CH_2 \xrightarrow{Br_2} (A) \xrightarrow[(ii)\ CH_3I]{(i)\ NaNH_2\ (3.0\ \text{equiv.})} (B)$

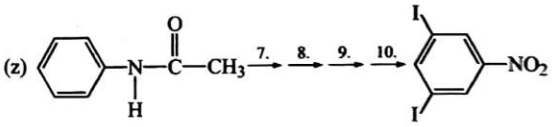
(IIT 1998)

(w) 

$\xrightarrow[(ii)\ H^+,\ \text{Heat}]{(i)\ LiAlH_4} (D)$ (IIT 1998)

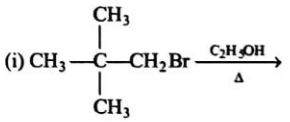
(x)  (IIT 1999)

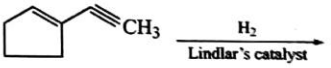
(y) 

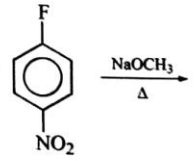
(z) 

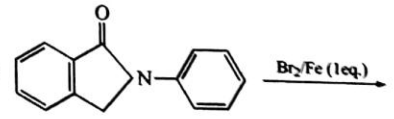
(IIT 1999)

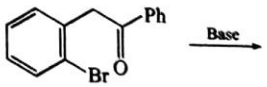
93. What would be the major product in each of the following reactions? **(IIT 2000)**

(i) 

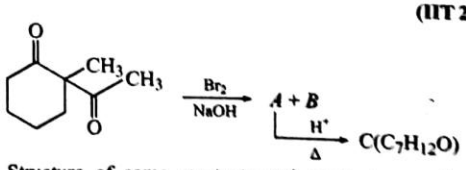
(ii) 

(iii) 

(iv) 

(v) 

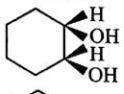
94. Idenfity (A), (B) and (C) and give their structures. **(IIT 2000)**

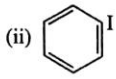


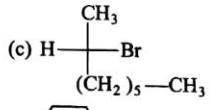
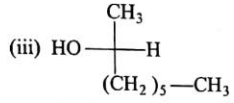
95. Structure of some reactants and products are given in columns I and II respectively. First match the appropriate

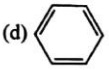
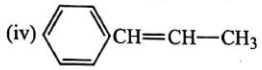
reactant-product pair from columns I and II and then suggest another suitable reagent for each pair. **(Roorkee 2001)**

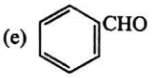
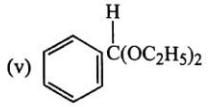
Column I **Column II**

(a) $R—CH=CH_2$ (i) 

(b) (ii) 

(c)  (iii) 

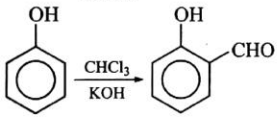
(d)  (iv) 

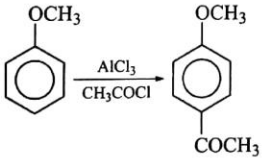
(e)  (v) 

(f) (vi) $R—CHCl—CH_2—CCl_3$

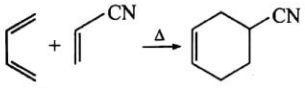
96. Match the name reactions in **list I** with the transformations provided in **list II.**

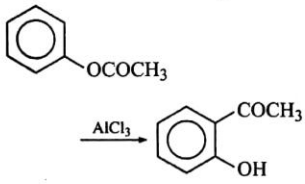
List I **List II**

(1) Friedel-Crafts reaction (A) 

(2) Hofmann's rearrangement (B) 

(3) Diels-Alder reaction (C) $RCONH_2 \xrightarrow[Br_2]{NaOH} RNH_2$

(4) Fries rearrangement (D) 

(5) Reimer-Tiemann reaction (E) 

97. Draw the various structures of molecular C_4H_6 on the basis of following characteristics :

(a) If C_4H_6 reacts with ammoniacal $AgNO_3$.

(b) If C_4H_6 does not react with ammoniacal $AgNO_3$ but reacts with hot alkaline $KMnO_4$ to give CH_3COOH.

(c) If C_4H_6 decolourises Br_2 water and by catalytic hydrogenation (using 1 mole) and subsequent reaction with alkaline $KMnO_4$ gives CH_3COOH.

(d) If C_4H_6 on ozonolysis gives succinic acid.

98. An alkane (*A*), C_5H_{12} on chlorination at 300°C gives a mixture of four different monochlorinated derivatives, (*B*), (*C*), (*D*) and (*E*). Two of these derivatives give the same stable alkene (*F*) on dehydrohalogenation. On oxidation with hot alkaline $KMnO_4$, followed by acidification, (*F*) gives two products (*G*) and (*H*). Give structures of (*A*) to (*H*) with proper reasoning. **(Roorkee 1995)**

99. There are six different alkenes (*A*), (*B*), (*C*), (*D*), (*E*) and (*F*). Each on addition of one mole of hydrogen gives (*G*) which is the lowest molar mass hydrocarbon containing only one asymmetric carbon atom. None of the above alkenes give acetone as a product on ozonolysis. Give structures of (*A*) to (*F*). Identify the alkene which is likely to give a ketone containing more than five carbon atoms on treatment with a warm conc. solution of alkaline $KMnO_4$. Show various configurations of (*G*) in Fischer projections. **(Roorkee 1992)**

100. Draw the various structures of compound (*A*) having molecular formula $C_5H_{10}O$ on the basis of following characteristics :

(a) If (*A*) undergoes Cannizzaro's reaction.

(b) If (*A*) gives iodoform test and forms isobutyric acid salt and iodoform.

(c) If (*A*) reacts with Na and decolorises Br_2 water and shows geometrical isomerism.

(d) If (*A*) reduces Tollens reagent and has chiral carbon atom.

(e) If (*A*) does not reduces Tollens reagent but gives iodoform test and forms white crystalline solid with $NaHSO_3$.

(f) If (*A*) gives red-orange solid with 2-4 dinitro phenyl hydrazine but does not give white crystalline solid with $NaHSO_3$.

101. How many g of Br_2 will react with 5 g of :

(a) Pent-1-ene (b) Pent-1-yne (c) Pentane?

102. (a) A halide $C_5H_{11}X$ on treating with alc. KOH gives pentene-1. What is halide?

(b) A halide $C_5H_{11}X$, on treating with (alc.) KOH gives only pentene-2. What is halide?

103. Identify (*X*), (*Y*) and (*Z*) in the following synthetic scheme and write their structures.

$$CH_3CH_2C\equiv CH \xrightarrow[(ii)\ CH_3CH_2Br]{(i)\ NaNH_2} (X) \xrightarrow{H_2/Pd\text{-}BaSO_4} (Y) \xrightarrow{\text{Alkaline } KMnO_4} (Z)$$

Is the compound (*Z*) optically active? **(IIT 2002)**

104. An unsaturated hydrocarbon (A), C_9H_{16} which reacts with one mole of Br_2, on ozonolysis gives compound (B) and two carbon containing aldehyde (C), of which one of the compound undergoes reaction with cold and conc. NaOH to give products (D) and (E) in equimolar proportion, both containing same number of carbon atoms. Identify (A), (B), (C) and gives reactions.

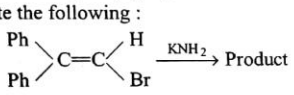
105. An unknown optically active hydrocarbon (X) (M.F. C_8H_{12}) gives an optically inactive compound (Y) (M.F. C_8H_{18}) after hydrogenation. The compound (X) gives no precipitate with $[Ag(NH_3)_2]^+$ and gives optically inactive compound (Z) (M.F. C_8H_{14}) with H_2 and Na/liq. NH_3. Determine the structures of (X), (Y) and (Z).

106. A hydrocarbon (X) was found to have a molar mass of 80-85 g mol^{-1}. A 10.02 mg sample took up 8.40 mL of H_2 gas measured at 0°C and 760 mm pressure. Ozonolysis of (X) yields only HCHO and CHO-CHO. What was hydrocarbon?

107. A hydrocarbon of formula $C_{10}H_{16}$ absorbs only one mole of H_2 upon hydrogenation. On ozonolysis it yields 1,6-cyclodecane dione. What is the hydrocarbon?

108. Out line all the steps for the conversion of *trans*-1-phenyl propene to *cis*-1-phenyl propene.

109. Complete the following :



110. An organic compound (A), C_4H_9Cl on reacting with aqueous KOH gives (B) and on reaction with alcoholic KOH gives (C) which is also formed on passing the vapours of (B) over heated copper. The compound (C) readily decolorises bromine water. Ozonolysis of (C) gives two compounds (D) and (E). Compound (D) reacts with NH_2OH to give (F) and the compound (E) reacts with NaOH to give an alcohol (G) and sodium salt (H) of an acid. (D) can also be prepared from propyne on treatment with water in presence of Hg^{2+} and H_2SO_4. Identify (A) to (H) with proper reasoning. **(Roorkee 1996)**

111. An organic compound (A), $C_6H_{10}O$, on reaction with CH_3MgBr followed by acid treatment gives compound (B). The compound (B) on ozonolysis gives compound (C), which in presence of a base gives 1-acetyl cyclopentene (D). The compound (B) on reaction with HBr gives compound (E). Write the structures of (A), (B), (C) and (E). Show how (D) is formed from (C). **(IIT 2000)**

112. $A\ (C_6H_{12}) \xrightarrow{HCl} \underset{(C_6H_{13}Cl)}{B+C}$

$B \xrightarrow{\text{(alc.) KOH}} D$(isomer of A)

$D \xrightarrow{\text{Ozonolysis}} E$ (Negative test with Fehling solution but + ve iodoform test)

$A \xrightarrow{\text{Ozonolysis}} F+G$ (Both give positive test with Fehling solution but - ve iodoform test)

$F+G \xrightarrow{\text{Conc. NaOH}}$ HCOONa + a primary alcohol.

113. In the study of chlorination of propane four products (A, B, C and D) of the formula $C_3H_6Cl_2$ were isolated. Each was further chlorinated to provide trichloro products $C_3H_5Cl_3$. It was found that (A) provided one trichloro product, (B) gave two while (C) and (D) each gave three products. What are (A), (B), (C) and (D)?

114. A hydrocarbon (A) of molar mass 54 reacts with an excess of Br_2 in CCl_4 to give a compound (B) whose molar mass is 593% more than that of (A). However, on catalytic hydrogenation with excess of hydrogen. (A) forms (C) whose molar mass is only 7.4% more than that of (A). (A) reacts with CH_3CH_2Br in the presence of $NaNH_2$ to give another hydrocarbon (D) which on ozonolysis yields diketone (E). (E) on oxidation gives propanoic acid. Give structures of (A) to (E) with reason. **(Roorkee 1997)**

115. An organic compound C_4H_6 on ozonolysis gives HCHO, CO_2 and CH_3CHO. What is this?

116. An organic compound E (C_5H_8) on hydrogenation gives compound F (C_5H_{12}). Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E. **(IIT 1995)**

117. After complete ozonolysis of one mole of monomer of natural polymer gives two moles of CH_2O and one mole of CH_3COCHO. Identify the monomer and draw the all *cis*-forms of natural polymer. **(IIT 2005)**

118. One mole of the compound (A) (molecular formula C_8H_{12}), incapable of showing stereoisomerism, reacts with only one mole of H_2 on hydrogenation over Pd. (A) undergoes ozonolysis to give a symmetrical diketone (B) ($C_8H_{12}O_2$). What are the structure of (A) and (B)? **(IIT May 1997)**

119. A hydrocarbon (A) of the formula C_7H_{12} on ozonolysis gives a compound (B) which undergoes aldol condensation giving 1-acetyl cyclopentane. Identify (A) and (B). **(IIT May 1997)**

120. Hydrocarbon (A), C_6H_{10} on treatment with H_2/Ni, H_2/Lindlar's catalyst and Na/liquid ammonia forms three different reduction products (B), (C) and (D) respectively. (A) does not form any salt with ammoniacal $AgNO_3$ solution, but forms a salt (E) on heating with $NaNH_2$ in an inert solvent. Compound (E) reacts with CH_3I to give (F). Compound (D) on oxidative ozonolysis gives *n*-butanoic acid along with other product. Give structures of (A) to (F) with proper reasoning. **(Roorkee 1998)**

121. An organic compound (A), C_5H_9Br which readily decolorises bromine water and $KMnO_4$ solution, gives (B), $C_5H_{11}Br$ on treatment with Sn/HCl. The reaction of (A) with $NaNH_2$ produces (C) with evolution of ammonia. (C) neither reacts with sodium nor forms any metal acetylide but reacts with Lindlar's catalyst to give (D) and on reaction with Na/NH_3(*liq.*) produces (E). Both the compounds (D) and (E) are isomeric. Give structures of (A) to (E) with proper reasoning. **(Roorkee 1996)**

122. 1,4-Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound (*X*) which upon reaction with excess of Mg in dry ether forms (*Y*). Compound (*Y*) on treatment with ethyl acetate followed by dilute acid yields (*Z*). Identify the structures of compounds (*X*), (*Y*) and (*Z*). **(IIT 1995)**

123. Dehydrobromination of compounds (*A*) and (*B*) yield the same alkene (*C*). Alkene (*C*) can regenerate (*A*) and (*B*) by the addition of HBr in the presence and absence of peroxide respectively. Hydrolysis of (*A*) and (*B*) give isomeric products, (*D*) and (*E*) respectively. 1,1-diphenyl ethane is obtained on reaction of (*C*) with benzene in presence of H^+. Give structures of (*A*) to (*E*) with reasons. **(Roorkee 1997)**

124. An alkene (*A*) on passing through Br_2/CCl_4 gives a compound (*B*), which on dehydrobromination in the presence of $NaNH_2$ gives a hydrocarbon (*C*). Compound (*C*) yields (*D*) when warmed with dilute H_2SO_4 in the presence of $HgSO_4$. (*D*) gives a yellow precipitate of (*E*) on treatment with I_2 and NaOH and also forms sodium salt of 3,4-dimethylpentanoic acid. Give structures of (*A*) to (*E*) with reasons. **(Roorkee 2001)**

125. 36.4 g of 1,1,2,2-tetrachloropropane was heated with zinc dust and the product was bubbled through ammoniacal $AgNO_3$. What is the mass of precipitate obtained? Give equations for the reactions involved.

126. Write the structure and give IUPAC name of the alkene which gives only pentan-2-one on ozonolysis. **(Roorkee 1985)**

127. An alkyne with 5 carbon atoms per molecule when passed through dilute sulphuric acid containing mercuric sulphate gives a compound which forms an oxime, but has no effect on Fehling's solution. The compound on oxidation give dimethyl acetic acid. It reacts with sodamide to form a hydrocarbon. What is the structure of the alkyne?

128. Write the structure formulae and IUPAC names for the different alkanes formed when a mixture of 1-bromopropane and 2-bromopropane is reacted with sodium in presence of ether. What is the name of the reaction?

129. Which of the following has larger dipole moment? Explain?
1-Butyne or 1-Butene **(Roorkee 1999)**

130. An organic compound (*A*) composed of C, H and O gives characteristic colour with ceric ammonium nitrate. Treatment of (*A*) with PCl_5 gives (*B*) which reacts with KCN to form (*C*). The reduction of (*C*) with warm Na/C_2H_5OH produces (*D*) which on heating gives (*E*) with evolution of ammonia. Pyridine is obtained on treatment of (*E*) with nitrobenzene. Give structure of (*A*) to (*E*) with proper reasoning. **(Roorkee 1996)**

131. Alkenes (*A*) and (*B*) yield the same alcohol (*C*) on hydration. On vigorous oxidation with $KMnO_4$ (*A*) gives a carbonyl compound (*D*) and an acid (*E*), each containing four carbon atoms. On the other hand (*B*) gives an acid (*F*) and a carbonyl compound (*G*). In (*G*) no two identical groups are attached to the same carbon atom. Give structure of (*A*) to (*G*) with proper reasoning. **(Roorkee 1995)**

132. Compound (*A*) contains only carbon and hydrogen. It decolorises bromine in CCl_4 solution and reacts slowly with concentrate H_2SO_4. Compound (*A*) reacts with HBr to form (*B*). (*B*) reacts with NaOH to form (*C*). On oxidation (*C*) gives hexanone-3. Write the structures of (*A*), (*B*) and (*C*) and give reactions. **(Roorkee 1986)**

133. It required 0.7 g of a hydrocarbon (*A*) to react completely with Br_2 (2.0 g). On treatment of (*A*) with HBr it yielded monobromo alkane (*B*). The same compound (*B*) was obtained when (*A*) was treated with HBr in presence of peroxide. Write down the structure formulae of (*A*) and (*B*) and explain the reactions involved. **(Roorkee 1987)**

134. A liquid (*A*) is reacted with hot aqueous sodium carbonate solution. A mixture of two salts (*B*) and (*C*) are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid (*A*) again. Identify (*A*), (*B*) and (*C*) and write the equations involved. **(IIT May 1997)**

135. Compound (*A*) C_6H_{12} gives a positive test with bromine in carbon tetrachloride. Reaction of (*A*) with alkaline $KMnO_4$ yields only (*B*) which is the potassium salt of an acid. Write structure formulae and IUPAC names of (*A*) and (*B*). **(IIT July 1997)**

136. The silver salt of an unknown alkyne contains 67.08% of Ag. Assuming no other functional gp. present, what is the structure of alkyne?

137. A chloro compound (*A*) showed the following properties :
1. Decolorised bromine in CCl_4.
2. Absorbed hydrogen catalytically.
3. Gave a precipitate with ammonical cuprous chloride.
4. When vapourised 1.49 g of (*A*) gave 448 mL of vapours at STP. Identify (*A*) and write down the equations of reactions. **(Roorkee 1991)**

138. An unsaturated hydrocarbon (*A*), C_6H_{10} readily gives (*B*) on treatment with $NaNH_2$ in liquid NH_3. When (*B*) is allowed to react with 1-chloropropane, a compound (*C*) is obtained. On partial hydrogenation in the presence of Lindlar's catalyst, (*C*) gives (*D*), C_9H_{18}. On ozonolysis (*D*) gives 2,2-dimethylpropanal and 1-butanal. Give structures of (*A*), (*B*), (*C*) and (*D*) with proper reasoning. **(Roorkee 1992)**

139. An organic compound (*A*), C_6H_{10} on reduction first gives (*B*), C_6H_{12} and finally (*C*) C_6H_{14}. (*A*) on ozonolysis followed by hydrolysis gives two aldehydes (*D*) C_2H_4O and (*E*) $C_2H_2O_2$. Oxidation of (*B*) with acidified $KMnO_4$ gives acid (*F*), $C_4H_8O_2$. Determine the structures of (*A*) to (*F*) with proper reasoning. **(Roorkee 1993)**

140. A 10 g mixture of isobutane and isobutene requires 20 g of Br_2 (in CCl_4) for complete addition. If 10 g of the mixture is catalytically hydrogenated and the entire alkane is monobrominated in the presence of light at 127°C, which exclusive product and how much of it would be formed? (Atomic mass of bromine = 80). **(Roorkee 1998)**

141. A biologically active compound, Bombykol ($C_{16}H_{30}O$) is obtained from a natural source. The structure of the compound is determined by the following reactions :

(a) On hydrogenation, Bombykol gives a compound *A*, $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester.

(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O_3/H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.

Determine the number of double bonds in Bombykol. Write the structures of compound (*A*) and Bombykol. How many geometrical isomers are possible for Bombykol?

(IIT 2002)

142. An alkyl halide, (*X*) of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes (*Y*) and (*Z*) (C_6H_{12}). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of (*X*), (*Y*) and (*Z*). **(IIT 1996)**

143. One mole of each bromoderivative (*A*) and NH_3 react to give one mole of an organic compound (*B*). (*B*) reacts with CH_3I to give (*C*). Both (*B*) and (*C*) react with HNO_2 to give compounds (*D*) and (*E*), respectively. (*D*) on oxidation and subsequent decarboxylation gives 2-methoxy-2-methylpropane. Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1994)**

144. An organic compound (*A*) of molecular formula C_5H_8 when treated with sodium in liquid ammonia followed by reaction with *n*-propyl iodide yields (*B*), C_8H_{14}. (*A*) gives a ketone (*C*), $C_5H_{10}O$, when treated with dilute H_2SO_4 and $HgSO_4$. (*B*) on oxidation with alkaline $KMnO_4$ gives two isomeric acids (*D*) and (*E*), $C_4H_8O_2$. Give structures of compounds (*A*) to (*E*) with proper reasoning. **(Roorkee 1994)**

145. When gas (*A*) is passed through dry KOH at low temperature, a deep red coloured compound, (*B*) and a gas (*C*) are obtained. The gas (*A*) on reaction with but-2-ene, followed by treatment with Zn/H_2O yields acetaldehyde. Identify (*A*), (*B*) and (*C*).

146. When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute $KMnO_4$, in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? **(IIT 1994)**

147. 0.037 g of an alcohol, *R*OH, was added to CH_3MgI and the gas evolved measured 11.2 cm^3 at STP. What is the molar mass of *R*OH? On dehydration, *R*OH gives an alkene which on ozonolysis gives acetone as one of the products. *R*OH on oxidation easily gives an acid containing the same number of carbon atoms. Give structures of *R*OH and the acid with proper reasoning. **(Roorkee 1994)**

148. Hydrocarbon (*X*), C_7H_{12} on reaction with boron hydride followed by treatment with CH_3COOH yields (*A*). On reductive ozonolysis (*A*) yields a mixture of two aldehydes, (*B*) and (*C*). Of these, only (*B*) can undergo Cannizzaro's reaction. (*A*) exists in two geometrical isomers, (*A*–1) and (*A*–2), of which (*A*–2) is more stable. Give structures of (*X*), (*A*), (*B*), (*C*), (*A*–1) and (*A*–2) with proper reasoning. **(Roorkee 2000)**

149. A hydrocarbon (*A*), of the formula C_8H_{10}, on ozonolysis gives compound (*B*), ($C_4H_6O_2$) only. The compound (*B*) can also be obtained from the alkyl bromide, (*C*), (C_2H_5Br) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify (*A*), (*B*) and (*C*) and also give equations for the reactions. **(IIT 1996)**

150. An O.C. (*A*) reacts with H_2 to give (*B*) and (*C*) successively. On ozonolysis of (*A*), two aldehydes (*D*) C_2H_4O and (*E*) $C_2H_2O_2$ are formed. On ozonolysis of (*B*) only propanal is formed. What are (*A*) to (*E*) ?

151. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (*A*). The organometallic reacts with ethanal to give an alcohol (*B*) after mild acidification. Prolonged treatment of alcohol (*B*) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (*C*). Write the structures of (*A*), (*B*) and explain how (*C*) is obtained from (*B*)? **(IIT 2001)**

152. How will you distinguish divinyl ether and diethyl ether?

153. Arrange the following in order of increasing tendency for dehydrohalogenation with proper reasoning :

(i) $CH_3CH_2\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_3$

(ii) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$

(iii) $CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

(iv) $CH_3CH_2CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}H_2$

(v) CH_3CH_2Br

154. (a) An organic compound C_5H_8 on ozonolysis gives pentane-1,5-dial. Identify and convert 'C_5H_8' into cyclopentane-1,2-diol.

(b) A small amount of NaI catalyses the hydrolysis of *R*Cl.

155. A hydrocarbon (*A*) (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. (*A*) adds HBr in accordance with Markownikoff's rule to form a compound (*B*) which on reaction with silver hydroxide forms an alcohol (*C*), $C_5H_{12}O$. Alcohol (*C*) on oxidation gives a ketone (*D*), Deduce (*A*) to (*D*) and give the reactions involved.

156. 0.369 g of a bromo-derivative of a hydrocarbon (*A*) when vaporized occupied 67.2 mL at NTP. (*A*) on reaction with aqueous NaOH gives (*B*). (*B*) when passed over alumina at 250°C gives a neutral compound (*C*) while at 350°C it gives a hydrocarbon (*D*). (*D*) when heated with HBr gives an isomer of (*A*). When (*D*) is treated with conc. H_2SO_4 and the product is diluted with water and distilled, (*E*) is obtained. Identify (*A*) to (*E*) and explain the reactions.

157. Compound (x) (C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess of MeMgBr, 0.42 g of (x) gives 224 mL CH_4 at STP. Treatment of (x) with H_2 in presence of Pt catalyst followed by boiling with excess HI gives n-pentane. Suggest structure for (x) and write equations involved. **(IIT 1992)**

158. 0.535 g ethanol and acetaldehyde mixture when heated with Fehling solution gave 1.2 g of a red precipitate. What is the percentage of acetaldehyde in the mixture?
(Atomic mass of Cu = 63.8)

159. An organic compound (A) reacts with ethanol to give (B) and (C). On acid hydrolysis (C) yields (B) and (D). Oxidation of (D) gives (B). (B) is an acid and forms a salt with $Ca(OH)_2$ which on dry distillation gives (E), C_3H_6O. Give structures of (A) to (E) with proper reasoning.
(Roorkee 2000)

160. Compound (A) gives positive Lucas test in 5 minutes. When 6.0 g of (A) is treated with sodium metal, 1120 mL of hydrogen is evolved at STP. Assuming (A) to contain one atom of oxygen per molecule, write structure formula of (A). Compound (A) when treated with PBr_3 gives (B) which when treated with benzene in presence of anhydrous aluminium chloride gives (C). What are (B) and (C)?
(Roorkee 1990)

161. When 0.0088 g of compound (A) was dissolved in 0.50 g of camphor, the melting point of camphor was lowered by 8°C. Analysis of (A) gave 68.18% C and 13.16% H. Compound (A) showed the following reactions :
(i) It reacted with acetyl chloride and evolved hydrogen with sodium.
(ii) When reacted with HCl + $ZnCl_2$, a dense oily layer separated out immediately.
Compound (A) was passed over Al_2O_3 at 350°C to give compound (B). (B) on ozonolysis followed by hydrolysis gave two neutral compounds (C) and (D), which gave positive test wtih carbonyl reagents but only (C) gave a positive test with Fehling solution and resinous substance with NaOH. Identify (A), (B), (C) and (D) with proper reasoning. K_f for camphor = 40 K mol^{-1} kg.
(Roorkee 1991)

162. Compound (X) with molecular formula $C_9H_{10}O$ forms a semicarbazone and gives negative Tollens and iodoform tests. Upon reduction it gives n-propyl benzene. Deduce the structure of X.

163. An optically active alcohol (A) ($C_6H_{10}O$) absorbs two mole of hydrogen per mole of (A) upon catalytic hydrogenation and gives a product (B). The compound (B) is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of (A) and (B). **(IIT 1996)**

164. Give the aldol products and the corresponding alkenes (aq. NaOH or KOH used, 100°C) from :
(i) 2,5-hexanedione
(ii) 2,4-pentanedione

165. An aromatic ketone (X) has the M.F. ($C_{10}H_{12}O_2$) on vigorous oxidation, it gives (Y), a dibasic acid ($C_9H_8O_5$) which easily gives an anhydride on heating. The ketone (X) gives (Z) ($C_9H_{10}O_3$), a monobasic acid on heating with bromine and NaOH. (Z) on decarboxylation with soda lime gives 3-methyl anisole. Determine (X), (Y) and (Z).

166. Complete the following :

$$E(C_{11}H_{14}O_2) \xrightarrow{OH^-} F + CH_3CH_2COO$$

$$F \xrightarrow[2.\ H^+]{1.\ KMnO_4/OH} \text{(COOH, COOH)}$$

167. A compound (D), ($C_8H_{10}O$) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid (E), ($C_7H_6O_2$). Write the structures of (D), (E) and explain the formation of (E).
(IIT 1996)

168. $$A \xrightarrow[250°C]{Al_2O_3} (B) \xrightarrow[(ii)\ AgOH]{(i)\ HI} (C) \xrightarrow[150°C]{Al_2O_3} (B)B \xrightarrow[(ii)\ H_2O_2,\ OH]{(i)\ B_2H_6} (A)$$

In the above reactions scheme (A) and (C) are isomers. (B) has a formula of C_5H_{10} which can also be obtained from the product of the reactions of CH_3CH_2MgBr and $(CH_3)_2CO$. Give structures of (A), (B) and (C). **(Roorkee 2000)**

169. A compound (A) $C_4H_{10}O_4$ yields on acetylation (B) of formula $C_{12}H_{18}O_8$. How many hydroxyl groups are present in compound ? Also write structures of (A) and (B).

170. Compounds (A) and (B) on reaction in ether medium and subsequent acidification and oxidation give 2,5-dimethyl-3-hexanone. What are (A) and (B)? **(Roorkee 1998)**

171. The compound $C_4H_8Cl_2$ (A) on hydrolysis gives a compound C_4H_8O, (B). The compound (B) reacts with hydroxylamine and gives a negative test with Tollens reagent. What are (A) and (B)? Support your answer with proper reasoning and give the equations of reactions.
(Roorkee 1985)

172. An acid (A) contains carbon = 40.7%; hydrogen = 5.1% and its silver salt contains 65.1% silver. The ethylester of (A) has V.D. of 87 (H_2 = 1). What structure (A) may have? How would you distinguish between isomers?

173. Compound (A) $C_4H_8O_2$ has the following properties. What is this?
(i) It reacts with sodium bicarbonate to liberate CO_2.
(ii) On fusion with alkali gives propane.
(iii) With $Ca(OH)_2$ it gives $C_8H_{14}O_4Ca$ which on heating decomposes to di-isopropyl ketone.

174. A Grignard reagent (A) and a haloalkene (B) react together to give (C). Compound (C) on heating with KOH yields a mixture of two geometrical isomers, (D) and (E), of which (D) predominates. (C) and (E) have the same molecular formula and (C) gives 1-bromo-3-phenyl propane on reaction with HBr in the presence of a peroxide. Give structures of (A), (B) and (C) and configurations of (D) and (E) with reasons. **(Roorkee 2001)**

175. An acidic compound (A), $C_4H_8O_3$ loses its optical activity on strong heating yielding (B), $C_4H_6O_2$ which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$, which on reaction with $(CH_3)_2NH$ gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable compound (E) which decarboxylates readily to give (F), C_3H_6O. The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give structures of (A) to (G) with proper reasoning.

(Roorkee 1995)

176. An organic compound (A) C_5H_8O adds Br_2 to give $C_5H_8Br_2O$. It does not react with Tollens reagent but enters into reaction with phenyl hydrazine. Ozonolysis of (A) gives acetaldehyde and $C_3H_4O_2$ which readily loses CO to form acetaldehyde.

177. A compound has two isomers (A) and (B) of formula $C_5H_{10}O$. Isomer (A) on treating with NaOH(*aq.*) gives 2,2-dimethylpropan-1-ol and 2,2-dimethylpropanoic acid salt. The isomer (B) on treating with NaOH(*aq.*) gives 3-hydroxy, 2-propylheptanal. What are (A) and (B)?

178. An organic acid (A), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiff's test but (F) does not. Give structures of (A) to (F) with reasons.

(Roorkee 1997)

179. An organic compound (A) $C_4H_7Cl_3$ yields (B) with KOH(*aq.*). (B) on treating with NH_3 gives (C) which on heating gives (D). On heating (D) with P_2O_5, 2-methylpropannitrile is formed. What are (A), (B), (C) and (D)?

180. Two isomers (A) and (B) have formula $C_3H_6O_2$. (B) gives effervescenses with $NaHCO_3$ while (A) does not do so. (B) gives out H_2 when treated with metallic Zn but (A) has no reaction with it. (A) on treatment with excess of NaOH yields two compounds (C) and (D). Compound (C) when treated with dil. H_2SO_4 gives (E) which reduces Tollens reagent. (D), however, can form iodoform with I_2 and alkali. Identify (A) to (E).

181. An organic compound (A), $C_6H_{12}O_3$ on treatment with concentrated H_2SO_4 gives CO_2, H_2O and (B). Compound (B) can be prepared by passing vapours of pentanol-1 over heated copper at 570 K. Compound (A) on heating gives (C), $C_{12}H_{20}O_4$.
Give structures of (A) to (C) with proper reasoning.

(Roorkee 1998)

182. An ester has molar mass 102 g mol^{-1}. On aqueous hydrolysis it produces a monobasic acid and an alcohol. If 0.185 g of the acid produced completely neutralizes 25 mL of 0.1 *N* NaOH, find out the structure formulae of the produced alcohol, acid and the ester with proper reasoning.

(Roorkee 1990)

183. A liquid (X) having molecular formula $C_6H_{12}O_2$ is hydrolysed with water in presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are (X), (Y) and (Z)?

184. An organic compound (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidic conditions gives (B) and (D). Oxidation of (D) with $KMnO_4$ also gives (B). (B) on heating with $Ca(OH)_2$ gives (E) (Molecular formula C_3H_6O). (E) does not give Tollens test and does not reduce Fehling solution but forms 2,4-dinitrophenylhydrazone. Identify (A) to (E).

(IIT 1992)

185. Two mole of an ester (A) are condensed in presence of sodium ethoxide to give a β-keto ester (B) and ethanol. On heating in an acidic solution (B) gives ethanol and a β-keto acid (C). On decarboxylation (C) gives 3-pentanone. Identify (A), (B) and (C) with proper reasoning and give reactions. **(Roorkee 1992)**

186. Compound (A) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yielded two compound (B) and (C). The compound (B) on oxidation gave (D) which on treatment with alkali (aqueous) and subsequent heating furnished (E). The later on catalytic hydrogenation gave (C). The compound (D) was oxidized further to give (F) which was found to be monobasic acid (m.wt. 60.0). Deduce structures of (A) to (E). **(IIT 1990)**

187. Compound (A) $C_5H_8O_2$ liberated CO_2 on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yielded compound (B), $C_5H_{10}O_2$ on hydrogenation. Compound (B) can be separated into enantiomorphs. Write structures of (A) and (B).

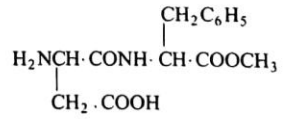
188. The sodium salt of a carboxylic acid, (A) was produced by passing a gas (B) into aqueous solution of caustic alkali at an elevated temperature and pressure. (A) on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid (C). A sample of 0.4 g of (C) on combustion gave 0.08 g of H_2O and 0.39 g of CO_2. The silver salt of the acid, weighing 1.0 g, on ignition yielded 0.71 g of Ag as residue. Identify (A), (B) and (C).

(IIT 1990)

189. An organic compound (A), $C_5H_8O_3$ on heating with soda lime gives (B), which reacts with HCl to give (C). The compound (C) reacts with thionyl chloride to produce (D) which on reaction with KCN gives compound (E). Alkaline hydrolysis of (E) gives a salt (F) which on heating with soda lime produces *n*-butane. Careful oxidation of (A) with dichromate gives acetic acid and malonic acid. Give structures of (A) to (F) with proper reasoning.

(Roorkee 1999)

190. Aspartame, an artificial sweetener, is a peptide and has the following structure :



(i) Identify the four functional groups.
(ii) Write the zwitterionic structure.
(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
(iv) Which of the two amino acids is more hydrophobic?
(IIT 2001)

191. From analysis and molar mass determination, the molecular formula of (*A*) is C_3H_7NO. The compound gave following reactions :
(1) On hydrolysis it gives an amine (*B*) and a cabroxylic acid (*C*).
(2) Amine (*B*) reacts with benzene sulphonyl chloride and gives a product which is insoluble in aqueous sodium hydroxide solution.
(3) Acid (*C*) on reaction with Tollens reagent gives a silver mirror, what are (*A*), (*B*) and (*C*)? Explain the reactions.

192. A basic volatile, nitrogen compound gave a foul smelling gas when treated with $CHCl_3$ and alcoholic KOH. A 0.295 g sample of the substance dissolved in aqueous HCl and treated with $NaNO_2$ solution at 0°C liberated a colourless; odourless gas whose volume correspond to 112 mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave yellow precipitate. Identify the original substance. Assume it contains one N-atom per molecule.
(IIT 1993)

193. An organic compound (*A*) containing C, H, N and O, on analysis gives 49.32% C, 9.59% H and 19.18% N. (*A*) on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid (*B*). The silver salt of (*B*) contains 59.67% silver. Deduce structures of (*A*) and (*B*). **(IIT 1988)**

194. Compound '*X*' containing chlorine, on treatment with NH_3 gives a solid '*Y*' which is free from chlorine. (*Y*) analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br_2 and caustic soda to give a basic compound (*Z*), (*Z*) reacts with HNO_2 to give ethanol. Suggest structures for (*X*), (*Y*) and (*Z*). **(IIT 1992)**

195. Write the structure of alanine at pH = 2 and pH = 10.
(IIT 2000)

196. Compound (*A*), $C_5H_{11}NO$ is not soluble in cold dilute alkaline or acidic solutions. When (*A*) is refluxed in NaOH solution, a gas (*B*) is evolved and a salt (*C*) is formed. Acetyl chloride reacts with (*B*) to give (*D*), C_4H_9NO. (*B*) reacts with HNO_2 to give a yellow oil (*E*). Give structures of (*A*) to (*E*) with reason. **(Roorkee 2000)**

197. An organic compound $C_2H_7NO_2$, on slow distillation loses water and gives (*B*) which on further distillation with P_2O_5 forms (*C*). (*C*) on hydrolysis gives (*D*) which on treating with $P + Cl_2$ followed with hydrolysis forms glycollic acid. What are (*A*), (*B*), (*C*) and (*D*)?

198. As ester *A* ($C_4H_8O_2$), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol *B* as the sole organic product. Alcohol *B*, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of *A* and *B*. Show the reactions involved. **(IIT 1998)**

199. A mixture of an acid anhydride (*A*) and a monobasic acid (*B*) on heating produces another monobasic acid (*C*) of equivalent mass 74 and an anhydride (*D*). The acids and anhydrides remain in equilibrium. The anhydride (*D*) contains two identical fluoroalkyl groups. The acid (*B*) contains a trifluoromethyl group and has an equivalent mass of 128.
Give structures of (*A*) to (*D*) with proper reasoning (Atomic mass of fluorine = 19). **(Roorkee 1998)**

200. Two isomeric compounds (*A*) and (*B*) have $C_4H_{11}N$ molecular formula. Both on separately treating with HNO_2 lose their N_2 producing two isomeric alcohols (*C*) and (*D*) respectively of molecular formula $C_4H_{10}O$. (*C*) reacts with Lucas reagent immediately and resists oxidation. (*D*) does not react with Lucas reagent in cold but can be easily oxidized. Complete methylation of either (*A*) or (*B*) is made which on decomposition does not produce butene-1.

201. An organic compound (*A*) $C_2H_5NO_2$ gave on hydrolysis an alcohol (*B*) of molar mass 46 g mol^{-1} and an acid. On reduction it gave the same alcohol (*B*) and NH_3 gas. What is (*A*)?

202. (a) Carry out the following transformation in not more than three steps.

$$CH_3—CH_2—C\equiv C—H \longrightarrow$$

$$CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$$ **(IIT 1999)**

(b) Discuss the hybridisation of carbon atoms in allene (C_3H_4) and show the π-orbital overlaps. **(IIT 1999)**
(c) Explain why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid. **(IIT 1999)**

203. Identify (*X*), (*Y*) and (*Z*) in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (*Z*) is treated with HBr and subsequently ozonolysed. Mark the (C*) carbon in the entire scheme.

$$Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow (X)\,(\text{gas})\ [C^* \text{ denotes } C^{14}]$$

$$CH_2=CH\cdot Br \xrightarrow[(ii)\,X,\ (iii)\,H_3O^+]{(i)\ Mg/Ether} (Y) \xrightarrow{LiAlH_4} (Z)$$

(IIT 2001)

204. Complete the reaction :
(a) $\cdot CH_2=CHCHO \xrightarrow{LiAlH_4}$ '*A*'
(b) $\dot{C}_6H_5CH=CHCHO \xrightarrow{LiAlH_4}$ '*B*'

205. (a) When bromobenzene is monochlorinated, two isomeric compounds (*A*) and (*B*) are obtained. Monobromination of (*A*) gives several isomeric products of formula $C_6H_3ClBr_2$ while monobromination of (*B*) yields only two isomers (*C*)

and (*D*). Compound (*C*) is identical with one of the compounds obtained from the bromination of (*A*), however, (*D*) is totally different from any of the isomeric compounds obtained from bromination of (*A*). Give structures of (*A*), (*B*) and (*D*) and also suggest structures of four isomeric monobrominated products of (*A*). Support answer with reasoning. **(Roorkee 1992)**

206. A phenolic compound (*A*), $C_7H_8O_2$ on mild oxidation gives a highly volatile oil (*B*). (*A*) forms (*C*) on reaction with dimethyl sulphate in alkali. Oxidation of (*C*) with hot $KMnO_4$ gives (*D*) which then reacts with bromine water to give (*E*) containing about 72% bromine. Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1997)**

207. A hydrocarbon (*A*) [C = 90.56%; vapour density 53] was subjected to vigorous oxidation to give a dibasic acid (*B*). 0.10 g of (*B*) required 24.1mL of 0.05 *N* NaOH for complete neutralization. When (*B*) was heated strongly with soda lime, it gave benzene. Nitration of (*B*) gave a single mono nitro derivative. Identify (*A*) and (*B*) with proper reasoning and also give their structures. **(Roorkee 1991)**

208. There are three isomeric compounds (*A*), (*B*) and (*C*) having molecular formula $C_8H_8O_2$.

(i) When heated with soda lime (*A*) gives C_6H_6, while (*B*) and (*C*) gives toluene.

(ii) (*A*) is neutral compound while (*B*) and (*C*) are monobasic acid.

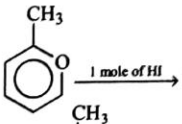
(iii) (*B*) on chlorination in sunlight gave a compound containing 3 chlorine atom per molecule which is easily hydrolysed to a dibasic acid (*D*). (*D*) with soda lime gave benzene. The photo chlorination of (*C*) gave a product which contains two Cl-atoms per molecule and is strong acid. Identify (*A*), (*B*), (*C*) and (*D*).

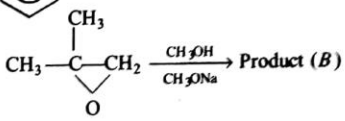
209. Catalytic dehydrogenation of methylcyclohexane, obtained from petroleum, gives a liquid which on treatment with chlorosulphonic acid at 370 K yields a mixture of two isomers (*A*) and (*B*), $C_7H_7SO_2Cl$. The major isomer (*A*) reacts with ammonia to form (*C*), which on oxidation with permanganate gives compound (*D*). On heating compound (*D*) gives a well known sweetening agent (*E*). The minor isomer (*B*) also reacts with ammonia to give a compound (*F*) which on treatment with NaClO/NaOH gives an antiseptic (*G*). Identify (*A*) to (*G*) with proper reasoning. **(Roorkee 1999)**

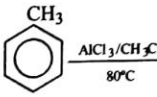
210. An alkene (*A*) ($C_{16}H_{16}$) on ozonolysis gives only one product (*B*) (C_8H_8O). Compound (*B*) on reaction with $NaOH/I_2$ yields sodium benzoate. Compound (*B*) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (*C*) (C_8H_{10}). Write the structure of compounds (*B*) and (*C*). Based on this information two isomeric structures can be proposed for alkene (*A*). Write their structures and identify the isomer which on catalytic hydrogenation (H_2/Pd-C) gives a racemic mixture. **(IIT 2001)**

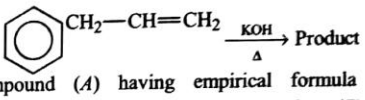
211. (a) Prepare 3-chloroaniline from benzene (In three steps).

(b) Identify the products in each case.

(i)  Product (*A*)

(ii)  Product (*B*)

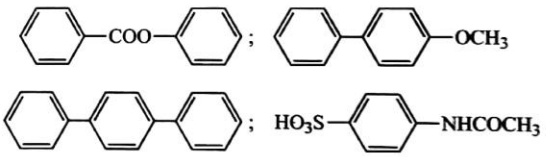
(iii)  Major product (only mono substitution)

(iv)  Product

212. Compound (*A*) having empirical formula C_7H_8 is chlorinated in sunlight to give a product (*B*) which on hydrolysis gives a compound (*C*). (*C*) gives a positive test with Tollens reagent and with sodium acetate and acetic anhydride gives an acid (*D*) with an equivalent mass 148.15. Identify (*A*), (*B*), (*C*) and (*D*) and explain the reactions involved.

213. (a) An organic compound C_8H_{18} on monochlorination gives a single monochloride. Write the structure of hydrocarbon.

(b) Write the structures of possible major monosubstituted products formed when Br^+ attacks the following molecules. Justify your answer. **(Roorkee 1999)**



214. An aromatic compound (*A*), $C_7H_5NO_3Cl_2$ on reduction with Sn/HCl gives (*B*) which on reaction with $NaNO_2$/HCl gives (*C*). Compound (*B*) does not form a dye with β-naphthol. However, (*C*) gives red colour with ceric ammonium nitrate and on oxidation gives an acid (*D*) of equivalent mass 191. Decarboxylation of (*D*) gives (*E*) which forms a single mononitro derivative (*F*) on nitration. Give structure of (*A*) to (*F*) with proper reasoning. **(Roorkee 1995)**

215. Compound (*A*) C_7H_8O is insoluble in aqueous sodium bicarbonate but dissolves in aqueous sodium hydroxide and gives a characteristic colour with aqueous ferric chloride. When treated with bromine, (*A*) forms a compound (*B*) $C_7H_5OBr_3$.

(i) Give structure formulae of (*A*) and (*B*).

(ii) What would be structure of (*A*) if it neither dissolves in aqueous sodium hydroxide nor gives a characteristic colour with $FeCl_3$? **(Roorkee 1993)**

216. An organic compound (A) gives positive Liebermann reaction and on treatment with $CHCl_3/KOH$ followed by hydrolysis gives (B) and (C). Compound (B) gives colour with Schiff's reagent but not (C), which is steam volatile. (C) on treatment with $LiAlH_4$ gives (D), $C_7H_8O_2$ which on oxidation gives (E). Compound (E) reacts with $(CH_3CO)_2O/CH_3COOH$ to give a pain reliever (F). Give structures of (A) to (F) with proper reasoning.

(Roorkee 1995)

217. An organic compound (A) of molar mass 140.5 has 68.32% C and 6.4% H and 25.26% Cl. Hydrolysis of (A) with dilute acid gives compound (B) $C_8H_{10}O$. Compound (B) can be oxidized under mild conditions to compound (C), C_8H_8O. Compound (C) forms a phenyl hydrazone (D) with $PhNHNH_2$ and gives positive iodoform test. Deduce the structures of (A) to (D) with proper reasoning.

(Roorkee 1990)

218. An organic compound (A), $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound (B). The compound (B) on treatment with PCl_5, followed by reaction with $H_2/Pd(BaSO_4)$ gives compound (C), which on reaction with hydrazine gives a cyclised compound (D) ($C_{14}H_{10}N_2$). Identify (A), (B), (C) and (D). Explain the formation of (D) from (C). **(IIT 2000)**

219. An acid (A), $C_8H_7O_2Br$ on bromination in the presence of $FeBr_3$ gives two isomers, (B) and (C) of formula $C_8H_6O_2Br_2$. Vigorous oxidation of (A), (B) and (C) gives acids (D), (E) and (F) respectively. (D), $C_7H_5O_2Br$ is the strongest acid among all of its isomers, whereas (E) and (F) each has a molecular formula of $C_7H_4O_2Br_2$. Give structures of (A) to (F) with justification. **(Roorkee 2000)**

220. Two different Grignard reagents, (X) and (Y) produce $C_6H_5CH_2C(CH_3)_2OH$ on reaction with (P) and (Q) respectively. Give structures of (X), (Y), (P) and (Q).

(Roorkee 2000)

221. A mixture of two aromatic compounds (A) and (B) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing (A), when heated with alcoholic solution of KOH produce (C) C_7H_5N associated with unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds (D) and (E) of molecular formula $C_7H_6O_2$. Identify (A) to (E). **(IIT 1990)**

222. (A), (B), (C), (D), (E), (F) and (G) are amines, each of which forms a hydrochloride containing 32.42% chlorine. (A), (B), (C) and (D) evolve N_2 on reaction with HNO_2, but (E), (F) and (G) do not. Give structures of (A) to (G) with reasons.

(Roorkee 2001)

223. An O.C. (A) $C_7H_7NO_2$ on reduction gives a solid (B). (B) on diazotization gives (C) which on treating with Cu_2Cl_2/HCl gives (D). (D) on oxidation by alkaline $KMnO_4$ gives (E) which on reduction by Ni-Al/NaOH gives benzoic acid.

224. An organic compound (A) $C_9H_{13}N$ dissolves in dil. HCl and releases N_2 with HNO_2 giving an optically active alcohol (B). (B) on oxidation gives dicarboxylic acid, which on heating form anhydride. What are (A) and (B)?

225. The percentage of carbon, hydrogen and nitrogen in a disubstituted aromatic compound (A) is 71.11, 6.67 and 10.37 respectively. Its molecule contains a single atom of nitrogen. Compound (A) evolves NH_3 when heated with NaOH to form salt (B), from which an acid (C) is obtained on acidification. If an electrophilic substitution is carried on (C), an entering electrophile can occupy either of the two identical positions available in the ring. Acid (C) on heating with PCl_5, gives (D) which reacts with (B) to give an organic product (E). Give structures of (A) to (E) with proper reasoning. **(Roorkee 1996)**

226. Compound (A), $C_{10}H_{12}O$ gives off hydrogen on treatment with sodium metal and also decolourises Br_2 in CCl_4 to give (B), $C_{10}H_{12}OBr_2$. (A) on treatment with I_2 in NaOH gives iodoform and an acid (C) after acidification. Give structures of (A) to (C) and also of all the geometrical and optical isomers of (A). **(Roorkee 1997)**

227. An organic compound containing C, H and O exists in two isomeric forms (A) and (B). 0.108 g of an isomer gives 0.308 g of CO_2 and 0.072 g of H_2O. (A) is insoluble in NaOH and $NaHCO_3$, while B is soluble in NaOH. (A) reacts with conc. HI to give (C) and (D). (C) can be separated from (D) by ethanolic $AgNO_3$ solution and (D) is soluble in NaOH. (B) reacts readily with bromine water to give compound (E) of molecular formula $C_7H_5OBr_3$. Identify (A) to (E).

(IIT 1991)

228. Two isomeric mononitro derivatives (B) and (C) are obtained by the nitration of an organic compound (A), C_7H_8O. Treatment of (A) with acetyl chloride produces (D) which on reaction with CrO_2Cl_2 gives (E) whose oxidation with neutral $KMnO_4$ followed by acidification gives (F). The compound (F) on heating gives phenol. (A) on treatment with alkaline $C_6H_5SO_2Cl$ produces (G) which on oxidation with $KMnO_4$ gives (H). Hydrolysis of (H) also gives (F). Give structures of (A) to (H) with proper reasoning. **(Roorkee 1996)**

229. An aromatic hydrocarbon (A) $C_{16}H_{16}$ shows the following reactions :

(i) It decolourises Br_2 in CCl_4.

(ii) It adds one mole of H_2.

(iii) Oxidation with hot $KMnO_4$ gives a dicarboxylic acid (B) $C_6H_4(COOH)_2$. (B) on bromination shows only one monobromo substitution product.

Deduce the structure of (A) and report its stereoisomers if any.

230. A mono substituted alkyl benzene (A) of the formula $C_{10}H_{14}$ resists vigorous oxidation to an aryl carboxylic acid. Name the compound and write down its various mono substituted isomers.

231. Compound A (C_8H_8O) on treatment with $NH_2OH \cdot HCl$ gives (B) and (C). (B) and (C) rearrange to give (D) and (E), respectively, on treatment with acid. (B), (C), (D) and (E) are all isomers of molecular formula (C_8H_9NO). When (D)

is boiled with alcoholic KOH an oil (*F*) (C_6H_7N) separates out. (*F*) reacts rapidly with CH_3COCl to give back (*D*). On the other hand, (*E*) on boiling with alkali followed by acidification gives a white solid (*G*) ($C_7H_6O_2$). Identify (*A*) to (*G*). **(IIT 1999)**

232. Two isomeric forms of an organic compound (*A*), $C_{11}H_{13}OCl$ readily decolourise bromine water and give same compound (*B*) on catalytic hydrogenation. Both the isomeric forms on vigorous oxidation give (*C*) which on treatment with soda lime gives 2-chloroethoxybenzene. However, (*C*) on treatment with Ni/Al alloy in alkaline medium gives 3-ethoxy benzoic acid. Only one of the isomers of (*A*) give geometrical isomers (*D*) and (*E*). Identify (*A*) to (*E*) with proper reasoning. **(Roorkee 1997)**

233. An organic compound (*A*) of molar mass 135 on boiling with NaOH evolves a gas which gives white dense fumes on bringing a rod dipped in HCl near it. The alkaline solution thus, obtained on acidification gives the precipitate of a compound (*B*) having molar mass 136. Treatment of (*A*) with HNO_2 also yields (*B*), whereas its treatment with Br_2/KOH gives (*C*). Compound (*C*) reacts with cold HNO_2 to give (*D*), which gives red colour with ceric ammonium nitrate. On the other hand (*E*) an isomer of (*A*) on boiling with dil. HCl gives an acid (*F*), having molar mass 136. On oxidation followed by heating, (*F*) gives an anhydride (*G*) which condenses with benzene in presence of $AlCl_3$ to give anthraquinone. Give structures of (*A*) to (*G*) with proper reasoning. **(Roorkee 1999)**

234. Two isomeric compound (*A*) and (*B*) have the same formula $C_{11}H_{13}OCl$. Both are unsaturated, yield the same compound (*C*) on catalytic hydrogenation and produce 4-chloro-3-ethoxybenzoic acid on vigorous oxidation. (*A*) exists in geometrical isomers, (*D*) and (*E*) but not (*B*). Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1994)**

235. An organic compound (*A*), $C_9H_{12}O$ was subjected to a series of tests in the laboratory. It was found that this compound :

(i) Rotates the plane of polarized light.

(ii) Evolves hydrogen with sodium.

(iii) Reacts with I_2 and NaOH to produce a pale yellow solid compound.

(iv) Does not react with Br_2/CCl_4.

(v) Reacts with hot $KMnO_4$ to form compound (*B*), $C_7H_6O_2$ which can also be synthesized by the reaction of benzene and carbonyl chloride followed by hydrolysis.

(vi) Loses optical activity as a result of formation of compound (*C*) on being heated with HI and P.

(vii) Reacts with Lucas reagent in about 5 min.

Give structures of (*A*) to (*C*) with proper reasoning and draw Fischer projections for (*A*). Give reactions for the steps wherever possible. **(Roorkee 1999)**

236. An organic compound (*A*), C_8H_6, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound (*B*), which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound (*B*), when treated with iodine in aqueous KOH, yields (*C*) and a yellow compound (*D*). Identify (*A*), (*B*), (*C*) and (*D*) with justification. Show how (*B*) is formed from (*A*)? **(IIT 1994)**

237. The aqueous solution of a nitrogen and chlorine containing organic compound (*A*) is acidic to litmus. (*A*) on treatment with aqueous NaOH gives a compound (*B*) containing nitrogen, but not chlorine. Compound (*B*) on treatment with $C_6H_5SO_2Cl$ in the presence of NaOH gives an insoluble product (*C*), $C_{13}H_{13}NO_2S$. Give structures of (*A*) and (*B*). **(Roorkee 2000)**

238. An aldehyde (*A*) ($C_{11}H_8O$), which does not undergo self aldol condensation, gives benzaldehyde and two mole of (*B*) on ozonolysis. Compound (*B*), on oxidation with silver ion, gives oxalic acid. Identify the compounds (*A*) and (*B*). **(IIT 1998)**

239. An organic compound (*A*), $C_{18}H_{20}O$ on ozonolysis gives (*B*), $C_{10}H_{12}O$ and (*C*), $C_8H_8O_2$. Compound (*B*) gives iodoform reaction and produces an oxime (*D*), $C_{10}H_{13}ON$ on treatment with NH_2OH. Compound (*D*) reacts with PCl_5 in dry ether to give (*E*) which on hydrolysis gives (*F*), $C_8H_{11}N$ and acetic acid. (*F*) on treatment with HNO_2 followed by oxidation gives phthalic acid. Compound (*C*) on mild oxidation gives (*G*) which gives effervescence with $NaHCO_3$. (*G*) on treatment with HI produces *p*-hydroxybenzoic acid and CH_3I. Give structures of (*A*) to (*G*) with proper reasoning. **(Roorkee 1998)**

240. An aromatic compound (*A*), C_8H_9Br reacts with $H_2C(COOC_2H_5)_2$ in the presence of C_2H_5ONa to give (*B*). Compound (*B*) on refluxing with dilute H_2SO_4 gives (*C*) which on vigorous oxidation gives (*D*). The compound (*D*) is a dibasic acid but on heating does not give an anhydride. It forms a mononitro derivative (*E*), in which all the substituents are at equidistant from one another. Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1998)**

241. A colourless substance (*A*) is sparingly soluble in water and gives (*B*) on heating with mineral acids. Compound (*B*) on reaction with $CHCl_3$ and alcoholic potash produces an obnoxious smell of carbylamine due to the formation of (*C*). Compound (*A*) on reaction with chlorosulphonic acid gives (*D*) which on treatment with ammonia gives (*E*). Compound (*E*) on acid hydrolysis gives sulphanilamide, a well known drug. Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1998)**

242. An organic acid (*A*) on heating with $AlPO_4$ at 700°C forms (*B*). Compound (*B*) also reacts with (*A*) to give (*C*). Compound (*C*) on reaction with 1,3,5-trimethyl benzene in presence of $AlCl_3$ gives a ketone (*D*) and CH_3COOH. (*D*) on treatment with Na(Hg)/HCl gives an aromatic hydrocarbon (*E*).

Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1998)**

243. Five isomeric para-disubstituted aromatic compounds (*A*) to (*E*) with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds :

(i) Both (*A*) and (*B*) form a silver mirror with Tollens reagent; also, (*B*) gives a positive test with $FeCl_3$ solution.

(ii) (*C*) gives positive iodoform test.

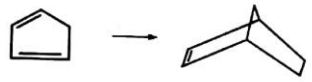
(iii) (*D*) is readily extracted in aqueous $NaHCO_3$ solution.

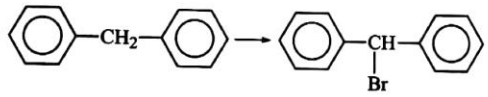
(iv) (*E*) on acid hydrolysis gives 1,4-dihydroxybenzene.

(IIT 2002)

244. Compound (*A*) of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form (*B*). On oxidation with $KMnO_4$, (*A*) gives *m*-chlorobenzoic acid. Identify (*A*) and (*B*). **(IIT 2003)**

245. Bring about following one step transformations :

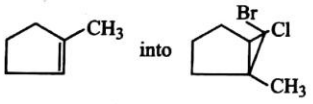
(i) 

(ii) 

246. Convert the following :

(a) 2-chlorobutanoic acid into 3-chlorobutanoic acid

(b) $(CH_3)_3CH$ to $(CH_3)_3CD$ (in two steps)

(c) 

(d) Isobutylene to 2,2,4-trimethyl pentane

(e) Convert $RCH{=}CH_2$ to RCH_2CH_2CHO

(f) Acetone into ketene

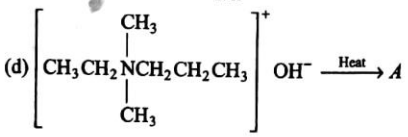
(g) Acetic acid into ketene

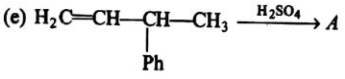
247. Give the products formed in the following reactions :

(a) 1,1,2-cyclohexane tricarboxylic acid $\xrightarrow{\Delta}$

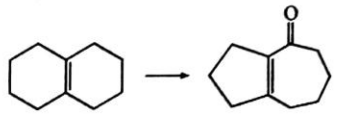
(b) Phthalic acid + $NH_3 \longrightarrow D \xrightarrow{300^\circ C} E$

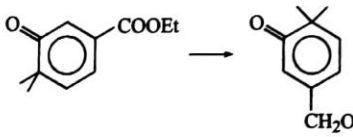
(c) $H_2C{=}CHCH_2CN \xrightarrow[2.\ H^+]{1.\ PhMgBr} A$

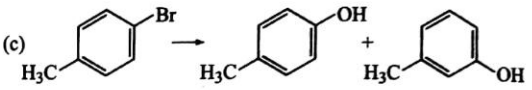
(d) 

(e) 

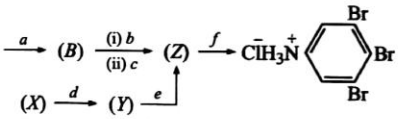
248. Suggest how following transformations will be brought in (may require more than one step) :

(a) 

(b) 

(c) 

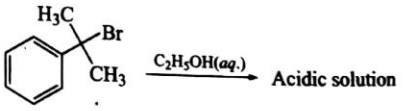
249. How would you synthesise 4-methoxyphenol from bromobenzene in not more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. **(IIT 2001)**

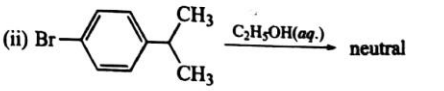
250. 

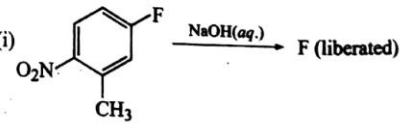
Give structures of (*A*), (*B*), (*X*), (*Y*) and (*Z*) in the above scheme of reactions, if reagents *a*, *b*, *c*, *d*, *e* and *f* are Br_2/CH_3COOH, $NaNO_2/H_2SO_4$, CuBr, HNO_3/H_2SO_4, Br_2/Fe and Sn/HCl respectively. **(Roorkee 2001)**

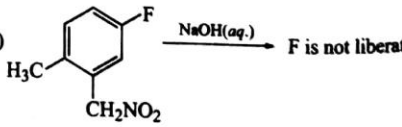
251. There is a solution of *p*-hydroxy benzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them. Also write the confirmatory tests of functional groups. **(IIT 2003)**

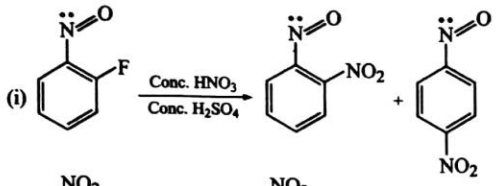
252. Give reasons :

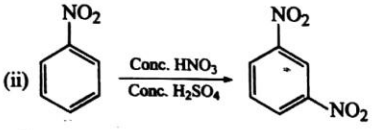
(a) (i) 

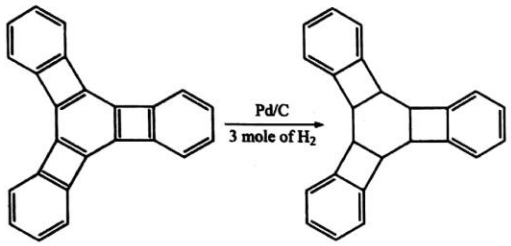
(ii) 

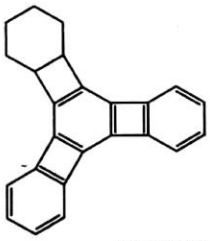
(b) (i) 

(ii) 

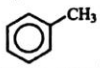
(c) (i) 

(ii) 

(d) 

is formed but not 

(IIT 2005)

253. (Brown fumes and pungent smell) $B \xleftarrow{NaBr+MnO_2} A \xrightarrow{Conc.\ HNO_3}$ 

C (Intermediate) $\longrightarrow$ D (Explosive product)

Find A, B, C and D. Also write equations A to B and A to C.

(IIT 2005)

254. If $\mu_{obs} = \Sigma \mu_i x_i$, where μ_i is the dipole moment of stable conformer and x_i is the mole fraction of that conformer.

(a) Write stable conformer for $Z—CH_2—CH_2—Z$ in Newman's projection. If $\mu_{solution} = 1.0$ D and mole fraction of anti form = 0.82, find μ_{Gauche}.

(b) Write most stable meso conformer of $\begin{matrix} CHDY \\ | \\ CHDY \end{matrix}$

If (i) $Y = CH_3$ about $C_2—C_3$ rotation and (ii) $Y = OH$ about $C_1—C_2$ rotation. **(IIT 2005)**

255. What are the relative powers of overlapping of sp, sp^2 and sp^3 with respect to s-orbitals?

256. Write various canonical forms of $CH_2=CH—CHO$ and predict their order of stability.

257. Arrange the following carbocations in order of their stability with explanations.

$(CH_3)_3C^+$, $CH_3\overset{+}{C}H_2$ and $\overset{+}{C}H_3$

258. Why is triphenylmethyl cation is highly stable?

259. Cyanide ion is an ambident nucleophile. From which end it acts as stronger nucleophile in aqueous medium.

260. Although phenoxide ion has more number of canonical forms than carboxylate ion but carboxylic acids are stronger than phenol.

261. Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethyl cyclohexanone does not. Why?

262. There are two $—NH_2$ groups in semicarbazide. However, only one NH_2 gp directly attached to $>CO$ gp is not involved in the formation of semicarbazones. Why?

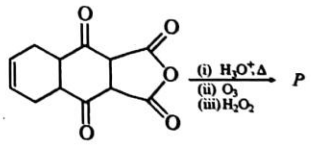
263. A tetrapeptide has —COOH group on alanine. This produces glycine (Gly), Valine (Val), Phenyl Alanine (Phe) and Alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with $—NH_2$ group attached to a chiral center is :

[JEE (Advanced) I 2013]

264. The total number of lone-pairs of electrons in melamine is :

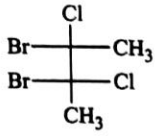
[JEE (Advanced) I 2013]

265. The total number of carboxylic acid groups in the product P is: **[JEE (Advanced) I 2013]**



266. $EDTA^{4-}$ is ethylenediaminetetraacetate ion. The total number of N—Co—O bond angles in $[Co(EDTA)]^{1-}$ complex ion is : **[JEE (Advanced) I 2013]**

267. The total number(s) of **stable** conformers with non-zero dipole moment for the following compound is/are :

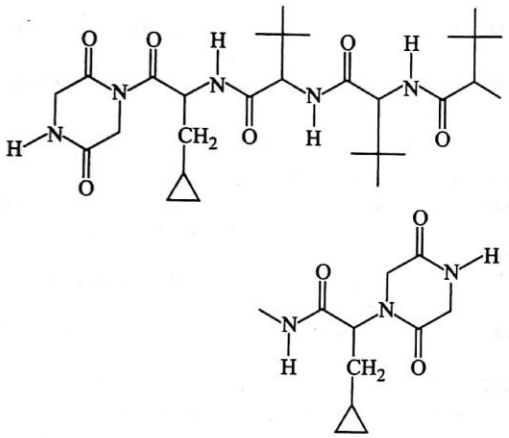


[JEE (Advanced) I 2014]

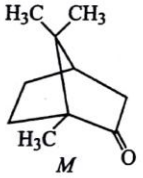
268. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$.

[JEE (Advanced) I 2014]

269. The total number of *distinct naturally occurring amino acids* obtained by complete acidic hydrolysis of the peptide shown ahead is : **[JEE (Advanced) I 2014]**

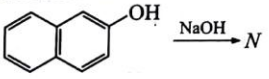


270. The total number of stereoisomers that can exist for *M* is :

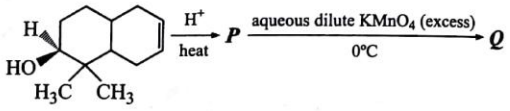


M

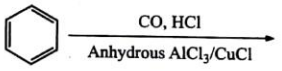
271. The number of resonance structures for *N* is :

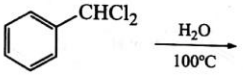


272. The number of hydroxyl group(s) in *Q* is :

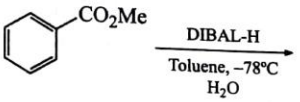


273. Among the following the number of reaction(s) that produce(s) benzaldehyde is :

(I) 

(II) 

(III)

(IV) 

SOLUTIONS (Numerical Problems)

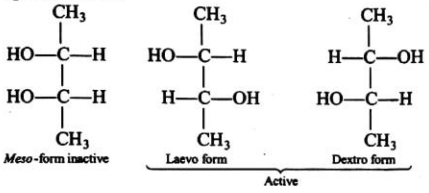
1. **Chiral :** An object which is non-superimposable on its mirror image is said to be chiral, *e.g.*,
Screw, scissor, spool of thread, glove, shoe, sock, helix, double helix, tennis racket, hand, foot, ear, rifle, letters (P, J, F).
Achiral : An object which is superimposable on their mirror image, *e.g.*, empty spool of thread and rest all not included in chiral examples.

2. (a) 2,3-Dihydroxybutane

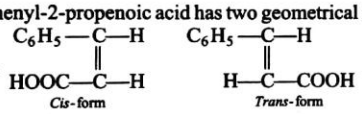
Note : This name is wrong. It should be butan-2,3-diol.

$CH_3 \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot CH_3$

where * shows asymmetric carbon atoms, thus compound has optical isomers.



(b) 3-Phenyl-2-propenoic acid has two geometrical isomers.



3. (a) When the molecule cannot be divided into two equal parts, *i.e.*, has no symmetry and n is the number of asymmetric carbon atoms, then

No. of optically active isomers, $a = 2^n$
Number of *meso* forms, $m = 0$
Total no. of racemic forms, $r = a/2$
Total no. of optical isomers $= a + m$

e.g., $CH_3 \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot COOH$

* represents asymmetric carbon atoms, *i.e.*, $n = 2$

$\therefore \quad a = 2^2 = 4$
$m = 0$
$r = 0$

Total optical isomers $= 4 + 0 = 4$

(b) When the molecule can be divided into two equal halves (*i.e.*, has symmetry) number of asymmetric carbon atoms is even, then

Number of optically active isomers, $a = 2^{n-1}$
Number of *meso* forms, $m = 2^{(n/2)-1}$
Number of racemic forms, $r = a/2$
Total number of optical isomers $= a + m$

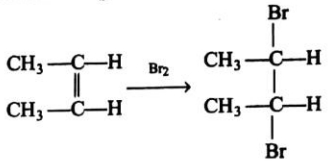
e.g., $COOH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot COOH$

* represents asymmetric carbon atoms, *i.e.*, $n = 2$

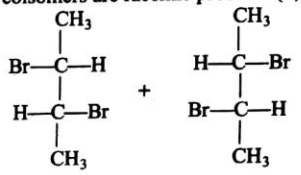
$\therefore \quad a = 2^{2-1} = 2$
$m = 2^{1-1} = 2^0 = 1$
$r = 1$

Total optical isomers $= 2 + 1 = 3$

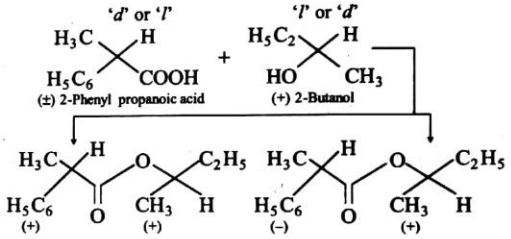
4. Addition of Br_2 is anti addition.



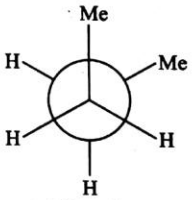
The stereoisomers are racemic products (*d*, *l*)



5.

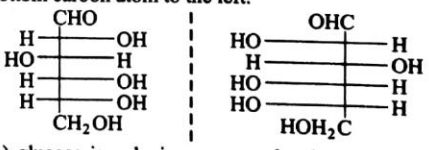


6. *n*-butane is $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$. The staggered form of butane is :

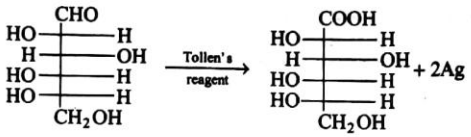


The relative lower stability of staggered form of *n*-butane is due to van der Waals' repulsion between the methyl groups.

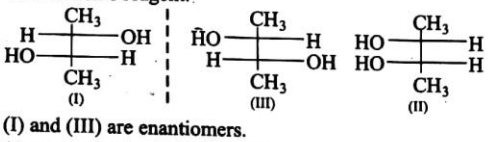
7. (a) *L*-(–) glucose is an enantiomer, *i.e.*, mirror image of *D*-(+) glucose. Also, *D*-form has hydroxyl group next to bottom carbon atom to the left.



(b) *L*-(–) glucose is reducing agent and reduces Tollen's reagent to metallic silver, it self being oxidised to *L*-(–) gluconic acid.

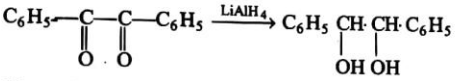


8. In (*B*) both the rings are present in acetal form and thus, it will not hydrolyse in solution and thus, will not reduce Tollen's reagent. In (*A*) one ring is present in hemiacetal form and thus, it will hydrolyse and will give positive test with Tollen's reagent.

9. 

(I) and (III) are enantiomers.

(I) and (II); (II) and (III) are diastereomers.

10. 

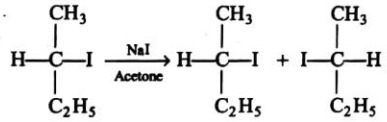
The molecule after reduction possesses two asymmetric carbon with symmetry in molecule

Thus, $a = 2^{n-1} = 2^{2-1} = 2$

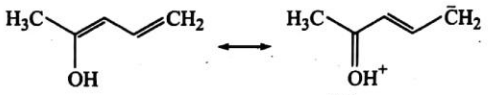
$m = 2^{n/2-1} = 2^0 = 1$

$\therefore$ No. of stereoisomers = 2 + 1 = **3.**

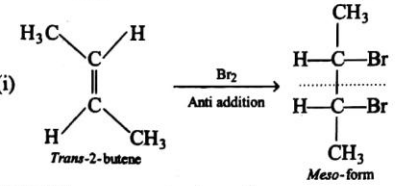
11. The C–I bond is broken and reformed to give racemic mixture of 2-iodobutane and thus remains optically inactive. The presence of I^- provides opportunities for the remaking of the C–I bond.



12.

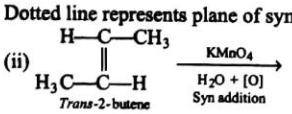


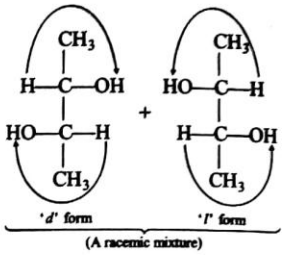
13. (i)



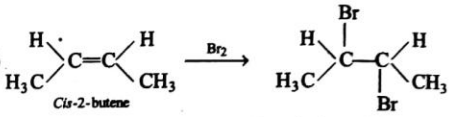
Dotted line represents plane of symmetry.

(ii)

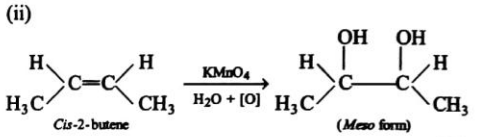


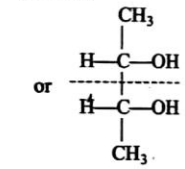


14. (i)



(ii)

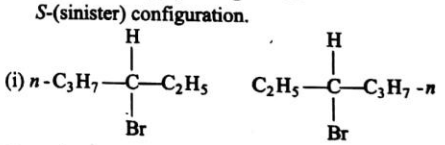




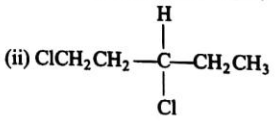
15. (a) (i) *R*, (ii) *R*, (iii) *S*, (iv) *R*, (v) *S*, (vi) *S*.

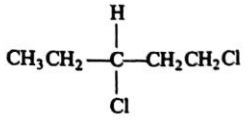
(b) *R*-(rectus or right) configuration

S-(sinister) configuration.



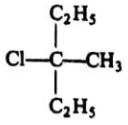
Precedence order : Br > C_3H_7 > C_2H_5 > H





Precedence order : Cl > CH_3CH_2Cl > CH_2CH_3 > H

(iii) It is an achiral molecule and does not have optical isomers.



(iv) $BrCH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-C_2H_5$ $\quad C_2H_5-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Br$

Precedence order : $Br > CH_2Br > C_2H_5 > CH_3$

(v) $t\text{-}C_4H_9-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-C_4H_9\text{-iso}$ $\quad \text{iso-}C_4H_9-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-C_4H_9\text{-}t$

Precedence order : $Cl > t\text{-}C_4H_9 > \text{iso-}C_4H_9 > H$

(vi) $H-\underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{C}}-OH$ $\quad HO-\underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{C}}-H$

Precedence order : $OH > COOH > CH_3 > H$

(vii) $n\text{-}C_3H_7-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-D$ $\quad D-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-C_3H_7\text{-}n$

Precedence order : $Cl > C_3H_7 > D > H$

16. Either of the two explanations may be given.

(a) $\underset{C_2H_5}{\overset{CH_3}{\rangle}}CH-OH+H^+ \longrightarrow \underset{C_2H_5}{\overset{CH_3}{\rangle}}C^+-H+H_2O$

$\underset{C_2H_5}{\overset{CH_3}{\rangle}}C^+-H+H_2O \longrightarrow \underset{C_2H_5}{\overset{CH_3}{\rangle}}\overset{OH}{\underset{|}{C}}-H+$

$\underset{C_2H_5}{\overset{CH_3}{\rangle}}\overset{OH}{\underset{|}{C}}-OH$

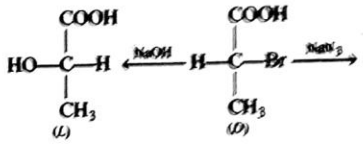
(b) $\underset{C_2H_5}{\overset{CH_3}{\rangle}}CHOH+H^+ \rightleftharpoons \underset{C_2H_5}{\overset{CH_3}{\rangle}}\overset{+}{C}HOH_2$

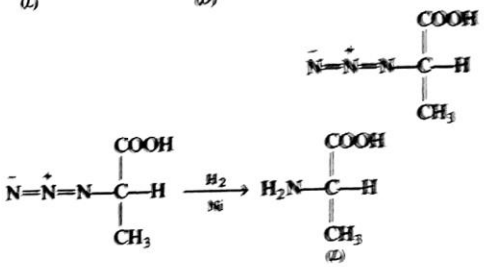
$\underset{C_2H_5}{\overset{CH_3}{\rangle}}\overset{+}{C}HOH_2+H_2O \longrightarrow H_2O\overset{-\delta}{\cdots\cdots}\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdots\cdots OH_2^{+\delta}$

$\downarrow$

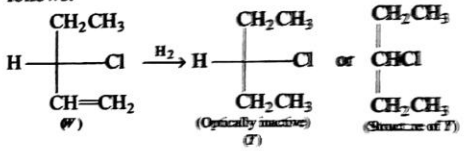
$H^+ + HO-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{CH}}-C_2H_5 \rightleftharpoons H_2O-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}^+ + H_2O$

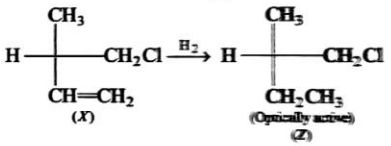
17. Catalytic hydrogenation is S_N2 . S_N2 reactions are accompanied with 100% inversion.





18. The given statements suggest that (*W*) and (*X*) are as follows:





19. (1) (*A*) reacts with Na to give H_2 and thus it contains —OH gp.

(2) Molar mass of (*A*) $(C_4H_{10}O_2) = 90\ g\ mol^{-1}$

If one OH gp. then,

90 g (*A*) with Na gives 11200 mL H_2 (*i.e.*, half mole H_2)

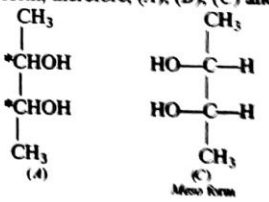
$\therefore$ 0.90 " " " $\dfrac{11200\times0.90}{90}$ mL H_2 at NTP

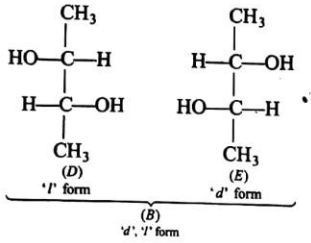
$= 112$ mL H_2 at NTP

Since, 0.90 g (*A*) gives 224 mL H_2 at NTP and thus, it contains two —OH gps.

(3) Keeping in view of above facts (*A*) is $C_4H_8\begin{matrix}OH\\OH\end{matrix}$

(4) (*A*) Shows optical isomerism of which (*B*) form is optically active having two isomers (*D*) and (*E*); (*C*) being inactive form, therefore, (*A*), (*B*), (*C*) and (*D*) are



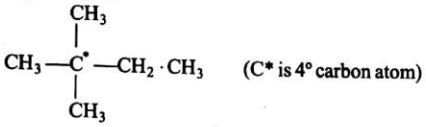


*represents two asymmetric (C) atoms.

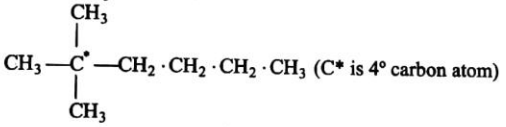
20. Heptane is C_7H_{16}.

Homologues of heptane are C_6H_{14} and C_8H_{18}

(1) Molecule of hexane having one quaternary C-atom : 2,2-Dimethylbutane is

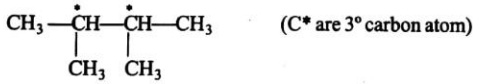


Molecule of octane having one quaternary C-atom : 2,2-Dimethylhexane is

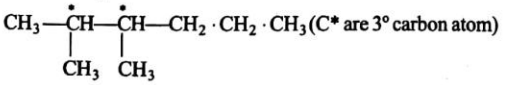


Note : Other structures with one quaternary may also be formed with octane.

(2) Molecule of hexane having two tertiary C-atoms : 2,3-Dimethylbutane is



Molecule of octane having two tertiary C-atoms : 2,3-Dimethylhexane is



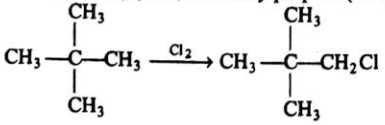
21. V.D. = 36

$\therefore$ Molar mass = $2 \times 36 = 72$ g mol^{-1}

An examination of molar mass suggests it to be alkane, *i.e.*, C_nH_{2n+2}.

$$12n + 2n + 2 = 72$$
$$n = 5$$

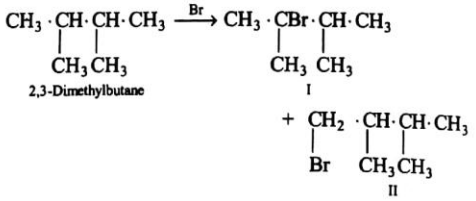
$\therefore$ Alkane (*A*) is C_5H_{12}, gives only one product on substitution, thus (*A*) is 2,2-dimethylpropane (neo pentane).



22. Alkane is C_nH_{2n+2}; Molar mass = 86 g mol^{-1}

$\therefore$ $12n + 2n + 2 = 86$ $\quad\therefore$ $n = 6$

$\therefore$ Alkane is C_6H_{14} which on bromination giving two products as :



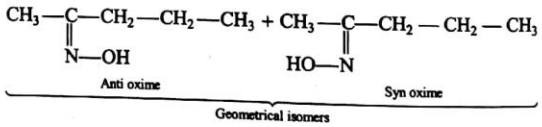
23. $CH_3 \cdot CH{=}CH{-}\underset{\displaystyle Cl}{CH_2} \xrightarrow{AgNO_3}$ White ppt; allylic chlorine

$CH_3 \cdot CH{=}\underset{\displaystyle Cl}{C} \cdot CH_3 \xrightarrow{AgNO_3}$ No reaction ; vinylic chlorine

24. $CH_3{-}\underset{\text{3-Methyl pent-1-ene optically active due to chiral nature of } C_3 \text{ atom}}{\underset{|}{CH_3}\,CH_2\,CH\cdot CH{=}CH_2} \xrightarrow[\text{catalyst}]{H_2} \underset{\text{3-Methyl pentane (optically inactive)}}{CH_3\,CH_2\,\underset{|}{CH_3}\,CH{-}CH_2CH_3}$

25. (i) Ring-chain isomerism (ii) Tautomerism (iii) Position isomerism (iv) Metamerism.

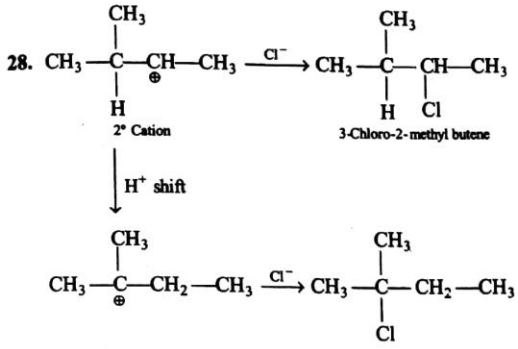
26. $\underset{\text{Pentan-2-one}}{CH_3COCH_2CH_2CH_3} \xrightarrow{NH_2OH}$



$CH_3{-}CH_2{-}CO{-}CH_2{-}CH_3 \xrightarrow{NH_2OH}$ $CH_3{-}CH_2{-}\underset{\displaystyle NOH}{\underset{\|}{C}}{-}CH_2{-}CH_3$

27. $MeO^- > Me_2CH_2O >$ $> Me_2CHO^- > Me_3CO^-$

As *R*'s accumulate on the carbon bonded to O^-, the nucleophile becomes bulkier and its backseat approach to the displacement site is retarded causing a decline in rate. Although (I) is an R_2CHO^- alkoxide, its *R*'s are 'tied back' away from the O^-. This arrangement permits a more facile approach than by Me_2CHO^-. The S_N2 reactivity is susceptible to steric hindrance by the nucleophile as well as by the *R*'s around the site of displacement.

28. 

29. $CH_3 \cdot CH_2 \cdot \underset{Br}{CH} \cdot CH_2 \cdot CH{=}CH_2 \xrightarrow{-HBr}$

$CH_3CH_2 \cdot CH{=}CH{-}CH{=}CH_2$ + $CH_3CH{=}CH \cdot CH_2 \cdot CH{=}CH_2$

Major(conjugated diene)

30. $CH_3CH_2CH_2CH_2\underset{C_2H_5}{\underset{|}{C}}{=}CH_2 \xrightarrow[CBrCl_3]{H_2O_2}$

$CH_3CH_2CH_2CH_2\underset{C_2H_5}{\underset{|}{C^{\bullet}}}{-}CH_2 \cdot CCl_3$

3° Radical

$CH_3(CH_2)_4CH_2CH{=}CH_2 \xrightarrow{H_2O_2}$

$CH_3(CH_2)_4CH_2\dot{C}H{-}CH_2 \cdot CCl_3$

2° Radical

3° Radical is more stable than 2° radical and forms faster.

31. $RCH{=}CH_2 + IN_3 \longrightarrow R{-}\underset{I^{\oplus}}{CH}{-}CH_2 + N_3^- \longrightarrow$

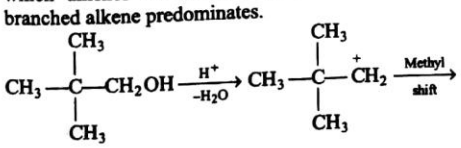
$R{-}\underset{N_3}{\underset{|}{CH}}{-}CH_2I$

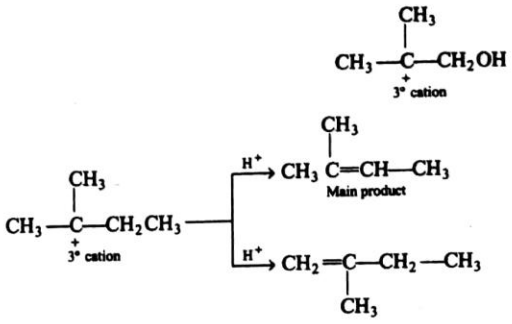
This is heterolytic addition *via* a cyclic iodonium ion and is analogous to the addition of X_2 and HOX and takes place with the same orientation.

32. $CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{HCl} CH_3{-}\underset{1,2\text{-Addition}}{CHCl \cdot CH{=}CH_2}$

$CH_3{-}\underset{1,4\text{-Addition}}{CH{=}CH{-}CH_2Cl}$

33. The first step is the formation of 1° carbocation. This rearranges by methyl shift to the more stable 3° cation, from which alkenes are formed. As usual the more highly branched alkene predominates.

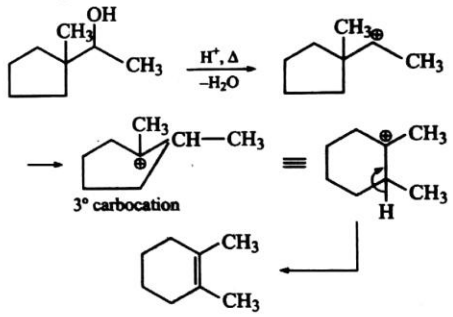


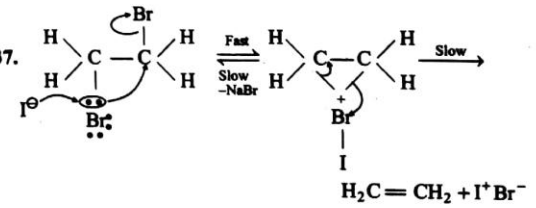


34. $\overset{+}{H_3O}$; HBr ; Stronger acid dry HBr; In aqueous solution, HBr reacts to yield weaker acid $\overset{+}{H_3O}$; Electrophilic addition is more easier in HBr dry.

35. (i) Allylic bromination (ii) α-elimination
(iii) Rearrangement (iv) γ-elimination.

36. Rearrangement of carbocation leads to a change in the size of the ring.



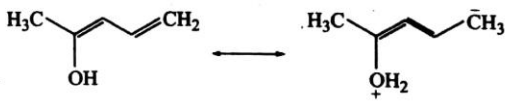
37. 

$H_2C{=}CH_2 + I^+Br^-$

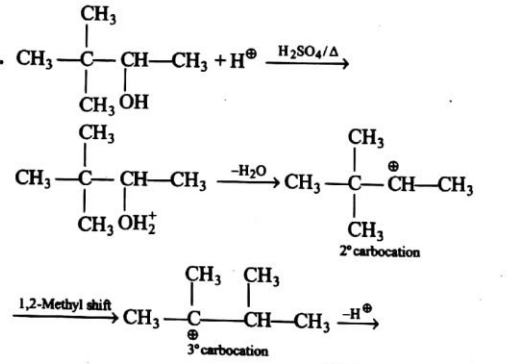
38. $BrCH_2C{\equiv}C \cdot CH_2Br \xrightarrow[\Delta]{Zn} \underset{\text{Butatriene}}{CH_2{=}C{=}C{=}CH_2} \xrightarrow[H_2O/Zn]{O_3}$

$2HCHO + 2CO_2$

39.

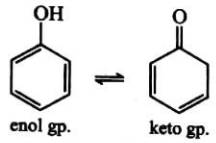


40.



$(CH_3)_2C{=}C(CH_3)_2$

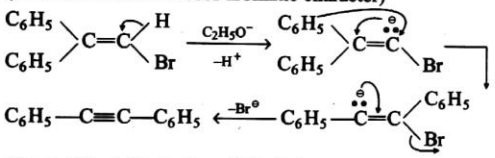
41.



enol gp. keto gp.

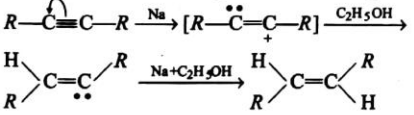
(unstable because it loses aromatic character)

42.

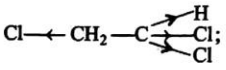


This is Fritsch-Buttenberg-Wiechel rearrangement.

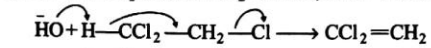
43.



44.



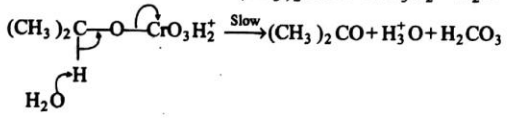
the *–IE* of two Cl-atoms is greater than that of one. Consequently, the proton of $CHCl_2$ is removed more easily by OH^-, than a proton of CH_2Cl. Thus, the E^2 mechanism.



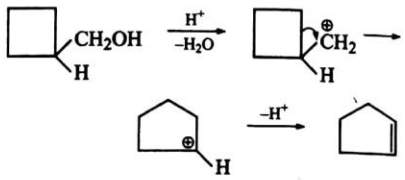
45.

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons HCrO_4^-$$

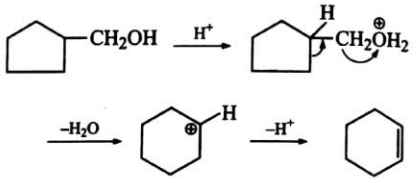
$$(CH_3)_2CHOH + HCrO_4^- + 2H^+ \rightleftharpoons (CH_3)_2CH{\cdot}O{\cdot}CrO_3H_2^+ + H_2O$$



46.



47.



48. (a)

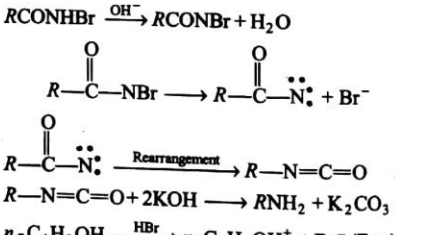
$$Cl_2 \xrightarrow{h\nu} Cl^\bullet + Cl^\bullet \quad \text{Chain initiation}$$

$$\left.\begin{aligned} Cl^\bullet + RH &\longrightarrow R^\bullet + HCl \\ R^\bullet + SO_2 &\longrightarrow RSO_2^\bullet \\ RSO_2^\bullet + Cl_2 &\longrightarrow RSO_2Cl + Cl^\bullet \end{aligned}\right\} \text{Chain propagation}$$

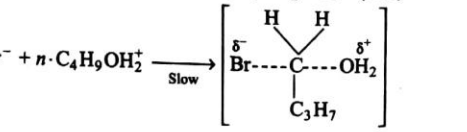
This is Reed reaction having free radical chain mechanism.

(b) $Br_2 + 2NaOH \longrightarrow NaBr + \overset{+}{N}aBrO^- + H_2O$

This is Hoffmann's bromamide reaction.

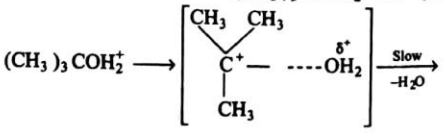


(c) $n\text{-}C_4H_9OH \xrightarrow{HBr} n\cdot C_4H_9OH_2^+ + Br^-$ (Fast)



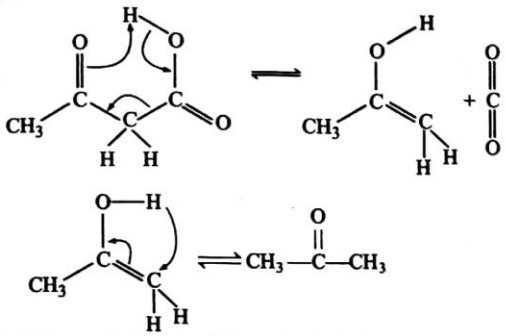
(d)

$$(CH_3)_3C{\cdot}OH + HBr \longrightarrow (CH_3)_3C{\cdot}OH_2^+ + Br^- \text{ (Fast)}$$

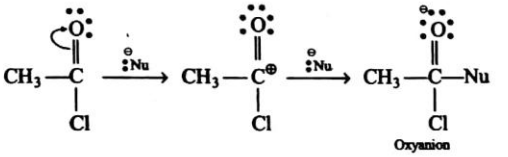


$$(CH_3)_3C^+ \xrightarrow[\text{Fast}]{Br^-} (CH_3)_3CBr \ (S_N1)$$

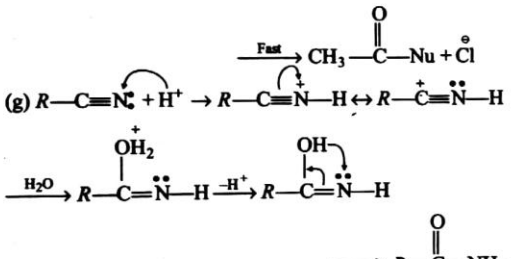
(e)



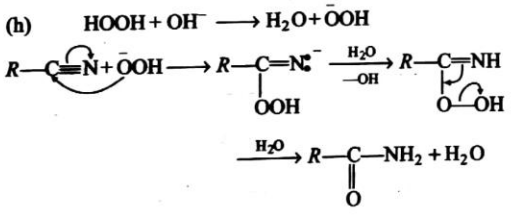
(f) This is called nucleophilic acyl substitution.



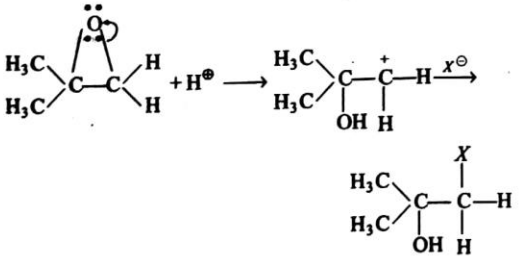
Oxyanion



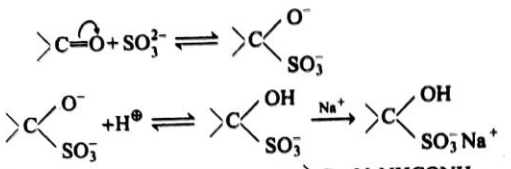
(h) $HOOH + OH^- \longrightarrow H_2O + \bar{O}OH$



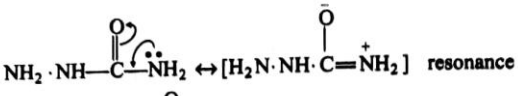
49.



50. $NaHSO_3 \longrightarrow Na^+ + HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$

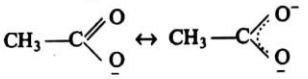


51. $>C{=}O + H_2N{\cdot}NHCONH_2 \longrightarrow >C{=}N{\cdot}NHCONH_2$



stabalization of $-\overset{\overset{O}{\|}}{C}-NH_2$.

52. **Acetic acid :** $CH_3COOH \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-O^- + H^+$



Peroxy acetic acid : $CH_3CO_3H \rightleftharpoons CH_3COOO^- + H^+$;

Negative charge is not delocalised with $-\overset{\overset{O}{\|}}{C}-$ gp.

53. $(CH_3)_3C{\cdot}CHOH{\cdot}CH_3 \xrightarrow[(ii)\ -H_2O]{(i)\ H^+} (CH_3)_3C{\cdot}CH^+{\cdot}CH_3$

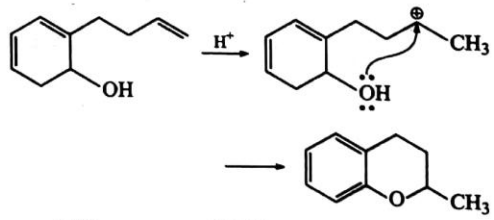
$\xrightarrow[\text{shift}]{CH_3^-} (CH_3)_2C^+CH(CH_3)_2 \xrightarrow{-H^+} (CH_3)_2C{=}CH(CH_3)_2$

54. (a) (i) $C_6H_5CH(OH)C{\equiv}CH \xrightarrow{H_3\overset{\oplus}{O}} C_6H_5\underset{\underset{OH_2^+}{|}}{CH}-C{\equiv}CH$

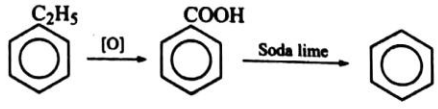
$\xrightarrow{-H_2O} C_6H_5CH{=}C{=}\overset{+}{C}H \xrightarrow{OH^-} C_6H_5CH{=}C{=}\underset{\underset{OH}{|}}{CH}$

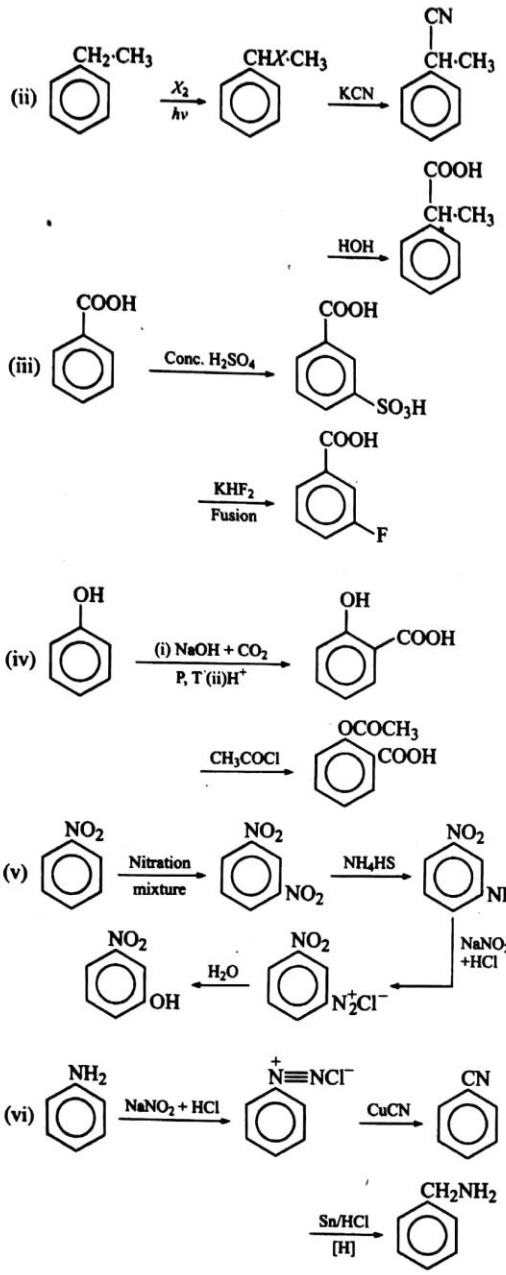
$\underset{\text{Tautomerisation}}{\rightleftharpoons} C_6H_5CH{=}CH{\cdot}CHO$

(ii)

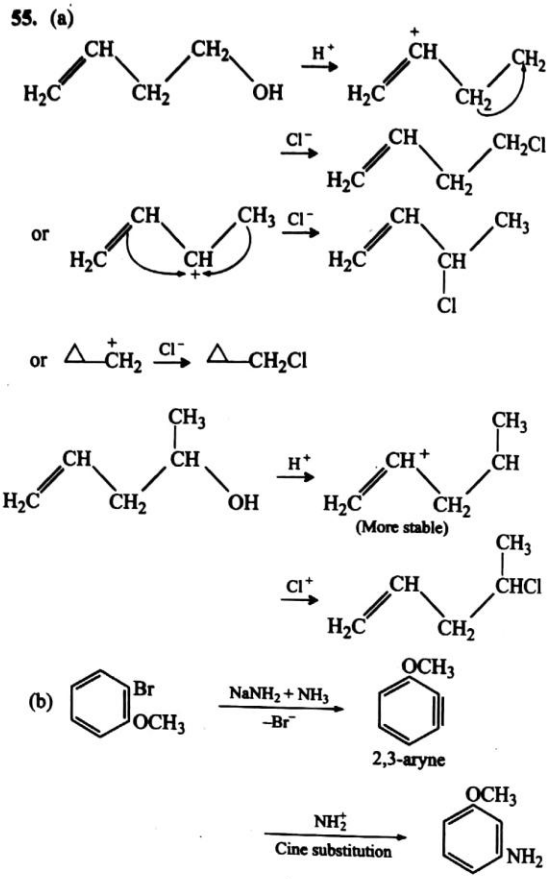


(b) (i)





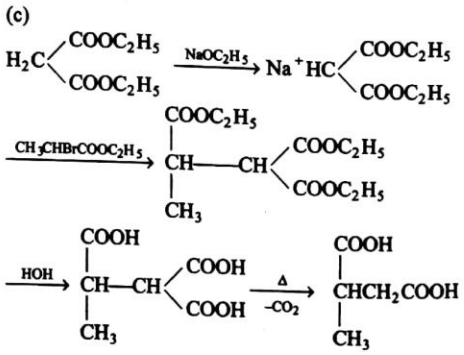
55. (a)



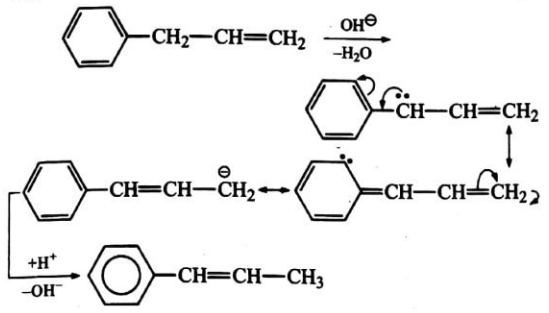
(b)

2,3-aryne

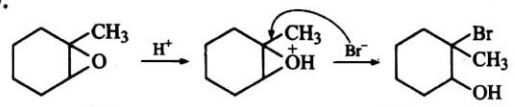
(c)



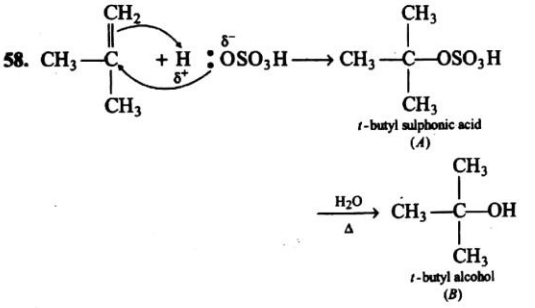
56.



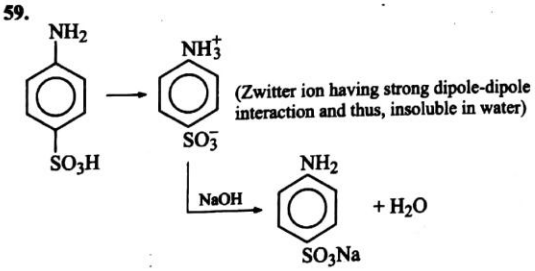
57.



58.



59.

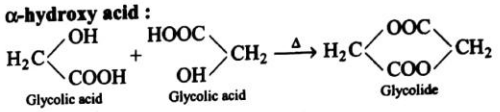


(Zwitter ion having strong dipole-dipole interaction and thus, insoluble in water)

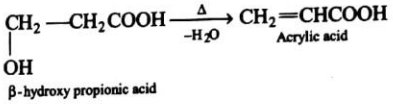
In acid, SO_3^- fails to accept H^+ and thus insoluble in acid whereas in alkalies the strong basic OH^- abstracts a proton from $-NH_3^+$ to make it a water soluble salt.

60. The carbon atoms in $-C\equiv C-$ are *sp*-hybridised and better electron withdrawing group than $>C=C<$ where carbon atoms are sp^2-hybridised. Thus, 3-butynoic acid (pK_a = 3.32) is stronger acid than 3-butenoic acid (pK_a = 4.35).

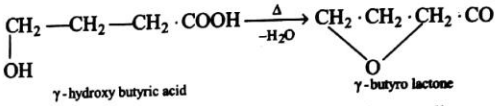
61. **α-hydroxy acid :**



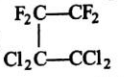
β-hydroxy acids:



γ-hydroxy acids:



62. $:CCl_3$ is less basic than $:CF_3$ because fluorine can disperse charge by inductive effect only while chlorine (having empty 3*d*-orbital) can disperse charge by *–IE* as well as by $p\pi - d\pi$ bonding delocalization.

63. (i)  (ii)

64. In presence of $FeBr_3$, Br_2 produces Br^+ (an electrophile) which attacks the benzene ring at *o*-, *p*-position to give *p*-bromotoluene. In presence of light, side chain is attacked to produce benzyl bromide.

65. (i) *t*-butyl benzene does not contain benzylic hydrogen and thus, this side chain [$-C(CH_3)_3$] cannot be oxidised to —COOH group.

(ii) $CH_2=CH_2$ is less acidic than $CH\equiv CH$ since the latter has *sp*-hybridised carbon atoms which increases the electronegativity of carbon atom and hence acidic character in C—H bond increases. Also, weaker is the acid (C_2H_4), stronger is its conjugate base ($CH_2=CH^-$).

(iii) Benzene has resonance stabilization due to delocalisation of π-electrons. Also, during electrophilic addition reactions, it loses its aromaticity. In electrophilic substitution reactions aromaticity is retained.

(iv) Diethyl ether is Lewis base and anhy. $AlCl_3$ is Lewis acid, thus oxygen atom of diethyl ether readily donates the lone pair to 3*p*-orbital Al-atom of anhydrous $AlCl_3$. In case of hydrated $AlCl_3$, Al-atom is already coordinated by oxygen atom of H_2O. Thus, anhydrous $AlCl_3$ is more soluble in diethyl ether.

66. (a) Wrong; Tollens reagent converts $CH_3CH=CH\cdot CHO$ to $CH_3\cdot CH=CH\cdot COOH$

(b) True

(c) Wrong; Desulphonation occurs to give C_6H_6

(d) Wrong ; It not only gives 3-iodo-2,2-dimethyl butane but also 2-iodo-2,3-dimethyl butane or 3-iodo-2,3-dimethyl butane.

67. 7-bromo-1,3,5-cycloheptatriene forms aromatic ion, a stable ion and thus exists in ionic form

5-bromo-1,3-cycloheptatriene forms antiaromatic ion even in presence of Ag^+.

68. $CH_3 \cdot CH{=}CH \cdot CH_3$ (But-2-ene)
- $\xrightarrow{HBr}$ $CH_3 \cdot CHBr \cdot CH_2 \cdot CH_3$ (2-Bromobutane)
- $\xrightarrow[\text{Peroxide}]{HBr}$ $CH_3 \cdot CHBr \cdot CH_2CH_3$

$CH_3{-}C(CH_3){=}CH_2$ (2-Methylpropene)
- $\xrightarrow{HBr}$ $(CH_3)_2 \cdot CBr \cdot CH_3$ (2-Bromo, 2-methylpropane)
- $\xrightarrow[\text{Peroxide}]{HBr}$ $(CH_3)_2CH \cdot CH_2Br$ (1-Bromo-2-methylpropane)

Note : See only one product is formed in symmetrical alkene, *i.e.*, but-2-ene.

69. 2,3-dimethyl but-2-ene $\left[(CH_3)_2C{=}C(CH_3)_2\right]$ has no olefinic H-atom and thus it does not decolorise Br_2/CCl_4 as the reaction following free radical addition does not take place. On the other hand reaction of 2,3-dimethyl but-2-ene with Br_2/H_2O involves electrophilic addition and thus Br_2-water is decolorised.

70. These are S_N2 reactions which invert configuration and the product is

(S)-Et O C(=O)–C(CH$_3$)(H)–CN

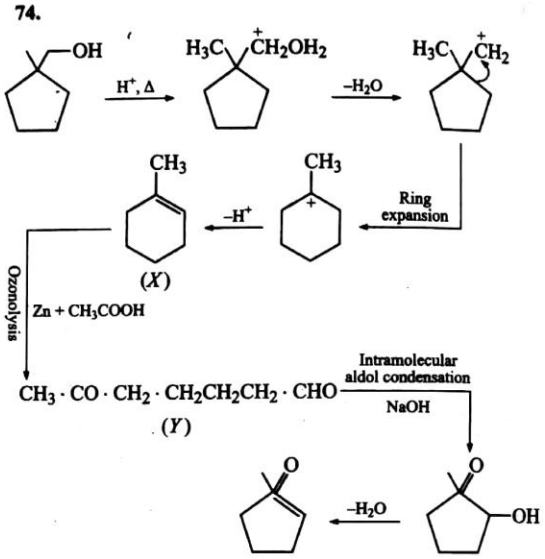
Although inversion occurs, the priority order changes and the product is (R)

71. $CH_3CH_2CH_2CH_2CHBr_2 \xrightarrow[200°C]{KOH(s)} CH_3CH_2C{\equiv}CCH_3$

72. $C_6H_5CH_2CH_2OH$

73. (A) and (B) are $C_6H_5{-}C(D)(CH_3){-}OH$

74.



75. (a) $(CH_3 \cdot CH_2)_2C{=}CHCH_3 \xrightarrow[O_2]{HBr}$ $(CH_3{-}CH_2)_2{-}CH(Br){-}CH{-}CH_3$

(b) $(CH_3 \cdot CH_2)_2{-}C{=}CH{-}CH_3 \xrightarrow{Br_2/H_2O}$ $(CH_3 \cdot CH_2)_2C(OH){-}CH(Br){\cdot}CH_3$

(c) $(CH_3 \cdot CH_2)_2C{=}CH{-}CH_3 \xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O} (C_2H_5)_3C{\cdot}OH$

76. $C_6H_5(CH_3)C{=}O \xrightarrow{NH_2OH} C_6H_5(CH_3)C{=}NOH$

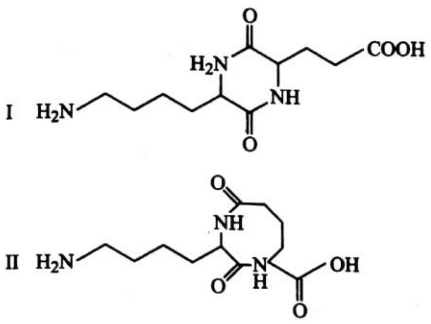
$C_6H_5{-}C(CH_3){=}N{-}OH$ (Syn) and $C_6H_5{-}C(CH_3){=}HO{-}N$ (Anti) (isomers)

77. $C_6H_5COCH_3 \xrightarrow[\text{Iodoform reaction}]{NaOI} \underset{(A)}{CHI_3} + \underset{(B)}{C_6H_5COONa}$

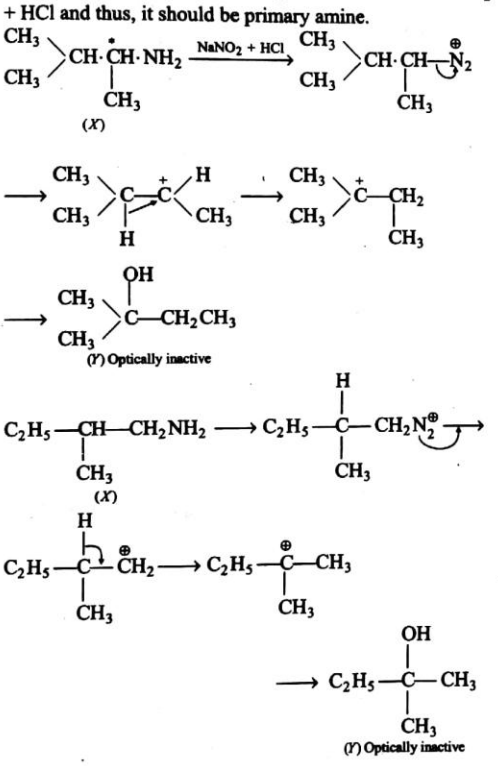
$\xrightarrow[\Delta]{Ag}$ $CH{\equiv}CH$ (C)

$\underset{(B)}{C_6H_5COONa} \xrightarrow{HOH} \underset{(D)}{C_6H_5COOH} \xrightarrow[H_2SO_4]{N_3H} \underset{(E)}{C_6H_5NH_2}$

78.



79. (X) is optically active and also it gives alcohol with $NaNO_2$ + HCl and thus, it should be primary amine.



80.

(a)

The two optically active forms are

(b) (i) Aniline no doubt undergoes Friedel-Crafts reaction. It is nitrobenzene which does not show Friedel-Crafts reaction. Question is wrong. However, the yield is poor because aniline being a base reacts with Lewis acid $AlCl_3$ to give $C_6H_5NH_2 \cdot AlCl_3$ and thus, resists the attack of carbocation. Also, formation of carbocation is hindered since $AlCl_3$ reacts with aniline.

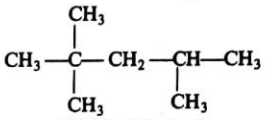
(ii) $C_6H_5NH_2 \xrightarrow{NaNO_2 + 2HCl} C_6H_5N{=}NCl$

The reaction requires HNO_2 + HCl and thus the mineral acid (HCl) is needed in more amount. Also, excess of mineral acid resists the hydrolysis of salt formed.

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

Also, excess of HCl prevents coupling of aniline with diazonium salt formed.

(c) $(CH_3)_2C{=}CH_2 + (CH_3)_2CHCH_3 \xrightarrow[\Delta]{HF}$

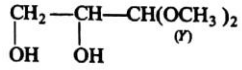


(2,2,4-dimethyl pentane)

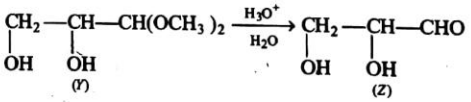
81. $CH_2{=}CH{-}CH_2OH \xrightarrow[CH_2Cl_2]{CrO_3,\ 2C_5H_5N} \underset{(W)}{CH_2{=}CHCHO}$

$CH_2{=}\underset{(W)}{CHCHO} \xrightarrow{CH_3OH,\ H^+} \underset{(X)}{CH_2{=}CH{-}CH(OCH_3)_2}$

$CH_2{=}\underset{(X)}{CH{-}CH(OCH_3)_2} \xrightarrow[\text{(cold, dil.)}]{KMnO_4,\ OH^-}$

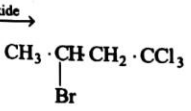


(Y)

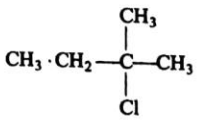


(Y) (Z)

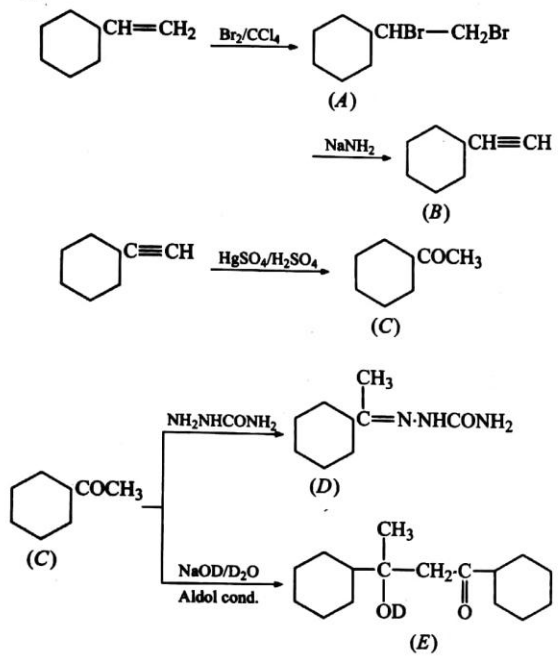
82. (i) $CH_3 \cdot CH{=}CH_2 + Br \cdot CCl_3 \xrightarrow{\text{Peroxide}}$



(ii) $CH_3 \cdot CH{=}\underset{CH_3}{\overset{|}{C}}{-}CH_3 + HCl \xrightarrow{\text{Peroxide}}$

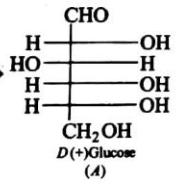


83.



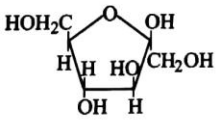
84. $CH_3-\underset{\underset{O}{\|}}{C}-O^{18}C_2H_5 \xrightarrow{HOH} \underset{(A)}{CH_3COOH} + \underset{(B)}{C_2H_5O^{18}H}$

85. (i) Sucrose $\longrightarrow$



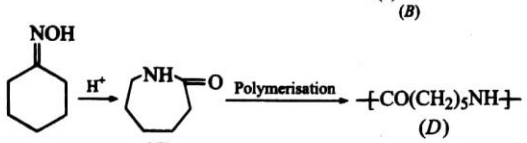
D(+)Glucose
(A)

+



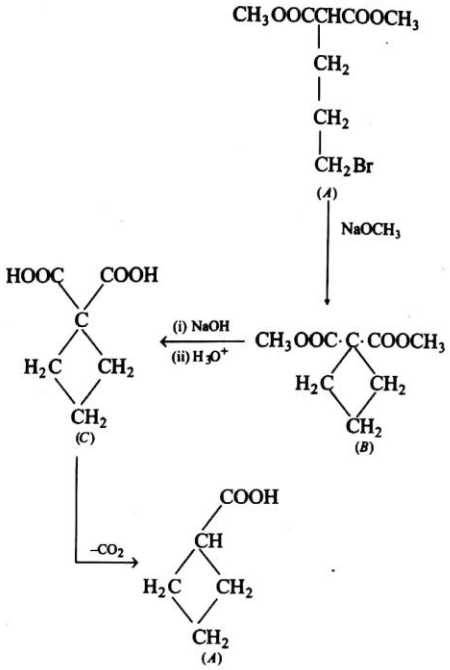
D(–)Fructose
(B)

(ii)

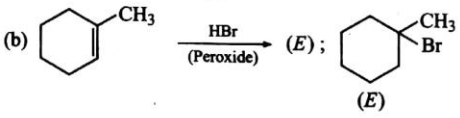


(C) (D)

86. (a) $CH_3OOCCH_2COOCH_3 \xrightarrow[(ii)\ BrCH_2CH_2CH_2Br]{(i)\ NaOCH_3}$

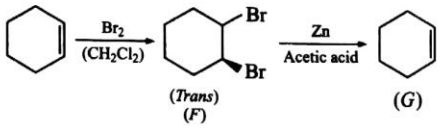


(b)

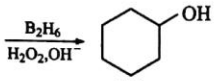


(E)

(c)

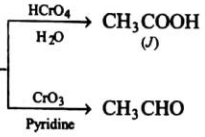


(Trans) (F) (G)



(H)

(d) CH_3CH_2OH (I)



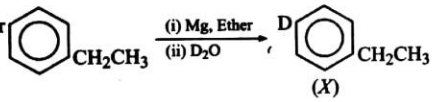
(e) $2CH_3COCH_3 \xrightarrow{OH^-} (CH_3)_2C(OH)CH_2COCH_3$ (K)

$(K) \xrightarrow[\Delta]{NaHSO_4} (CH_3)_2C{=}CHCOCH_3$

87. (a) $H_3C-\underset{CH=CH_2}{\overset{C_2H_5}{C}}-H + D_2 \xrightarrow{Pd}$ $H_3C-\underset{CH_2D}{\overset{C_2H_5}{C}}-H$ (*T*) + $H-\underset{CH_2D}{\overset{C_2H_5}{C}}-D$ (*U*)

(b) $R-\underset{O}{\overset{}{C}}-Cl \xrightarrow[(ii)\ H_2O]{(i)\ N_3H,\ \Delta} RNH_2$ (*V*)

(c) $I^- + CH_3CH_2CH_2-\underset{H}{\overset{D}{C}}-I \longrightarrow I-\underset{H}{\overset{D}{C}}-CH_2CH_2CH_3$ (*W*)

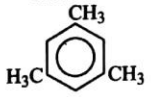
(d)  (*X*)

(e) $H_2C=\underset{CH_3}{\overset{}{C}}-COOH \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3/THF} CH_2(OH)-CH(CH_3)\cdot COOH$ (*Y*)

(f) $2CH\equiv CH \xrightarrow[O_2]{Cu^{2+}} HC\equiv C-C\equiv CH$ (*Z*)

88. (i) $3\ (CH_3)_2C=O \xrightarrow{Dry\ HCl}$ $(CH_3)_2C=CHCOCH=C(CH_3)_2$

Phorone

or $3CH_3COCH_3 \xrightarrow[\Delta]{Conc.\ H_2SO_4}$ 

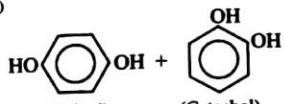
(Mesitylene)

(ii) $CH_3COCl + H_2 \xrightarrow[Quinolene]{Pd/BaSO_4} CH_3CHO + HCl$

(Rosenmund's reaction)

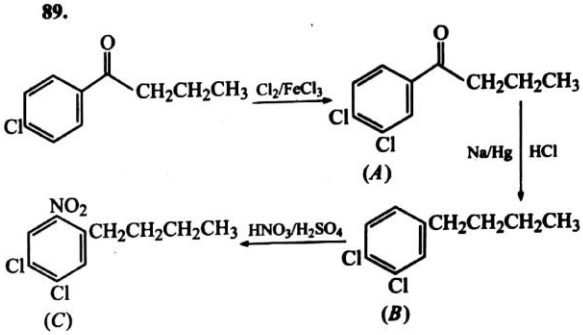
(iii) $(CH_3)_2CO \xrightarrow[C_2H_5ONa]{NH_2NH_2} CH_3CH_2CH_3$

(Wolff Kishner reaction)

(iv) $C_6H_5OH \xrightarrow[K_2S_2O_8\ (alk.)]{Elb's\ oxidation}$ 

(Quinol) (Catechol)

(v) $C_6H_5N_2Cl \xrightarrow[HCl]{Cu} C_6H_5Cl$ (Gattermann reaction)

89. 

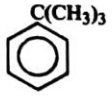
(*A*) (*B*) (*C*) (*D*) (*E*)

90. (*A*) This has reactive methylene group. $H_2C(CN)(Ph)$ and C_6H_5CHO attacks on CH_2 group giving (*B*)

(*B*) $C_6H_5CH=C(CN)(C_6H_5)$

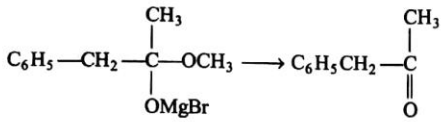
(*C*) $C_6H_5CH=C(COOH)(C_6H_5)$

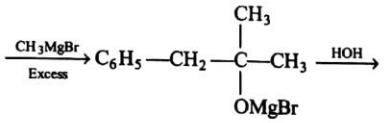
(*D*) $C_6H_5CH=C(CONHCH_3)(C_6H_5)$

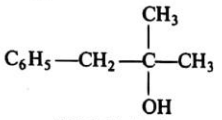
91. (i) $+ (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$ 

2-Methyl, 2-phenylpropane

(ii) $C_6H_5CH_2COOCH_3 \xrightarrow{CH_3MgBr}$

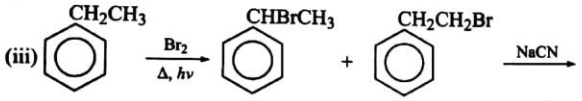






2-Methyl, 1-phenyl propan-2-ol

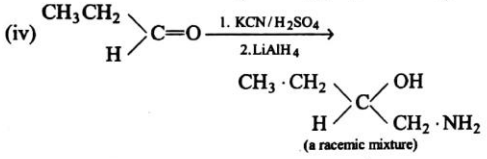
(iii)



(Major) (Minor)

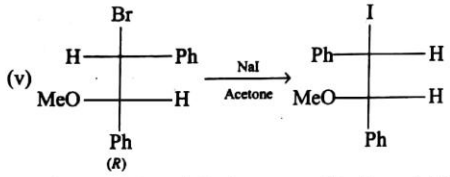
(2-Phenylpropane nitrile)

(iv)



(a racemic mixture)

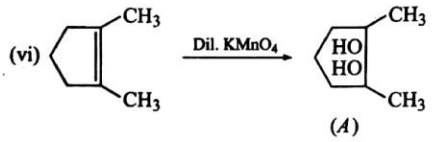
(v)



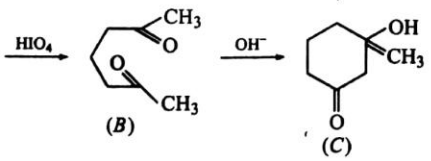
(R)

enantiomer of the original compound is formed following S_N2 mechanism (S)

(vi)

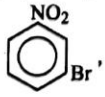
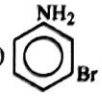
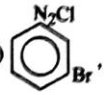


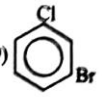
(A)



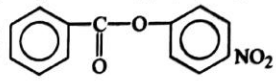
(B) (C)

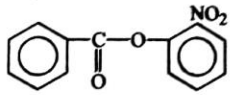
92. (a) (A) CH_3Cl, (B) $C_6H_5CH_2Cl$, (C) KCN, (D) $C_6H_5CH_2COOH$

(b) (A)  , (B)  , (C)  ,

(D) 

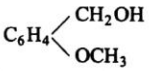
(c) (A) $CH_3CH_2 \cdot CH_2Br$, (B) $CH_3 \cdot CH{=}CH_2$, (C) $CH_3CHBr \cdot CH_3$, (D) $CH_3CHNH_2 \cdot CH_3$

(d) (A)  +



(e) (A) C_6H_5CN (B) C_6H_5COOH

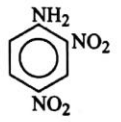
(f) (A)

(g) (A)  (B) HCOOK

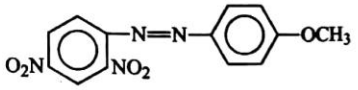
(h) $CH_3 \cdot CH_2 \cdot COOH \xrightarrow[\text{Bromine}]{\text{P and}} \underset{(A)}{CH_3 \cdot CHBr \cdot COBr}$

$CH_3CHBr \cdot COBr \xrightarrow[\text{(ii) } H^+]{\text{(i) KOH (alc.)}} \underset{(B)}{CH_2{=}CH \cdot COOH} + HBr$

(i)



$\xrightarrow[\text{2. Anisole}]{\text{1. } NaNO_2 \text{ and HCl at 5°C}}$

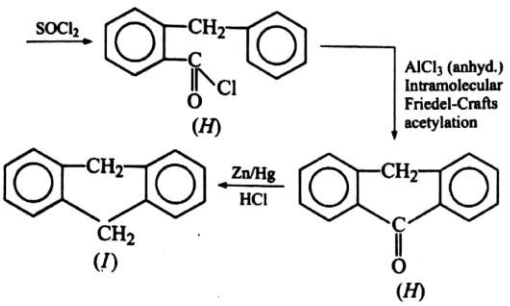


(C)

(j) $C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[\text{absolute } C_2H_5OH,\ \Delta]{NaOC_2H_5 \text{ in}}$ (Claisen condensation)

$\underset{(D)}{C_6H_5CH{=}CHCOOC_2H_5}$

(k) *o*-HOOC—C_6H_4—CH_2—C_6H_5

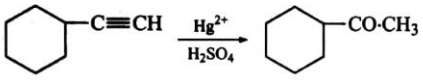


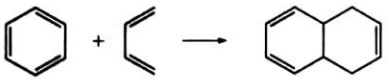
(l) (*A*) CH_3COOH, (*B*) CH_3COCl, (*C*) CH_3CH_2OH, (*D*) $CH_3 \cdot CH_2Br$

(m) $R—\underset{\underset{NOH}{\|}}{C}—R' \xrightarrow[\text{(Beckmann's rearrangement)}]{\text{Acidic reagent}} R—NH—\underset{\underset{O}{\|}}{C}—R'$

(n) $R—COCl + H_2 \xrightarrow{Pd/BaSO_4} R \cdot CHO$

(o) $Br \cdot CH_2 \cdot CH_2Br \xrightarrow{KOH(alc.)} C_2H_2$

(p) 

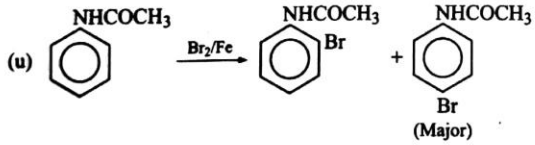
(q) 

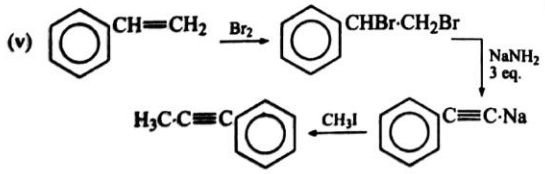
1,4-Dihydronaphthalene

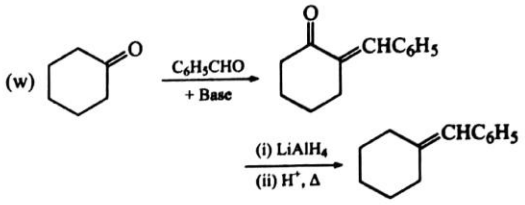
(r) $C_6H_5CH_2 \cdot CHClC_6H_5 \xrightarrow[\Delta]{KOH(alc.)} C_6H_5 \cdot CH{=}CH \cdot C_6H_5$ (*Cis* and *Trans*-forms)

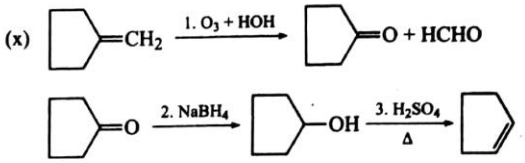
(s) $CH_3 \cdot CH_2 \cdot NH_2 \xrightarrow[\Delta]{(CH_3CO)_2O} CH_3 \cdot CH_2NHCOCH_3 + CH_3COOH$

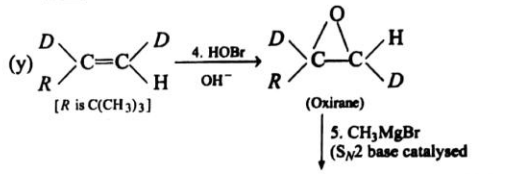
(t) $(CH_3)_2CH \cdot O \cdot CH_3 \xrightarrow[\Delta]{HI(excess)} (CH_3)_2CHI + CH_3I$

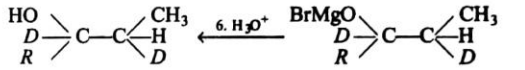
(u) 

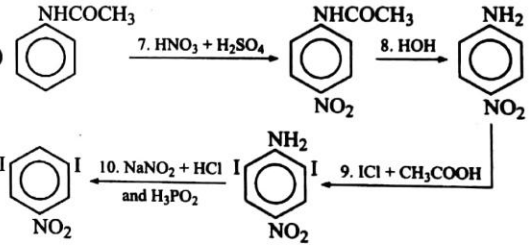
(v) 

(w) 

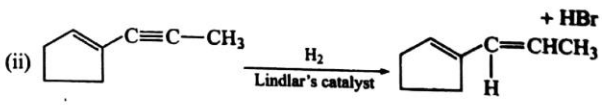
(x) 

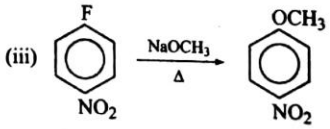
(y) 

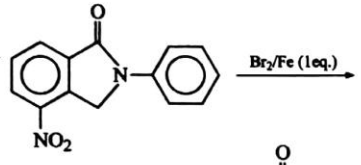


(z) 

93. (i) $(CH_3)_3 \cdot C \cdot CH_2Br \xrightarrow[\Delta]{C_2H_5OH} (CH_3)_2C{=}CH—CH_3$

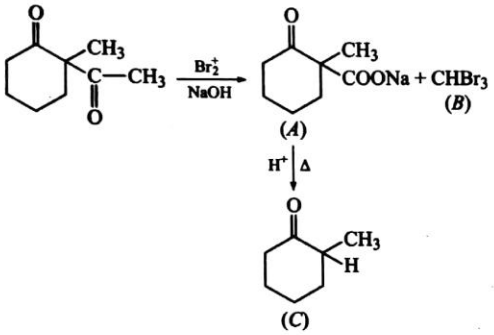
(ii) 

(iii) 

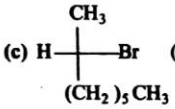
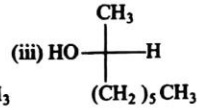
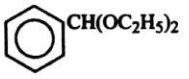
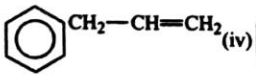
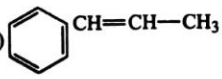
(iv) 

(v)

94.



95.

	Reagent	Product	Other reagent
(a)	$R-CH=CH_2$	(vi) $RCH(Cl)-CH_2\cdot CCl_3$	CCl_4/Peroxide
(b)		(i)	Baeyer's reagent or HCOOH or OsO_4 / (*aq.*) $NaHSO_3$
(c)		(iii) 	KOH(*aq.*)
(d)		(ii)	($I_2 + HNO_3$ or ICl)
(e)		(v) 	C_2H_5OH/dry HCl
(f)		(iv) 	KOH + Heat

96.

List I	List II
1	(B)
2	(C)
3	(D)
4	(E)
5	(A)

97. (a) $CH_3CH_2C\equiv CH \xrightarrow[\text{(A test for terminal alkyne)}]{\text{Amm. } AgNO_3} CH_3CH_2C\equiv C\cdot Ag$

(1-Butyne)

(b) $CH_3-C\equiv C-CH_3 \xrightarrow{\text{Alk. } KMnO_4,\ \Delta} 2CH_3COOH$

(2-Butyne)

(c) $CH_2=CH-CH=CH_2 \xrightarrow{Br_2} CH_2(Br)-CH(Br)-CH(Br)-CH_2(Br)$

(1,3-Butadiene)

Addition of 1 mole of H_2 follows 1,4 addition a characteristic reaction of conjugated alkadienes.

$CH_2=CH-CH=CH_2 \xrightarrow{H_2,\ 1\ mole} CH_3-CH=CH-CH_3$

(2-Butene)

(d) (Cyclobutene) $\xrightarrow{\text{Ozonolysis}}$ $\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}$

98. Alkane (*A*) C_5H_{12} on chlorination gives four mono chloro product and thus, (*A*) is isopentane

$CH_3\cdot CH(CH_3)-CH_2\cdot CH_3 \xrightarrow{\text{Chlorination}} CH_2Cl\cdot CH(CH_3)\cdot CH_2\cdot CH_3$

(*A*) (*B*)

$\xrightarrow[\text{halogenation}]{\text{Dehydro-}} CH_2=C(CH_3)-CH_2\cdot CH_3$

$CH_3\cdot CCl(CH_3)\cdot CH_2\cdot CH_3 \longrightarrow (CH_3)_2C=CH\cdot CH_3$

(*C*) (*F*)

$CH_3\cdot CH(CH_3)\cdot CHCl\cdot CH_3 \longrightarrow (CH_3)_2C=CH\cdot CH_3$

(*D*) (*F*)

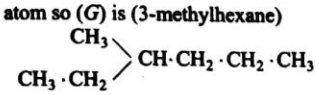
$\xrightarrow{[O]} (CH_3)_2CO + CH_3COOH$

(*G*) (*H*)

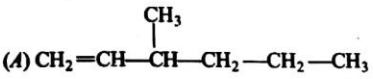
$CH_3\cdot CH(CH_3)\cdot CH_2\cdot CH_2Cl \longrightarrow (CH_3)_2CH=CH_2$

(*E*)

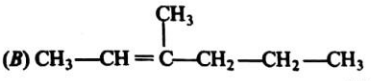
99. (1) (*G*) is lowest mol. mass alkane with one asymmetric carbon atom so (*G*) is (3-methylhexane)



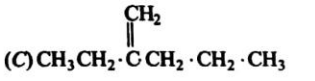
(2) Thus, possible alkenes which can produce (*G*) on hydrogenation are (also none of them on ozonolysis gives acetone).



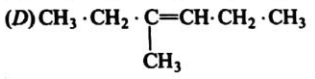
3-Methylhex-1-ene



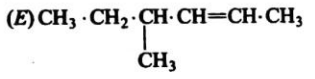
3-Methylhex-2-ene



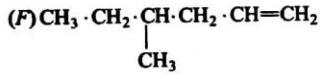
2-Ethylpent-1-ene



3-Methylhex-3-ene

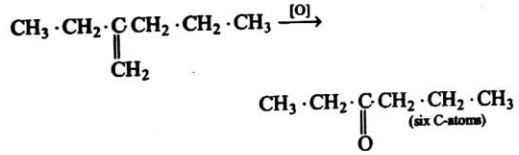


4-Methylhex-2-ene

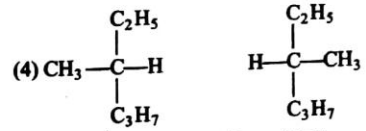


4-Methyl hex-1-ene

(3) Only alkene (*C*) gives a ketone containing more than five C-atoms on treatment with warm conc. alk. $KMnO_4$.

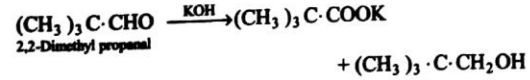


(six C-atoms)

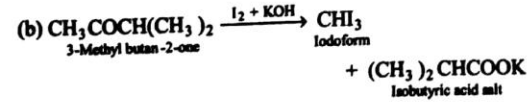
(4) 

These are Fischer projections of (*G*).

100. (a) Aldehydes lacking with α-H-atom undergoes Cannizzaro's reaction:



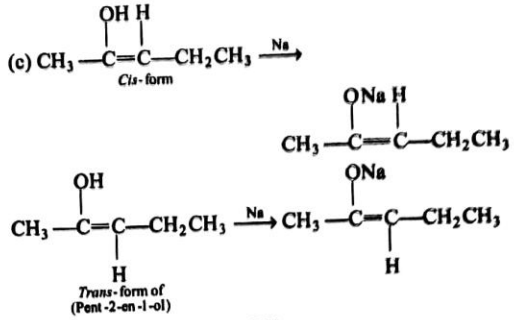
2,2-Dimethyl propanal



3-Methyl butan-2-one

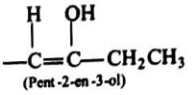
Iodoform

Isobutyric acid salt



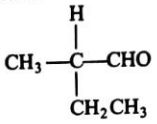
Cis-form

Trans-form of (Pent-2-en-1-ol)

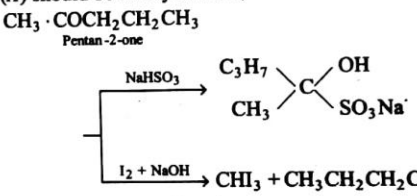
It may also be, 

(Pent-2-en-3-ol)

(d) (*A*) should have —CHO gp. and at least one chiral carbon atom.



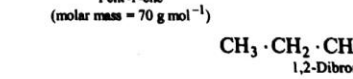
(e) (*A*) should be methyl ketone,



Pentan-2-one

(f) (*A*) should be a carbonyl compound and not a methyl ketone or aldehyde. $NaHSO_3$ gives white solid with all aldehydes and methyl ketones.

Pentan-3-one

101. (a) 

(molar mass = 70 g mol^{-1})

1,2-Dibromopentane

$\because$ 70 g C_5H_{10} requires 160 g Br_2

$\therefore$ 5 g C_5H_{10} requires $\frac{160\times 5}{70}$ g Br_2 = **11.43 g Br_2**

(b)

(molar mass = 68 g mol^{-1})

1,1,2,2-Tetrabromopentane

$\because$ 68 g C_5H_8 requires 320 g Br_2

$\therefore$ 5 g C_5H_8 requires $\frac{320\times 5}{68}$ g Br_2 = **23.53 g Br_2**

(c) $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3 \xrightarrow{Br_2} C_5H_{11}Br + HBr$
Pentane (molar mass = 72 g mol^{-1})

$\because$ 72 g C_5H_{12} requires 160 g Br_2

$\therefore$ 5 g C_5H_{12} requires $\frac{160\times5}{72}$ g Br_2 = **11.11 g Br_2**

102. (a) (1) Given,

$$C_5H_{11}X \xrightarrow[-HX]{KOH(alc.)} \underset{\text{Pent-1-ene}}{CH_3 \cdot CH_2 \cdot CH_2CH=CH_2}$$

(2) Thus, possible structure of halide may be (I) or (II). However, elimination of HX, according to Saytzeff's rule, suggests that structure (II) is correct as it gives only pent-1-ene.

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CHX \cdot CH_3$ (I)
↓ (alc.) KOH

$CH_3 \cdot CH_2CH=CH \cdot CH_3$ Major
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH=CH_2$ Minor

or $CH_3CH_2 \cdot CH_2CH_2 \cdot CH_2X$ (II)
↓ (alc.) KOH

$\underset{\text{Pent-1-ene (only)}}{CH_3 \cdot CH_2 \cdot CH_2CH=CH_2}$

Thus, halide is $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2X$ *i.e.*, 1-halopentane.

(b) (1) Given, $C_5H_{11}X \xrightarrow[-HX]{KOH(alc.)} CH_3 \cdot CH_2 \cdot CH=CH \cdot CH_3$

(2) Thus, possible structure of halide may be (I) or (II). However elimination of HX according to Saytzeff's rule (the major product is one from which elimination of H occurs from less hydrogenated C-atom) structure (II) is correct as it gives only pent-2-ene.

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CHX \cdot CH_3$ (I) $\xrightarrow{(alc.)\ KOH}$ $\underset{\text{Major}}{CH_3 \cdot CH_2 \cdot CH=CH \cdot CH_3}$ + $\underset{\text{Minor}}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH=CH_2}$

$CH_3 \cdot CH_2 \cdot CHX \cdot CH_2 \cdot CH_3$ (II) $\xrightarrow{(alc.)\ KOH}$ $\underset{\text{Pent-2-ene (only)}}{CH_3 \cdot CH=CH \cdot CH_2 \cdot CH_3}$

Thus, halide is $CH_3 \cdot CH_2 \cdot CHXCH_2 \cdot CH_3$, *i.e.*, 3-halopentane.

103. $CH_3CH_2C\equiv CH \xrightarrow{NaNH_2} CH_3CH_2C\equiv C^-Na^+ \xrightarrow{CH_3CH_2Br}$
$CH_3CH_2C\equiv CCH_2CH_3$ (X)

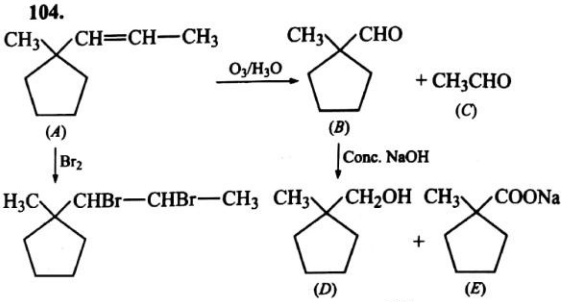
$CH_3CH_2C\equiv CCH_2CH_3$ (X) $\xrightarrow{H_2/Pd\text{-}BaSO_4}$
$\underset{\text{Cis-hexene (Y)}}{CH_3CH_2CH=CHCH_2CH_3}$

$CH_3CH_2CH=CHCH_2CH_3$ (Y) $\xrightarrow{\text{Alkaline } KMnO_4}$
$2CH_3CH_2COOK$
(Z) Pot. salt of propanoic acid

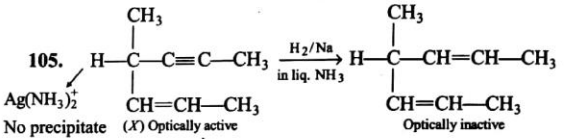
or $CH_3CH_2CH=CHCH_2CH_3$ (Y) $\xrightarrow{\text{if Baeyer's reagent}}$
$CH_3CH_2\underset{OH}{CH}\cdot\underset{OH}{CH}CH_2CH_3$ (Z)

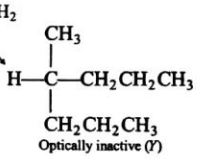
In both cases (Z) is optically inactive.

104.



105.





106. Mole of H_2 taken up = $\frac{8.40\times10^{-3}}{22.4} = 3.75\times10^{-4}$

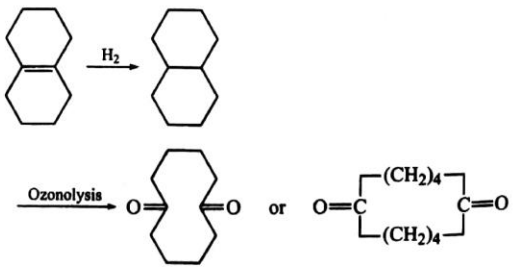
Mole of compound = $\frac{10.02\times10^{-3}}{80} = 1.253\times10^{-4}$

Thus, mole of H_2 taken up by

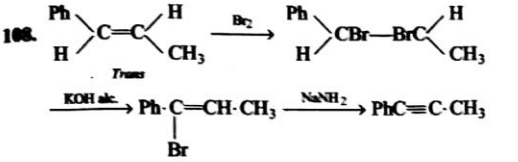
1 mole of compound = $\frac{3.75\times10^{-4}}{1.253\times10^{-4}} = 3$

Therefore, molecule has three double bond and it may be 1,3,5-hexatriene $CH_2=CH—CH=CH—CH=CH_2$.

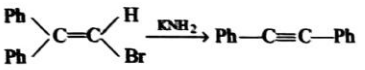
107.



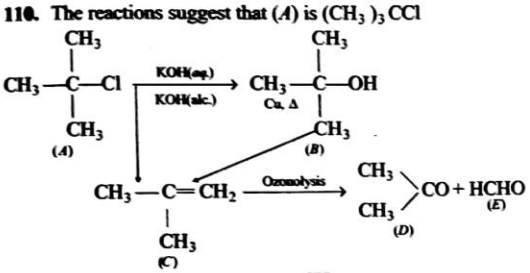
108.

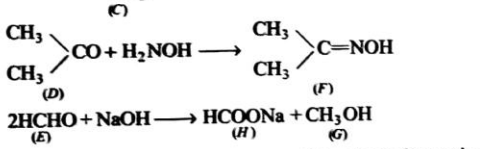


109.

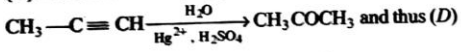


110. The reactions suggest that (*A*) is $(CH_3)_3CCl$





(i) (*D*) is obtained from propyne as

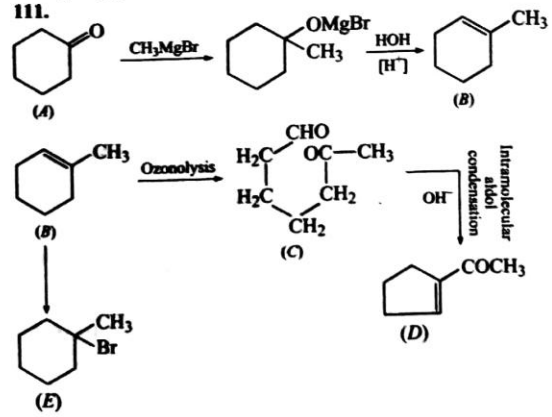


is acetone.

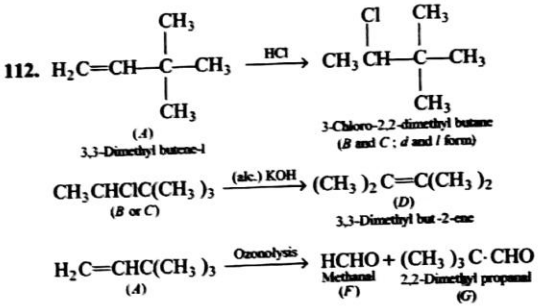
(ii) (*E*) undergoes Cannizzaro's reaction and thus HCHO [as (*D*) and (*E*) are formed from ozonolysis of (*C*)].

(iii) The alkene (*C*) formed by the action of KOH(alc.) on (*A*), on ozonolysis gives (*D*) and (*E*). Thus, (*C*) is $(CH_3)_2C{=}CH_2$ and (*A*) is $(CH_3)_3\cdot CCl$.

111.



112.



(*A*) 3,3-Dimethyl butene-1; 3-Chloro-2,2-dimethyl butane (*B* and *C*; *d* and *l* form)

(*D*) 3,3-Dimethyl but-2-ene

(*F*) and (*G*) both are aldehyde and give Fehling test but do not give iodoform test.

Ketone does not give Fehling test. Methyl ketones give iodoform test.

113. (i) Chlorination of propane gives :

$$CH_3\cdot CH_2CH_3 \xrightarrow{2Cl_2} CH_3\cdot CCl_2\cdot CH_3 \text{ 2,2-Dichloropropane}$$
$$+ CH_2Cl\cdot CH_2CH_2Cl \text{ 1,3-Dichloropropane}$$
$$+ CH_3CH_2\cdot CHCl_2 \text{ 1,1-Dichloropropane}$$
$$+ CH_3\cdot CHCl\cdot CH_2Cl \text{ 1,2-Dichloropropane}$$

(ii) Since, (*A*) on further chlorinaton gives one product and thus,

$$CH_3\cdot \underset{(A)}{CCl_2\cdot CH_3} \xrightarrow{Cl_2} CH_3\cdot CCl_2\cdot CH_2Cl$$

(iii) Since, (*B*) on further chlorination gives two products and thus,

$$CH_3Cl\cdot \underset{(B)}{CH_2\cdot CH_2Cl} \xrightarrow{Cl_2} CH_2Cl\cdot CHCl\cdot CH_2Cl$$
$$+ CH_2Cl\cdot CH_2\cdot CHCl_2$$

(iv)Since, (*C*) and (*D*) give three products on further chlorination and thus,

$$CH_3CH_2\underset{(C)}{CHCl_2} \xrightarrow{Cl_2} CH_3CHClCHCl_2 + CH_3CH_2\cdot CCl_3$$
$$+ CH_2Cl\cdot CH_2\cdot CHCl_2 \text{ or } \underset{(D)}{CH_3CHClCH_2Cl}$$

114. (i) Molar mass of (*A*) suggest it to be C_4H_6, *i.e.*, molar mass = 54

(ii) C_4H_6 has terminal triple bond as it reacts with CH_3CH_2Br in presence of $NaNH_2$.

(iii) $\underset{(A)}{CH_3\cdot CH_2\cdot C{\equiv}CH} \xrightarrow{Br_2} \underset{(B)}{CH_3\cdot CH_2\cdot CBr_2\cdot CHBr_2}$

Molar mass = 54 Molar mass = 374

Thus, molar mass of $(B) = \dfrac{593\times 54}{100} + 54 = 320 + 54 = 374$

(iv) $CH_3—CH_2·C\equiv CH \xrightarrow{H_2} \underset{\substack{(C)\\ \text{Mol. wt.} = 58}}{CH_3·CH_2·CH_2·CH_3}$

Thus, molar mass of $(C) = \frac{7.4}{100} \times 54 + 54 = 58$

(v) $\underset{(A)}{CH_3·CH_2·C\equiv CH} \xrightarrow[CH_3·CH_2Br]{NaNH_2} \underset{(D)}{CH_3·CH_2·C\equiv C·CH_2·CH_3}$

$(D) \xrightarrow{\text{Ozonolysis}} CH_3·CH_2—\underset{\underset{O}{\|}}{C}—\underset{\underset{O}{\|}}{C}—CH_2·CH_3 \xrightarrow{[O]}$

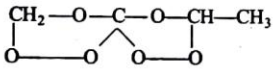
$\underset{(E)}{}$

$\rightarrow \underset{(F)}{CH_3·CH_2·COOH}$

115. (1) Since, 3 molecules are present and thus, rupture of C_4H_6 at two places occurs during ozonolysis so, C_4H_6 has two double bonds.

(2) Keeping in view of above facts, C_4H_6 is

$\underset{\substack{\text{Buta-1,2-diene}\\ [C_4H_6]}}{CH_2=C=CH·CH_3} \xrightarrow[\text{(II) HOH}]{\text{(I) } O_3}$



$\rightarrow \underset{\text{Methanal}}{HCHO} + CO_2 + \underset{\text{Ethanal}}{CH_3CHO}$

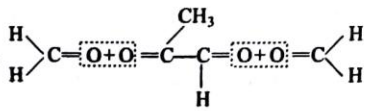
116. Compound (E) gives (F) on hydrogenation. Also, (E) on ozonolysis gives HCHO and 2-ketopropanal. Thus, (E) (C_5H_8) having two double bonds may be

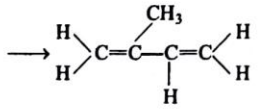
$CH_3—\underset{\underset{CH_2}{\|}}{C}—CH=CH_2$

$\xrightarrow{\text{Hydrogenation}} CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—CH_3$

$\xrightarrow{\text{Ozonolysis}} CH_3COCHO + 2HCHO$

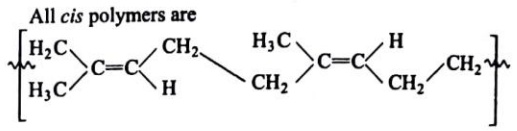
117.



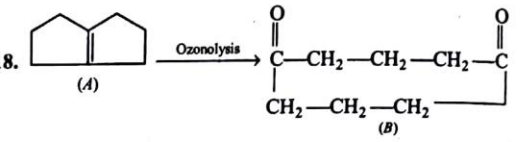


Thus, alkene is $CH_2=\underset{\underset{CH_3}{|}}{C}—CH=CH_2$ which on ozonolysis will give two moles of HCHO and one mole of CH_3COCHO.

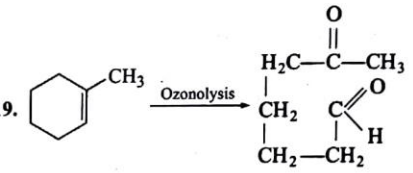
All *cis* polymers are

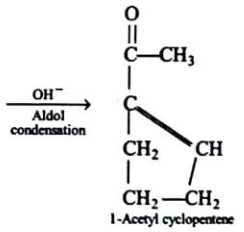


118.



119.

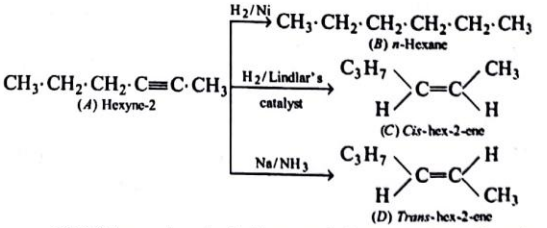




1-Acetyl cyclopentene

120. The given compound (A) is $CH_3·CH_2·CH_2·C\equiv C·CH_3$. This is confirmed by the following findings.

(i)



(ii) (A) is non-terminal alkyne as it does not give white salt with ammoniacal $AgNO_3$.

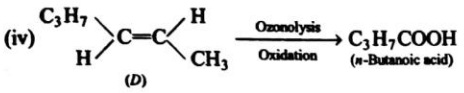
(iii) (A) forms (E) with $NaNH_2$ which reacts with CH_3I to give (F).

$\underset{\text{Hexyne-2}}{CH_3·CH_2·CH_2C\equiv C·CH_3} \xrightarrow[\Delta]{NaNH_2}$

$\underset{(E)}{CH_3·CH_2·CH_2·CH_2·C\equiv CNa}$

$\downarrow CH_3I$

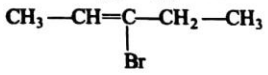
$\underset{(F)}{CH_3·CH_2·CH_2·CH_2·C\equiv C·CH_3}$

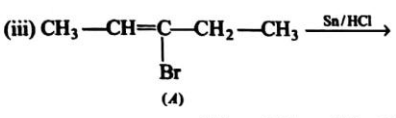
(iv) 

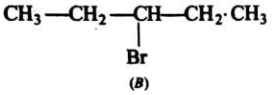
$+ CH_3COOH$

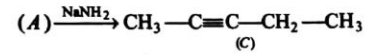
121. (i) (*A*) Decolorises bromine water and $KMnO_4$, thus it has unsaturation.

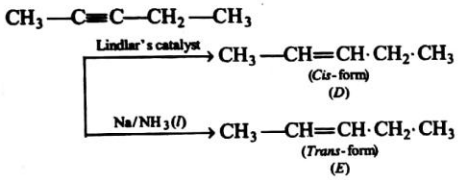
(ii) The reactions suggest (*A*) to be

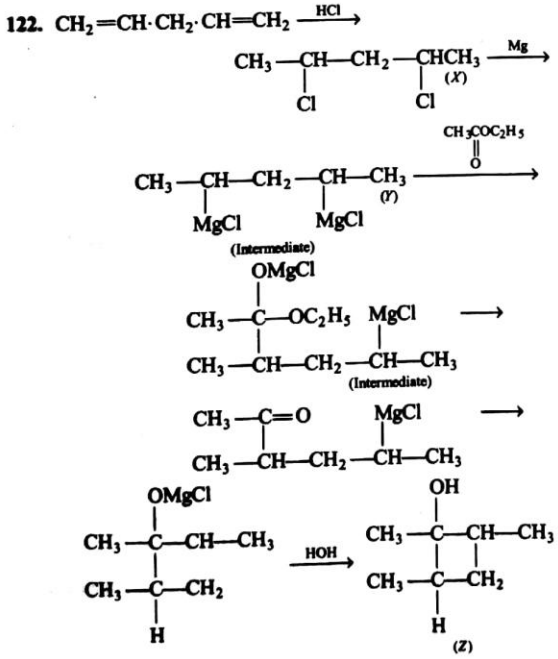


(iii) 







122. 

123. The given reactions suggest that:

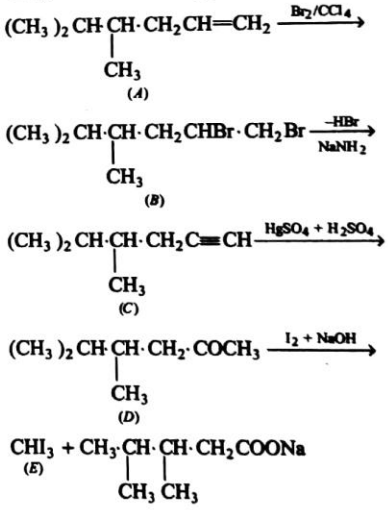
(i) (*B*) is

and (*A*) is

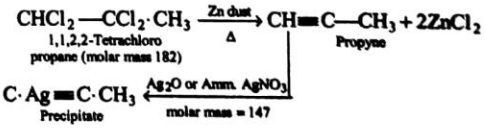
(ii) (*D*) and (*E*) are isomeric alcohols

(iii)

124. The given reactions suggest the following :



125. Given reactions are,



$\because$ 182 g compound (1,1,2,2-tetrachloropropane) gives = 147 g precipitate

$\therefore$ 36.4 g compound (1,1,2,2-tetrachloropropane) gives $= \frac{147 \times 36.4}{182}\text{ g} = 29.4\text{g}$

$\therefore$ Weight of precipitate = **29.4 g**

126. $CH_3 \cdot CH_2CH_2 - \underset{\underset{CH_3}{|}}{C} = \underset{\underset{CH_3}{|}}{C}CH_2 \cdot CH_2 \cdot CH_3 \xrightarrow{\text{Ozonolysis}}$

(4,5-Dimethyloct-4-ene)

$$2CH_3CH_2CH_2COCH_3 + H_2O_2$$

(Pentan-2-one)

127. $(CH_3)_2CH \cdot C \equiv CH \xrightarrow[H_2SO_4]{Hg^{2+}} (CH_3)_2CH \cdot CO \cdot CH_3$

(3-Methylbutyne) (3-Methylbutanone)

$$(CH_3)_2CH \cdot CO \cdot CH_3 \xrightarrow{NH_2OH} (CH_3)_2CH \cdot \underset{\underset{NOH}{\|}}{C}CH_3$$

(Oxime)

$$(CH_3)_2CH \cdot CO \cdot CH_3 \xrightarrow{[O]} (CH_3)_2 \cdot CH \cdot COOH + HCOOH$$

Note : However, the step showing oxidation of 3-methyl butanone will yield acetic acid and acetone and not dimethyl acetic acid according to Popf's rule. The step given in problem is not appropriate.

128. (1) The given reaction is **Wurtz reaction,** *i.e.*, reaction of alkyl halides with Na in presence of ether. When a mixture of halide reacts with Na in presence of ether, all possible alkanes are formed.

(a) $CH_3 \cdot CH_2 \cdot CH_2Br + 2Na + Br \cdot CH_2 \cdot CH_2 \cdot CH_3 \xrightarrow{\text{Ether}}$

1-Bromopropane

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$$

(Hexane)

(b) $CH_3 \cdot CH_2 \cdot CH_2Br + 2Na + BrCH(CH_3)_2 \xrightarrow{\text{Ether}}$

2-Bromopropane

$$CH_3 \cdot CH_2 \cdot CH_2 - CH(CH_3)_2$$

2-Methylpentane

(c) $(CH_3)_2CHBr + 2Na + BrCH(CH_3)_2 \xrightarrow{\text{Ether}}$

$$(CH_3)_2CH - CH(CH_3)_2$$

129. 1-butyne has more dipole moment because *sp*-hybridised carbon has more electronegativity in comparison to 1-butene (sp^2-hybridised carbon). It is evidenced by acidic nature of butyne-1.

$$\underset{sp}{CH_3}\underset{sp}{CH_2}C \equiv \underset{sp}{CH} \qquad \underset{sp^2}{CH_3}\underset{sp^2}{CH_2}CH = CH_2$$

130. (i) (*A*) gives characteristic colour with ceric ammonium nitrate and thus, it has OH group.

(ii) Reactions suggest that (*A*) is

$$CH_2(CH_2OH)_2 \xrightarrow{PCl_5} CH_2(CH_2Cl)_2 \xrightarrow{KCN}$$

(*A*) (*B*)

$$CH_2(CH_2CN)_2 \xrightarrow{Na/C_2H_5OH} CH_2(CH_2CH_2NH_2)_2 \xrightarrow{\Delta}$$

(*C*) (*D*)

$$CH_2(CH_2CH_2)_2NH \longrightarrow$$

(*E*)

Piperidine

Pyridine

131. (i) Since, alkene (*A*) on oxidation gives a carbonyl compound (*D*) and acid (*E*) of four carbon atoms each and thus

$$CH_3CH_2 \cdot C(CH_3) = CH \cdot CH_2 \cdot CH_3 \xrightarrow[KMnO_4]{[O]}$$

(*A*)

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_3 + CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$$

(*D*) Butanone (*E*) Butanoic acid

(ii) Alkene (*A*) and (*B*) give same alcohol on hydration and thus, (*B*) can only be (Also not two groups on same carbon atom).

$$CH_3CH_2 \cdot CH_2 \cdot CH_2 \cdot C(CH_3) = CH \cdot CH_3 \xrightarrow[KMnO_4]{[O]}$$

(*B*)

$$CH_3COCH_2 \cdot CH_2 \cdot CH_2CH_3 + CH_3COOH$$

(*G*) Hexanone-2 (*F*) Acetic acid

(iii) The hydration of (*A*) and (*B*) give same alcohol

$$CH_3CH_2 \cdot C(CH_3) = CH \cdot CH_2 \cdot CH_2 \cdot CH_3 \xrightarrow{H_2O}$$

(*A*)

$$CH_3CH_2 \cdot C(CH_3)(OH) \cdot CH_2 \cdot CH_2 \cdot CH_3$$

(*C*)

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C(CH_3) = CHCH_3 \xrightarrow{H_2O}$$

(*B*)

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C(CH_3)(OH) \cdot CH_2 \cdot CH_3$$

(*C*)

(3-Methylheptan-3-ol)

132. (1) (*A*) contains carbon and hydrogen, decolorises Br_2 in CCl_4 and so (*A*) is unsaturated hydrocarbon.

(2) (*A*) $\xrightarrow{HBr}$ (*B*) $\xrightarrow{NaOH}$ (*C*) $\xrightarrow{\text{Oxidation}}$ Hexanone-3

Bromide Alcohol

(3) Since, oxidation of (*C*) gives ketone and thus, (*C*) should be secondary alcohol.

(4) The position of OH in (*C*) should be at '3' because hexan-3-one is formed.

(5) (*C*) is obtained by hydrolysis of (*B*) and thus, (*B*) and *C* are

$$CH_3\cdot CH_2\underset{\underset{Br}{|}}{CH}\cdot CH_2\cdot CH_2\cdot CH_3 \xrightarrow{NaOH}$$

3-Bromohexane

$$CH_3\cdot CH_2\cdot \underset{\underset{OH}{|}}{CH}\cdot CH_2\cdot CH_2\cdot CH_3$$

Hexan-3-ol

(6) (*B*) is formed by the action of HBr on (*A*) and thus, (*A*) can be

$$CH_3\cdot CH{=}CH\cdot CH_2\cdot CH_2\cdot CH_3$$

(*A*) Hex-2-ene

or $CH_3\cdot CH_2\cdot CH{=}CH\cdot CH_2\cdot CH_3$

(*A*) Hex-3-ene

Reactions:

$$CH_3\cdot CH{=}CH\cdot CH_2\cdot CH_2\cdot CH_3 \xrightarrow{HBr} CH_3\cdot CH_2\cdot \underset{\underset{Br}{|}}{CH}\cdot CH_2\cdot CH_2\cdot CH_3$$

(*A*) (*B*)

$$CH_3\cdot CH_2\cdot CH{=}CH\cdot CH_2\cdot CH_3 \xrightarrow{HBr} CH_3\cdot CH_2\cdot \underset{\underset{Br}{|}}{CH}\cdot CH_2\cdot CH_2\cdot CH_3$$

(*A*) (*B*)

$$CH_3\cdot CH_2\underset{\underset{Br}{|}}{CH}\cdot CH_2\cdot CH_2\cdot CH_3 \xrightarrow{NaOH(aq.)}$$

3-Bromohexane (*B*)

$$CH_3\cdot CH_2\cdot \underset{\underset{OH}{|}}{CH}\cdot CH_2\cdot CH_2\cdot CH_3$$

Hexan-3-ol (*C*)

$$CH_3\cdot CH_2\cdot \underset{\underset{OH}{|}}{CH}\cdot CH_2\cdot CH_2\cdot CH_3 \xrightarrow{Oxidation}$$

Hexan-3-ol (*C*)

$$CH_3\cdot CH_2\cdot \underset{\underset{O}{\|}}{C}\cdot CH_2\cdot CH_2\cdot CH_3$$

Hexan-3-one

133. (1) (*A*) reacts with HBr to give mono bromo alkane (*B*), so (*A*) is alkene.

(2) (*A*) gives same product on addition of HBr in absence and presence of peroxide and thus, (*A*) is symmetrical alkene.

(3) Now 2 g Br_2 reacts with 0.7 g of (*A*)

$\therefore$ 160 g Br_2 reacts with $\frac{0.7\times 160}{2} = 56$ g of (*A*)

$\therefore$ Molar mass of alkene = 56 g mol^{-1}

or $C_nH_{2n} = 56$

$\therefore$ $n = 4$

(4) Thus, alkene is C_4H_8 having structure

$$CH_3\cdot CH{=}CH\cdot CH_3$$

But-2-ene (*A*)

Reactions:

$$CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[HBr]{\text{Presence or absence of peroxide}} CH_3\cdot CHBr\cdot CH_2\cdot CH_3$$

(*A*) 2-Bromobutane (*B*)

134. $$R{-}\underset{\underset{O}{\|}}{C}{-}O{-}\underset{\underset{O}{\|}}{C}{-}R' \xrightarrow[Na_2CO_3]{Hot\ (aq.)} R{-}\underset{\underset{O}{\|}}{C}{-}ONa +$$

(*A*) (*B*)

$$R'{-}\underset{\underset{O}{\|}}{C}{-}ONa \xrightarrow{H_2SO_4} \underbrace{RCOOH + R'COOH}_{\text{(Acids)}}$$

(*C*)

$$\xrightarrow{Distill.} R{-}\underset{\underset{O}{\|}}{C}{-}O{-}\underset{\underset{O}{\|}}{C}{-}R'$$

(*A*)

135. (i) (*A*) gives positive test with Br_2 in CCl_4 and thus, it is alkene.

(ii) Oxidation of (*A*) with alkaline $KMnO_4$ yields only one salt of an acid and thus, (*A*) is symmetrical alkene, *i.e.*, hex-3-ene.

$$CH_3\cdot CH_2\cdot CH{=}CH\cdot CH_2\cdot CH_3$$

(*A*)

Reactions:

(i) $$\underset{\text{Hex-3-ene}}{CH_3\cdot CH_2\cdot CH{=}CH\cdot CH_2\cdot CH_3} \xrightarrow[CCl_4]{Br_2\ in}$$

(*A*)

$$CH_3\cdot CH_2\cdot CHBr\cdot CHBr\cdot CH_2\cdot CH_3$$

3,4-Dibromohexane

(ii) $$CH_3CH_2\cdot CH{=}CH\cdot CH_2\cdot CH_3 \xrightarrow{alk.\ KMnO_4} CH_3CH_2COOK$$

(*A*) (*B*) Pot. propanoate

136. (1) Alkyne is terminal as it gives Ag salt. Let alkyne be $R{-}C{\equiv}CH$ and so formula of Ag salt is $R{-}C{\equiv}C\cdot Ag$

$\because$ 67.08 g Ag then mass of silver salt = 100

$\therefore$ 108 g Ag then mass of silver salt = $\frac{100\times 108}{67.08} = 161.00$

$\therefore$ Molar mass of silver salt = 161.00 g mol^{-1}

Note : If it would have acetylene then molar mass would have been determined by 216 g Ag.

$\therefore$ $R{-}C{\equiv}C\cdot Ag = 161$

$R + 12 + 12 + 108 = 161$

$\therefore$ $R = 29$

or $C_nH_{2n+1} = 29$

$\therefore$ $n = 2$

$\therefore$ Alkyne is $CH_3\cdot CH_2\cdot C{\equiv}CH$

But-1-yne

137. (1) (*A*) decolorises Br_2 in CCl_4 and absorbs H_2 and thus, (*A*) is unsaturated molecule having double or triple bond.

(2) (*A*) gives a precipitate with ammonical Cu_2Cl_2 and thus, it has terminal alkyne linkage, *i.e.*, triple bond at corner.

(3) Molar mass of $(A) = \frac{22400 \times 1.49}{448} = 74.5$

(4) Since, (A) has Cl and one $\equiv$ bond at terminal so (A) may be

$$R\text{Cl}\cdot\text{C}\equiv\text{CH}$$

$\therefore \quad R + 35.5 + 12 + 12 + 1 = 74.5$

$\therefore \quad R = 14$

$\therefore \quad R$ is CH_2

(5) Thus, (A) is $CH_2Cl\cdot C\equiv CH$, *i.e.*, 3-chloropropyne

Reactions:

$$\underset{(A)}{CH_2Cl\cdot C\equiv CH} \xrightarrow{Br_2/CCl_4} \underset{\substack{\text{1,2-Dibromo, 3-chloroprop-1-ene}\\ \text{(Red ppt.)}}}{CH_2\cdot Cl\,C(Br)=CHBr}$$

$$\underset{(A)}{CH_2Cl\cdot C\equiv CH} \xrightarrow{H_2} \underset{\text{1-Chloropropane}}{CH_2Cl\cdot CH_2-CH_3}$$

$$\underset{(A)}{2CH_2Cl\cdot C\equiv CH} \xrightarrow[\text{or Am. } Cu_2Cl_2]{Cu_2O} \underset{\text{Red ppt.}}{2CH_2Cl\cdot C\equiv C\cdot Cu} + H_2O$$

138. (1) (D) gives 2,2-dimethylpropanal and 1-butanal on ozonolysis and thus,

$$\underset{(D)}{(CH_3)_3C-CH=CHCH_2CH_2CH_3} \xrightarrow{\text{Ozonolysis}}$$

$$\underset{\text{(2,2-Dimethylhept-3-ene)}}{} (CH_3)_3C\cdot CHO + CH_3CH_2CH_2CHO$$

(2) (D) is formed by partial hydrogenation (in presence of Lindlar's catalyst) of (C) and thus, (C) is

$$\underset{\text{(2,2-Dimethylhept-3-yne) (C)}}{(CH_3)_3C\equiv CCH_2CH_2CH_3} \xrightarrow[\text{catalyst}]{H_2}$$

$$\underset{(D)}{(CH_3)_3C-CH=CHCH_2CH_2CH_3}$$

(3) (A) reacts with $NaNH_2/NH_3$ to give (B) which indicates a terminal triple bond in (A)

$$\underset{(A)}{C_6H_{10}} \xrightarrow[NH_3]{NaNH_2} \underset{(B)}{C_4H_9C\equiv C\cdot Na}$$

(4) (B) reacts with 1-chloropropane to give (C)

$$\underset{(B)}{C_4H_9C\equiv C\cdot Na} + Cl\cdot CH_2\cdot CH_2\cdot CH_3 \longrightarrow$$

$$\underset{(C)}{C_4H_9C\equiv C\cdot CH_2\cdot CH_2\cdot CH_3}$$

But (C) is $(CH_3)_3C-C\equiv C\cdot CH_2\cdot CH_2\cdot CH_3$

A comparison of two structures of (C) suggests that (B) and (A) are

$(CH_3)_3C-C\equiv CNa$, $\underset{\substack{\text{(3,3-Dimethylbut-1-yne)}\\ (A)}}{(CH_3)_3C-C\equiv CH}$

139. (1) (A), C_6H_{10} either has one triple bond or two double bonds.

(2) Ozonolysis of (A) suggests that it has two double bonds.

$$\underset{(A)}{C_6H_{10}} \xrightarrow{\text{Ozonolysis}} \underset{(D)}{C_2H_4O} + \underset{(E)}{C_2H_2O_2}$$

Since, (D) and (E) are aldehydes, *i.e.*, $\underset{\text{Ethanal } (D)}{CH_3CHO}$ and $\underset{\text{Ethane-1,2-dial } (E)}{CHO\cdot CHO}$

$\therefore$ (A) is $\underset{\text{Hexa-2,4-diene}}{CH_3CH=CH-CH=CH\cdot CH_3}$

(3) (A) gives (B) on reduction and finally gives (C).

$$\underset{(A)}{CH_3\cdot CH=CH-CH=CH-CH_3} \xrightarrow{H_2}$$

$$\underset{(B)\text{ Hex-2-ene}}{CH_3\cdot CH_2\cdot CH_2CH=CH\cdot CH_3} \xrightarrow{H_2}$$

$$\underset{\text{Hexane}}{CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3}$$

$$CH_3\cdot CH_2\cdot CH_2\cdot CH=CH\cdot CH_3 \xrightarrow{[O]}$$

$$\underset{(F)}{CH_3\cdot CH_2\cdot CH_2\cdot COOH} + CH_3COOH$$

Note : The above problem may also be given as : If acid (F) should have been given $C_3H_6O_2$. Then it would have been solved as :

$$\underset{(A)}{CH_3\cdot CH=CH-CH=CH-CH_3} \xrightarrow{H_2}$$

$$\underset{(B)}{CH_3\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH_3} \xrightarrow{\text{Oxidation}} \underset{\substack{\text{Propanoic acid}\\ (F)}}{CH_3CH_2COOH}$$

Note : Conjugated alkadienes, *i.e.*, alkenes with alternate single and double bonds, show I addition at 1,4 position giving rise to double bond at 2,3 positions.

$$CH_2=CH-CH=CH_2 \xrightarrow{X_2} \underset{X}{CH_2\cdot CH=CH-CH_2} \underset{X}{}$$

140. Let isobutane be a g and isobutene be b g. Thus, $a + b = 10$

$$\underset{\text{(Isobutene)}}{CH_3(CH_3)C=CH_2} \xrightarrow{Br_2} \underset{\text{Br}}{CH_3(CH_3)C-CH_2Br}$$

$$\underset{\text{(Isobutane)}}{CH_3(CH_3)CH\cdot CH_3} \xrightarrow{Br_2} \text{No reaction of addition}$$

Now, $\because$ 160 g Br_2 is needed for 56 g isobutene

$\therefore$ 20 g Br_2 is needed for $\frac{56 \times 20}{160} = 7$ g

Thus, isobutene, *i.e.*, $b = 7$ g

isobutane, *i.e.*, $a = 3$ g

Now, 7 g isobutene is converted to isobutane by reduction to give $\frac{58 \times 7}{56}$ g isobutane = 7.25 g.

Now isobutane reacts with Br_2 to give monobromo product in light.

$$C_4H_{10} + Br_2 \longrightarrow C_4H_9Br + HBr$$

$\because$ 58 g C_4H_{10} gives product = 137 g C_4H_9Br

$\therefore$ (7.25 + 3) g C_4H_{10} gives product

$$= \frac{137 \times 10.25}{58} \text{ g } C_4H_9Br$$

$$= \mathbf{24.21\ g\ C_4H_9Br}$$

141. (a) $\underset{\text{Bombykol}}{C_{16}H_{30}O} \xrightarrow{\text{Hydrogenation}} \underset{(A)}{C_{16}H_{34}O}$

Thus, Bombykol has two double bonds or one triple bond.

(b) (i) Bombykol reacts with acetic anhydride to give an ester, thus, it has —OH group.

$$C_{16}H_{29}OH + (CH_3CO)_2O \longrightarrow \underset{\text{Ester}}{C_{16}H_{29}OOC \cdot CH_3} + CH_3COOH$$

(ii) The ester on ozonolysis gives

$$CH_3CH_2CH_2COOH + \begin{matrix}COOH\\|\\COOH\end{matrix} + CH_3COO(CH_2)_9 \cdot COOH$$

Therefore, ester is

$CH_3CH_2CH_2 \cdot CH{=}CH{-}CH{=}CH(CH_2)_9 \cdot OOC \cdot CH_3$

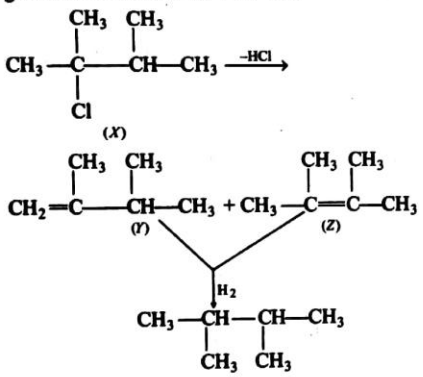
Thus, Bombykol is

$CH_3CH_2CH_2CH{=}CH{-}CH{=}CH(CH_2)_8CH_2OH$

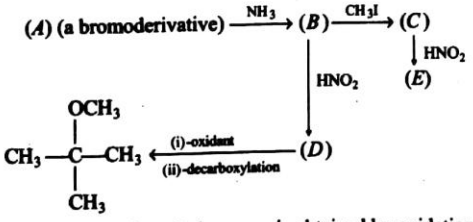
and (A) is $CH_3(CH_2)_{14}CH_2OH$

Bombykol has two double bonds (*i.e.*, $n = 2$) and thus, it has geometrical isomers $= 2^n = 2^2 = 4$.

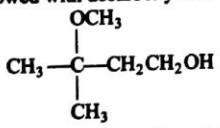
142.



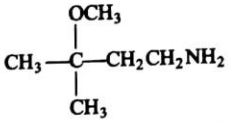
143.



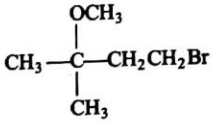
(i) 2-methoxy-2-methylpropane is obtained by oxidation of (D) followed with decarboxylation and thus, (D) is



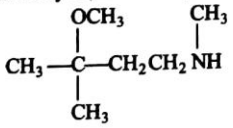
(ii) (D) is formed by the action of HNO_2 on (B) and thus, (B) is

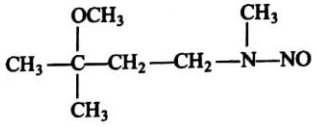


(iii) (B) is formed by the action of NH_3 over (A) a bromoderivative

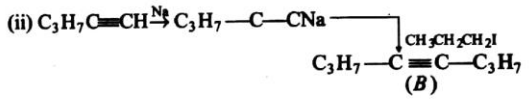
$\therefore$ (A) is 

(iv) (C) is obtained by action of CH_3I over (B)

$\therefore$ (C) is 

$\therefore$ (E) is 

144. (i) (A) reacts with sodium in ammonia and thus, it is terminal alkyne, *i.e.*, $C_3H_7C \equiv CH$

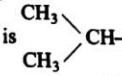
(ii) 

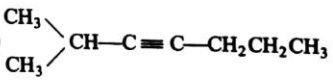
(iii) $C_3H_7{-}C{\equiv}CH \xrightarrow[H_2SO_4]{HgSO_4} \underset{(C)}{C_3H_7{-}CO{-}CH_3}$

(iv) $C_3H_7{-}C{\equiv}C{-}CH_2{-}CH_2{-}CH_3 \xrightarrow[KMnO_4]{[O]}$

$$\underset{(D)}{CH_3CH_2CH_2COOH} + \underset{(E)}{C_3H_7COOH}$$

Since, (D) and (E) are isomers and thus, (E) is $(CH_3)_2CH \cdot COOH$

$\therefore$ (A) is 

(B) 

145. (A) is ozone as it reacts with but-2-ene to show ozonolysis

$$CH_3{-}CH{=}CH{-}CH_3 + \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} 2CH_3CHO$$

The deep red coloured compound is potassium ozonide, KO_3 and gas is O_2

$$\underset{(A)}{5O_3} + 2KOH \longrightarrow \underset{(B)}{2KO_3} + H_2O(v) + \underset{(C)}{5O_2}$$

146. The alcohol is readily oxidised by dil. $KMnO_4$ and thus, primary alcohol, *i.e.*, *n*-butanol. Tertiary alcohols are not oxidized by dil. $KMnO_4$.

$$CH_3CH_2CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2CH_2CHO$$
$$\downarrow [O]$$
$$CH_3CH_2CH_2COOK + \underset{\text{(Brown ppt.)}}{MnO_2} + KOH$$

147. $ROH + CH_3MgI \longrightarrow CH_4 + Mg\begin{matrix}OR\\ I\end{matrix}$

$\because$ 11.2 mL gas CH_4 is obtained by 0.037 g *R*OH

$\therefore$ 22400 mL gas is obtained by $\frac{0.037 \times 22400}{11.2} = 74$ g

$\therefore$ Molar mass of *R*OH = 74 g mol^{-1}

Since, *R*OH on oxidation gives acid of same number of carbon atoms and thus, *R*OH is primary alcohol, *i.e.*, $C_nH_{2n+1}CH_2OH$.

$\therefore$ $12n + 2n + 1 + 12 + 2 + 16 + 1 = 74$

$\therefore$ $n = 3$

$\therefore$ Alcohol is $C_3H_7CH_2OH$. The reactions suggest the structure as

$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!CHCH_2OH \xrightarrow[\Delta]{H_2SO_4} \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!C=CH_2 \xrightarrow{\text{Ozonolysis}}$$
$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!CO + HCHO$$
$$\xrightarrow{[O]} \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!CHCOOH$$

148. The given reactions suggest the following

(i) $(A) \xrightarrow{\text{Ozonolysis}} \underset{(B)}{R'CHO} + \underset{(C)}{R'CHO}$

(*B*) cannot be HCHO however it gives Cannizzaro's reaction because then (*A*) must have $R'C{=}CH_2$ structure which will not give geometrical isomer.

(ii) $\underset{(X)}{C_7H_{12}} \xrightarrow[CH_3COOH]{B_2H_6} \underset{(A)}{C_7H_{14}}$

The reaction of alkyne to give alkene takes place through vinylic boranes as intermediate and *cis* alkene predominates.

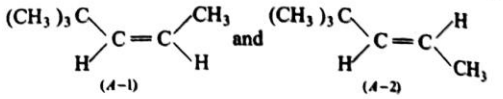
(iii) Thus, (*A*) is

$$\underset{(A)}{(CH_3)_3CCH{=}CHCH_3} \xrightarrow{\text{Ozonolysis}} \underset{(B)}{(CH_3)_3C{\cdot}CHO} + \underset{(C)}{CH_3CHO}$$

(*B*) does not have α-H atom and will show Cannizzaro's reaction.

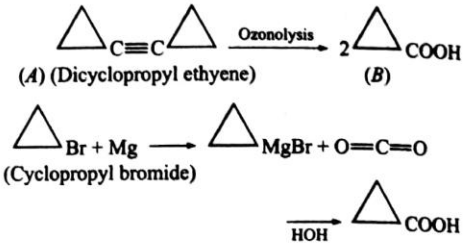
(iv) (*X*) is therefore $(CH_3)_3C{\cdot}C{\equiv}C{\cdot}CH_3$

(v) Two geometrical isomers of (*A*) are



(*A*-1) (*A*-2)

149.



150. (i) (*A*) reacts with H_2 to give (*B*) and (*C*) successively and thus, it has either two double bonds or one triple bond.

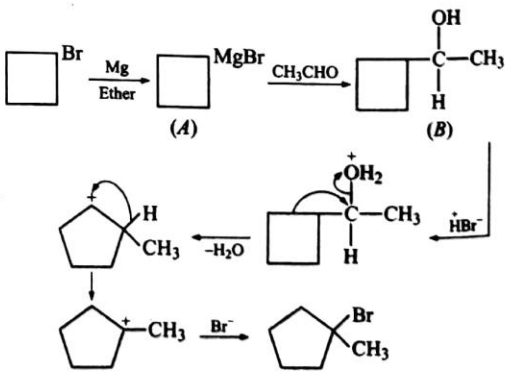
(ii) Ozonolysis of (*A*) gives (*D*), an aldehyde C_2H_4O, *i.e.*, CH_3CHO and (*E*) $C_2H_2O_2$, *i.e.*, $\begin{matrix}CHO\\ |\\ CHO\end{matrix}$ and thus,

$$\underset{(A)}{CH_3{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CH_3} \xrightarrow{\text{Ozonolysis}} 2CH_3CHO + \begin{matrix}CHO\\ |\\ CHO\end{matrix}$$
$$\downarrow H_2\,(I)$$
$$\underset{(B)}{CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_3} \xrightarrow[(II)]{H_2} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

(iii) $\underset{(B)}{CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_3} \xrightarrow[\text{Hexane}]{\text{Ozonolysis}} \underset{\text{(Hexene-3)}}{} \underset{\text{Propanal}}{2CH_3{\cdot}CH_2{\cdot}CHO}$

Note : Addition of H_2 in I case is a characteristic reaction of conjugated (alternate single and double bond) alkadienes where it occurs at 1,4-position and double bond is shifted to 2,3 position.

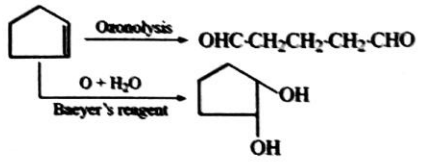
151.



152. Unsaturated ether (divinyl ether) will decolourise Br_2 water or Baeyer's reagent.

153. V < IV < III < II < I; The reactivity for E_2 dehydrohalogenation depends chiefly on the stability of the alkenes being formed.

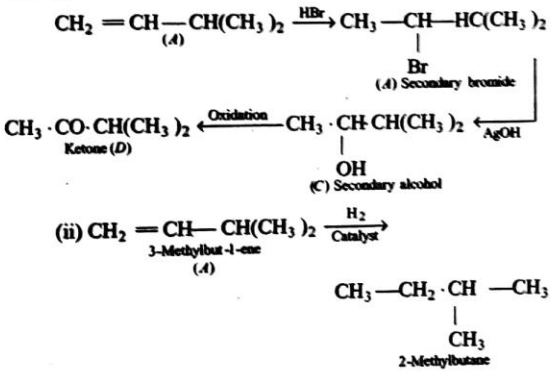
154. (a)



(b) NaI reacts with *R*Cl to form *R*I. The alkyl iodides having larger C—I bond length are more reactive than *R*Cl and thus readily hydrolysis.

$$RCl + NaI \longrightarrow RI + NaCl$$
$$RI + HOH \longrightarrow ROH + HI$$

155. (i)



(ii) $CH_2 = \underset{\text{3-Methylbut-1-ene}}{\underset{(A)}{CH—CH(CH_3)_2}} \xrightarrow[\text{Catalyst}]{H_2}$

156. (1) Molar mass of bromo-derivative

$$(A) = \frac{0.369 \times 22400}{67.2} = 123$$

(2) Let bromo-derivative be *R*Br

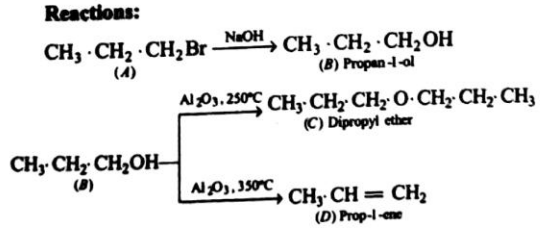
Then, molar mass of $R = 123 - 80 = 43$

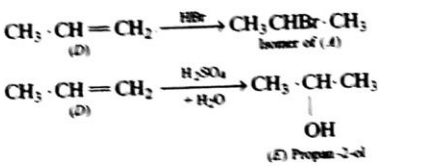
$\therefore \quad C_nH_{2n+1} = 43$

$\therefore \quad n = 3,$

Thus, bromo-derivative is C_3H_7Br

Reactions:

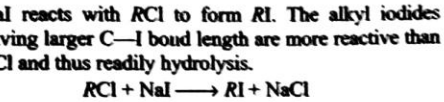




157. (1) (*x*), C_5H_8O does not react with Lucas reagent appreciably at room temperature but gives precipitate with ammoniacal $AgNO_3$ and thus, (*x*) has terminal alkyne linkage as well as primary alcoholic gp.

(2) (*x*) on hydrogenation and then reacting with HI gives pentane and thus, (*x*) is straight chain compound.

(3) Keeping in view of the above facts (*x*) may be



(4) Its reaction with MeMgBr gives CH_4, (It has two acidic or active H*-atoms) and thus, 1 mole of (*x*) will give two mole of CH_4.

$\because$ 84 g (*x*) gives 2×22.4 litre CH_4

$\therefore$ 0.42 g (*x*) will give $\frac{2 \times 22.4 \times 0.42}{84} = \mathbf{224\ mL\ CH_4}$

Given fact is confirmed.

158. $C_2H_5OH + CH_3CHO = 0.535\,g$

Let *a* g C_2H_5OH and *b* g CH_3CHO be present in mixture

$\therefore \quad a + b = 0.535$

Now mixture reacts with Fehling solution to give a red precipitate, which suggests a characteristic reaction for aldehyde, *i.e.*,

$$CH_3CHO + \underset{\text{Fehling solution}}{2CuO} \longrightarrow CH_3COOH + \underset{\text{Red ppt.}}{Cu_2O}$$

$\because$ 143.6 g Cu_2O is given by 44 g CH_3CHO

$\therefore$ 1.2 g Cu_2O is given by $\frac{44 \times 1.2}{143.6} = 0.368\,g\ CH_3CHO$

$\therefore \quad b = 0.368\,g$

$\therefore$ % of $CH_3CHO = \frac{0.368}{0.535} \times 100 = \mathbf{68.78\%}$

159. The given statements suggest the following :

(i) (*B*) is acetic acid since it reacts with $Ca(OH)_2$ which on dry distillation gives (*E*) C_3H_6O, *i.e.*, acetone.

$$CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca$$
$$(CH_3COO)_2Ca \xrightarrow[\text{distillation}]{\text{dry}} \underset{(E)}{CH_3COCH_3} + CaCO_3$$

(ii) (*A*) reacts with ethanol to give (*B*), *i.e.*, CH_3COOH and (*C*), thus, (*A*) is $CH_3COOOCCH_3$

$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O + C_2H_5OH \longrightarrow \underset{(B)}{CH_3COOH} + \underset{(C)}{CH_3COOC_2H_5}$$

(iii) (*C*) on acid hydrolysis gives (*B*), *i.e.*, CH_3COOH and (*D*); oxidation of (*D*) gives (*B*). Thus,

$$CH_3COOC_2H_5 + HOH \longrightarrow \underset{(B)}{CH_3COOH} + \underset{(D)}{C_2H_5OH}$$

$$\underset{(D)}{C_2H_5OH} \xrightarrow{[O]} \underset{(B)}{CH_3COOH}$$

160. (1) (*A*) gives Lucas test within 5 minutes and thus, (*A*) is secondary alcohol.

(2) (*A*) contains one O-atom and thus, only one OH gp. in (*A*). Thus, (*A*) is $C_nH_{2n+1}OH$.

(3) ∵ 1120 mL H_2 is given by the action of Na over 6 g (*A*).

∴ 11200 " " $\dfrac{6\times 11200}{1120} = 60$ g (*A*)

∴ Molar mass of (*A*) = 60 g mol^{-1}

Since, one mole of an alcohol having one OH gp. gives 11200 mL H_2 at STP with Na.

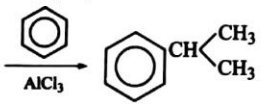
(4) Thus, $C_nH_{2n+1}OH = 60$

∴ $n = 3$

or (*A*) is C_3H_7OH; being secondary alcohol its formula is $CH_3\cdot CHOH\cdot CH_3$

Reactions:

$$\underset{\text{(Propan-2-ol)}}{\underset{(A)}{CH_3\cdot CHOH\cdot CH_3}} \xrightarrow{PBr_3} \underset{\text{(2-Bromopropane)}}{\underset{(B)}{CH_3CHBr\cdot CH_3}}$$



(*C*) 2-Phenylpropane

This is Friedel-Crafts reaction.

161. (1) Molar mass of $A = \dfrac{1000\times K'\times w}{\Delta T\times W}$

$$= \frac{1000\times 40\times 0.0088}{8\times 0.5} = 88 \text{ g mol}^{-1}$$

(2) For empirical formula

Element	%	Relative no. of atoms	Simplest ratio
C	68.18	5.68	$4.8\approx 5$
H	13.16	13.16	$11.2\approx 11$
O	18.66	1.17	1 1

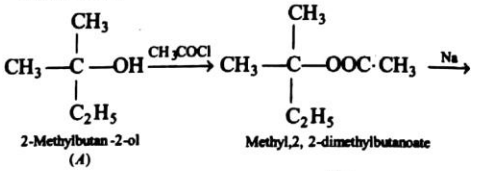
∴ Empirical formula of (*A*) = $C_5H_{11}O$; Empirical formula mass = 87 but molar mass = 88 and therefore, molecular formula = $C_5H_{12}O$.

(3) (*A*) reacts with acetyl chloride and gives H_2 with Na so, (*A*) is alcohol.

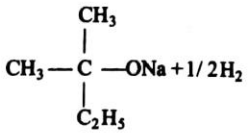
(4) (*A*) reacts with Lucas reagent (HCl + $ZnCl_2$), a dense oily layer separated immediately hence, (*A*) is a tertiary alcohol.

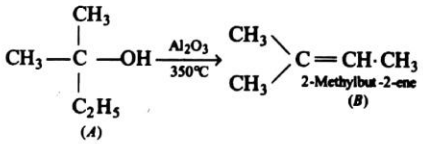
(5) Thus, (*A*) is $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle C_2H_5}{\overset{|}{\underset{|}{C}}}}-OH$, the only tertiary alcohol of 5 carbon atoms.

Reactions :

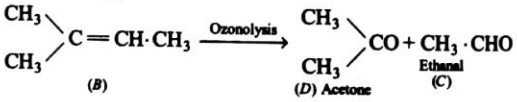


2-Methylbutan-2-ol (*A*) — Methyl,2, dimethylbutanoate





2-Methylbut-2-ene (*B*)



(*B*) — (*D*) Acetone — Ethanal (*C*)

Both (*C*) and (*D*) give test with carbonyl reagents such as HCN, $NaHSO_3$ forming addition products but only (*C*) gives test with Fehling solution. Thus, (*C*) is aldehyde and (*D*) is ketone, each having CH_3CO- unit.

162. (i) (*X*) forms semicarbazone and thus possesses carbonyl gp.

$$\rangle C=O + H_2N\cdot NHCONH_2 \longrightarrow \rangle C=N\cdot NHCONH_2$$

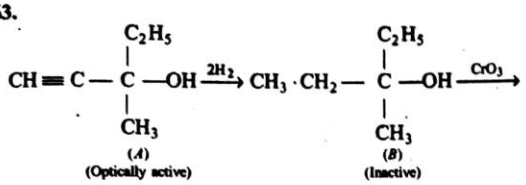
(ii) It does not give Tollen's reagent test and thus it is ketone.

(iii) It does not give iodoform test and thus it is not methyl ketone.

(iv) Keeping in view of the above facts and molecular formula; (*X*) is $C_6H_5-\underset{\displaystyle O}{\overset{\displaystyle \|}{C}}\cdot CH_2\cdot CH_3$

(v) This on reduction will give *n*-propyl benzene.

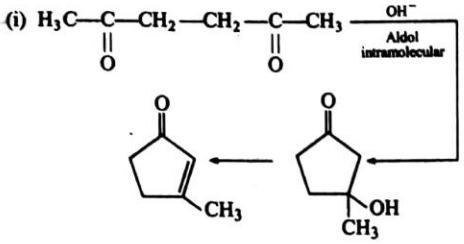
163.



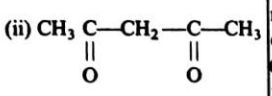
(*A*) (Optically active) (*B*) (Inactive)

Resistant to oxidation as it is tertiary alcohol.

164. (i)

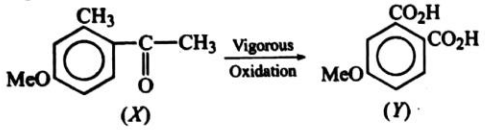


(ii)



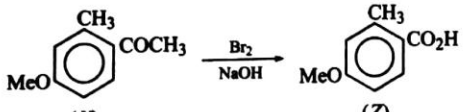
It would merely form the stable carbonion and react no further. The C^1 carbanion does not add to C^4 because a strained four-membered ring would result.

165. The statements provides the following informations regarding (*X*), (*Y*) and (*Z*).

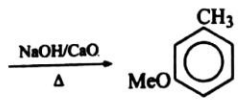


(*X*) (*Y*)

$\xrightarrow{\Delta}$ Can form anhydride

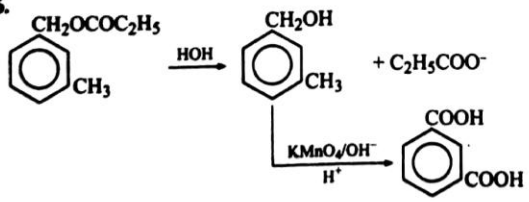


(*X*) (*Z*)



3-Methyl anisole

166.



167. $C_6H_5CHOH\cdot CH_3 \xrightarrow[\text{Iodoform reaction}]{\text{(i) } I_2 + NaOH,\ \text{(ii) HOH}} \underset{(D)\ \text{White}}{C_6H_5COOH} + \underset{(E)\ \text{Yellow}}{CHI_3}$

168. The reactions given are :

$$\underset{(A)}{C_5H_{11}OH} \xrightarrow[250^\circ C]{Al_2O_3} \underset{(B)}{C_5H_{10}} \xrightarrow[\text{(ii) AgOH}]{\text{(i) HI}} \underset{(C)\ \text{(an isomer of } A)}{C_5H_{11}OH}$$

$$\underset{(A)}{C_5H_{11}OH} \xrightarrow[150^\circ C]{Al_2O_3} \underset{(B)}{C_5H_{10}} \xrightarrow[H_2O_2,\,OH^-]{B_2H_6} (A)$$

This is possible only when (*A*) is $(CH_3)_2CHCHOHCH_3$.

$$\underset{(A)}{(CH_3)_2CHCHOHCH_3} \xrightarrow[250^\circ C]{Al_2O_3} \underset{(B)}{(CH_3)_2CH=CHCH_3}$$

$$(B) \xrightarrow{HI} (CH_3)_2\underset{I}{C}H-CH_2CH_3 \xrightarrow{AgOH} \underset{(C)}{(CH_3)_2\overset{OH}{C}HCH_2CH_3}$$

$$(C) \xrightarrow[150^\circ C]{Al_2O_3} (CH_3)_2CH=CHCH_3 \xrightarrow[B_2H_6,\,H_2O_2]{OH^-} \underset{(A)}{(CH_3)_2CHCHOHCH_3}$$

Also,

$$(CH_3)_2C=O + CH_3CH_2MgBr \longrightarrow (CH_3)_2C\begin{matrix}\diagup OMgBr \\ \diagdown CH_2CH_3\end{matrix}$$

$$\xrightarrow{HOH} (CH_3)_2C\begin{matrix}\diagup OH \\ \diagdown CH_2CH_3\end{matrix} \xrightarrow[-H_2O]{150^\circ C} \underset{(B)}{(CH_3)_2C=CHCH_3}$$

169. (i) (*A*) undergoes acetylation and thus, contains OH gps.

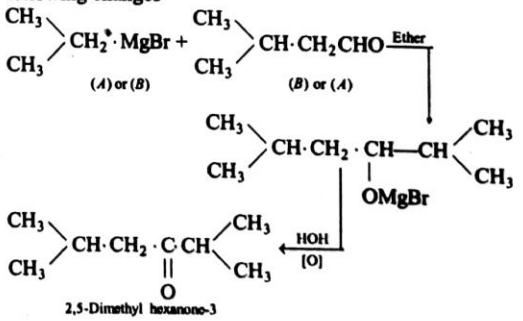
$$-OH \xrightarrow{CH_3COCl} -OOCCH_3 + HCl$$

(ii) Presence of one OH gp. enhances C_2H_2O structure in molecule. Since, (*B*) shows an increase in $4(C_2H_2O)$ units and thus, (*A*) has four OH gps.

(iii) Thus, (*A*) is $\underset{OH}{CH_2}\cdot\underset{OH}{CH}\cdot\underset{OH}{CH}\cdot\underset{OH}{CH_2}$ Butan-1,2,3,4-tetra-ol

$$(B)\ \underset{OOC\cdot CH_3}{CH_2}-\underset{OOC\cdot CH_3}{CH}-\underset{OOC\cdot CH_3}{CH}-\underset{OOC\cdot CH_3}{CH_2}$$

170. The given statement about (*A*) and (*B*) suggests the following changes



2,5-Dimethyl hexanone-3

171. (i) (*B*) reacts with hydroxyl amine and thus, (*B*) has carbonyl gp. *i.e.*, $>C=O$ gp. either ketonic ($>C=O$) or aldehyde ($-\overset{|}{\underset{H}{C}}=O$) gp.

(ii) (*B*) gives negative test with Tollen's reagent and thus, (*B*) is ketone.

(iii) (*B*) is obtained by hydrolysis of (*A*) and thus, both Cl-atoms should be on same carbon atom, *i.e.*, (*A*) must be gem dihalide as well as not on corners. Thus, only possibility of (*A*) is $CH_3 \cdot CCl_2 \cdot CH_2 \cdot CH_3$.

Reactions :

(i) $\underset{\text{2,2-Dichlorobutane}(A)}{CH_3 \cdot C \cdot Cl_2 \cdot CH_2 \cdot CH_3} \xrightarrow{HOH} CH_3 \cdot \underset{\underset{\underset{(B)\text{ Butan-2-one}}{O}}{\|}}{C} \cdot CH_2 \cdot CH_3$

(ii) $\underset{(B)}{CH_3 \cdot CH_2 \cdot \overset{CH_3}{\overset{\diagdown}{\underset{\diagup}{}}}C=O} + \underset{\text{Hydroxylamine}}{H_2NOH} \longrightarrow CH_3 \cdot CH_2 \cdot \overset{CH_3}{\overset{\diagdown}{\underset{\diagup}{}}}C=NOH$ (Oxime)

(iii) $CH_3CH_2 \cdot \overset{CH_3}{\overset{\diagdown}{\underset{\diagup}{}}}C=O \xrightarrow{\text{Tollen's reagent}}$ No reaction

172. For empirical formula

C = 40.7/12	= 3.39	1
H = 5.1/1	= 5.1	1.5
O = 54.4/16	= 3.4	1.0

$\therefore$ Empirical formula of acid is $C_2H_3O_2$

$$\frac{\text{mass of Ag}}{\text{E. mass of Ag}} = \frac{\text{mass of acid salt}}{\text{E. mass of acid salt}}$$

$\therefore$ E. mass of acid salt = $(100 \times 108)/65.1 = 165.89$

$\therefore$ E. mass of acid $165.89 - 108 + 1 = 58.89$

$\because$ Molar mass of ethyl ester is 174 and thus, acid is dibasic because molar mass of C_2H_5 gp. is only 29.

Thus, Molar mass of acid = $58.89 \times 2 = 177.78$

$\therefore$ Molecular formula of acid = $(C_2H_3O_2)_2 = C_4H_6O_4$

Thus, acid (*A*) is $CH_3 \cdot CH\overset{COOH}{\underset{COOH}{\diagup\diagdown}}$; the isomer of (*A*) may be $\begin{matrix}CH_2COOH \\ | \\ CH_2COOH\end{matrix}$ or *vice-versa*

The two may be distinguished by heating

$(A)\ CH_3CH\overset{COOH}{\underset{COOH}{\diagup\diagdown}} \xrightarrow{\Delta} \underset{\text{(Propanoic acid)}}{CH_3 \cdot CH_2 \cdot COOH} + CO_2$ (Methyl malonic acid)

$(B)\ \begin{matrix}CH_2COOH \\ | \\ CH_2COOH\end{matrix} \xrightarrow{\Delta} \begin{matrix}CH_2CO \\ | \\ CH_2CO\end{matrix}\!\!>O + H_2O$ (Succinic acid) (Succinic anhydride)

173. (i) $C_4H_8O_2$ reacts with $NaHCO_3$ to liberate CO_2 and so it contains —COOH group, *i.e.*, (*A*) is C_3H_7COOH.

(ii) $\underset{(A)}{C_3H_7COOH} \xrightarrow{NaOH + CaO} \underset{\text{Propane}}{C_3H_8} + Na_2CO_3$

Thus, (*A*) may be

$\underset{\text{(I) Butanoic acid}}{CH_3 \cdot CH_2 \cdot CH_2COOH}$ or $\underset{\underset{\text{2-Methylpropanoic acid}}{CH_3\ \text{(II)}}}{CH_3 \cdot \underset{|}{CH} \cdot COOH}$

Since, both gives propane on decarboxylation.

(iii) However, $C_8H_{14}O_4Ca$, *i.e.*, Ca salt of acid on heating gives

$\underset{\text{Di-isopropyl ketone}}{CH_3 \cdot \overset{CH_3}{\overset{\diagdown}{\underset{\diagup}{}}}CH \cdot CO \cdot CH\overset{CH_3}{\underset{CH_3}{\diagup\diagdown}}}$

Di-isopropyl ketone and thus, chain in acid is also not straight. Thus, structure (II) is correct, *i.e.*, (*A*) is

$\underset{(A)}{CH_3 \cdot \overset{CH_3}{\overset{\diagdown}{\underset{\diagup}{}}}CHCOOH}$ (2-Methylpropanoic acid)

$$2\left(\underset{(A)}{CH_3 \cdot \overset{CH_3}{\overset{\diagdown}{\underset{\diagup}{}}}CHCOO}\right)_2 Ca \longrightarrow CH_3 \cdot \overset{CH_3}{\overset{\diagdown}{\underset{\diagup}{}}}CHCOCH\overset{CH_3}{\underset{CH_3}{\diagup\diagdown}} + 2CaCO_3$$

174. The reactions suggest as :

$\underset{(B)}{CH_2{=}CH{-}CH_2X} + \underset{(A)}{C_6H_5MgX} \longrightarrow \underset{(C)}{C_6H_5CH_2 \cdot CH{=}CH_2}$

$\underset{(C)}{C_6H_5CH_2CH{=}CH_2} \xrightarrow{KOH} \underset{(D)}{C_6H_5 \cdot \overset{H}{\overset{\diagdown}{\underset{\diagup}{}}}C{=}C\overset{H}{\underset{CH_3}{\diagup\diagdown}}} + \underset{(E)}{C_6H_5 \cdot \overset{CH_3}{\overset{\diagdown}{\underset{\diagup}{}}}C{=}C\overset{CH_3}{\underset{H}{\diagup\diagdown}}}$

$\underset{(C)}{C_6H_5CH_2CH{=}CH_2} \xrightarrow[\text{Peroxide}]{HBr} C_6H_5CH_2CH_2 \cdot CH_2Br$

175. (i) (A) $C_4H_8O_3$ loses its optical activity on strong heating and gives (B) $C_4H_6O_2$. Thus, (A) may be $CH_3 \cdot CH_2CHOH \cdot COOH$ or $CH_3 \cdot CHOH \cdot CH_2COOH$.

(ii) Since, (B) is $C_4H_6O_2$ and thus (A) is β-hydroxy acid and not α-hydroxy acid because only β-hydroxy acids lose H_2O on heating.

Thus, (A) is

$$\underset{(A)}{CH_3 \cdot CHOH \cdot CH_2COOH} \xrightarrow{\Delta} CH_2 = CH \cdot CH_2 \cdot COOH$$

(iii) $$\underset{(B)}{CH_2 = CH \cdot CH_2COOH} \xrightarrow{SOCl_2} \underset{(C)}{CH_2 = CH \cdot CH_2COCl}$$

$$\xrightarrow{NH(CH_3)_2} \underset{(D)}{CH_2 = CH \cdot CH_2 \cdot CON(CH_3)_2}$$

(iv) $$\underset{(A)}{CH_3 \cdot CHOH \cdot CH_2COOH} \xrightarrow{[O]} \underset{(E)}{CH_3 \cdot CO \cdot CH_2COOH}$$

$$(E) \xrightarrow{\text{Decarboxylation}} \underset{(F)}{CH_3COCH_3} \xrightarrow{Zn/HCl} \underset{(G)}{CH_3CH_2 \cdot CH_3}$$

176. (i) (A) C_5H_8O adds one Br_2 molecule and thus, has one double bond.

(ii) It forms phenyl hydrazone with phenyl hydrazine and thus, carbonyl group is present in (A).

(iii) (A) does not reduce Tollen's reagent so carbonyl group is ketone and not aldehyde.

(iv) Ozonolysis of (A) gives CH_3CHO and $C_3H_4O_2$ and thus, in consideration of above facts (A) is

$$\underset{(A)}{CH_3CH = CH \cdot COCH_3} \xrightarrow{\text{Ozonolysis}} CH_3CHO + CH_3COCHO$$

$$\downarrow$$

$$CH_3CHO + CO$$

Note : α-keto aldehydes lose CO moderately to form aldehydes.

177. (i) $C_5H_{10}O$ has two isomers (A) and (B). Molecular formula suggests that they may be carbonyl compounds.

(ii) (A) on treating with $NaOH(aq.)$ gives 2,2-dimethyl-propanol and 2,2-dimethylpropanoic acid salts. Thus, (A) is an aldehyde lacking α-C-atom; since this is Cannizzaro's reaction.

$$\underset{\substack{2,2\text{-Dimethylpropanal} \\ (A)}}{(CH_3)_3 \cdot C \cdot CHO} \xrightarrow{NaOH} (CH_3)_3 \cdot C \cdot CH_2OH +$$

$$(CH_3)_3 \cdot C \cdot COONa$$

(iii) Isomer (B) reacts with NaOH to show aldol condensation product 3-hydroxy-2-propylheptanal and thus, (B) is pentanal-1, as condensation occurs at α-carbon atom.

$$\underset{\substack{\text{(Pentan-1-al, } B\text{)} \\ \| \\ O}}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C H} + \underset{|}{CH_2 \cdot CHO} \xrightarrow{NaOH(aq.)}$$

$$\underset{\substack{| \\ OH}}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH} - \underset{|}{CH \cdot CHO}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad C_3H_7$$

178. (i) (A) is an acid showing HVZ reaction in presence of $P + Br_2$. It suggests that (A) is $R \cdot CH_2 \cdot COOH$.

(ii) $R—CH_2 \cdot COOH \xrightarrow{Br_2/P} RCHBr \cdot COOH$ where R is C_3H_7.

(iii) $RCHBrCOOH$ has asymmetric C-atom represented by C*.

(iv) $RCHBr \cdot COOH \xrightarrow{-HBr} (C)$; since C has not geometrical isomers and thus, (C) may be

$$\underset{CH_3}{\overset{CH_3}{\diagdown}}C = CH \cdot COOH$$

(v) $$\underset{CH_3}{\overset{CH_3}{\diagdown}}C = \underset{(C)}{CH \cdot COOH} \xrightarrow{\text{Decarboxylation}} \underset{CH_3}{\overset{CH_3}{\diagdown}}C = \underset{(D)}{CH_2}$$

(vi) $$\underset{CH_3}{\overset{CH_3}{\diagdown}}C = CH_2 \xrightarrow{\text{Ozonolysis}} \underset{CH_3}{\overset{CH_3}{\diagdown}}\underset{(F)}{CO} + \underset{(E)}{HCHO}$$

Negative Schiff's reagent test and thus ketone — Positive Schiff's reagent test and thus aldehyde

(vii) Thus, (A) $\underset{CH_3}{\overset{CH_3}{\diagdown}}CH \cdot CH_2 \cdot COOH$

(B) $\underset{CH_3}{\overset{CH_3}{\diagdown}}CH \cdot CHBr \cdot COOH$

179. (1) (D) on heating with P_2O_5 gives 2-methylpropannitrile and so, (D) is $\underset{\text{2-Methylpropanamide}}{(CH_3)_2CH \cdot CONH_2}$

$$\underset{(D)}{(CH_3)_2CH \cdot CONH_2} \xrightarrow[\Delta]{P_2O_5} \underset{\text{2-Methylpropannitrile}}{(CH_3)_2CH \cdot CN}$$

(2) (D) is formed by heating the compound (C), whereas (C) is formed by the action of (B) over NH_3. Thus, (B) is an acid and (C) is its ammonium salt.

$$\underset{\substack{(B) \\ \text{2-Methylpropanoic acid}}}{(CH_3)_2CH \cdot COOH} + NH_3 \longrightarrow \underset{\substack{(C) \\ \text{2-Methylammonium-propanoate}}}{(CH_3)_2CH \cdot COONH_4} \longrightarrow \underset{(D)}{(CH_3)_2CH \cdot CONH_2}$$

(3) Acid (B) is formed by the hydrolysis of (A) hence all the three halogens must be present on terminal C-atom. Therefore, (A) is

$$\underset{\substack{(A) \\ \text{1, 1, 1-Trichloro,} \\ \text{2-methylpropane}}}{(CH_3)_2CH \cdot CCl_3} \xrightarrow{KOH\ (aq.)} \underset{(B)}{(CH_3)_2CH \cdot COOH}$$

180. (1) $C_3H_6O_2$ has two isomers (A) and (B). The molecular formula suggests, that they may be an acid or ester.

(2) (B) reacts with $NaHCO_3$ whereas (A) does not do so, therefore, (B) is acid and (A) is ester.

$\underset{\text{(Propanoic acid) }(B)}{CH_3CH_2COOH}$ $\underset{(A)}{HCOOC_2H_5}$ or $\underset{(A)}{CH_3COOCH_3}$

(3) (A) on reacting with NaOH gives (C) and (D); (D) gives iodoform test and thus, ester is $HCOOC_2H_5$.

$$\underset{\substack{(A)\\ \text{Ethyl formate}}}{HCOOC_2H_5} \xrightarrow{NaOH} \underset{(C)}{HCOONa} + \underset{\substack{(D),\text{ Ethanol}\\ \text{Gives iodoform test}}}{C_2H_5OH}$$

(4) Also, (C) on treating with dil. H_2SO_4 gives (E) which reduces Tollen's reagent.

$$HCOONa \xrightarrow[H_2SO_4]{HOH} \underset{(E)}{HCOOH} + NaOH$$

(Reduces Tollen's reagent)

181. (i) Compound (B) is obtained from pentanol-1 vapours on passing through Cu at 570 K and thus, it is an aldehyde (1° alcohols give aldehyde)

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2OH \xrightarrow[570\text{ K}]{Cu}$$

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO$$

Pentanal-1 (B)

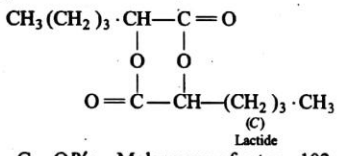
(ii) Compound (B), *i.e.*, pentanal-1 is also obtained along with CO and H_2O from (A) on heating with H_2SO_4. Thus, (A) is $CH_3(CH_2)_3\cdot CHOH\cdot COOH$.

$$\underset{(A)}{CH_3(CH_2)_3\cdot CHOH\cdot COOH} \xrightarrow{H_2SO_4}$$

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO + H_2O + CO$$

(iii) (A) on heating gives (C), *i.e.*,

$$\underset{(A)}{CH_3(CH_2)_3\cdot CHOH\cdot COOH} \xrightarrow{\Delta}$$



Lactide

182. (1) Ester is $R-\underset{\underset{O}{\|}}{C}-OR'$; Molar mass of ester = 102

$\therefore$ Molar mass of $R + R' = 102 - 44 = 58$

(2) Given, $\underset{(A)}{R-COOR'} \xrightarrow{HOH} \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$

mM of acid = mM of NaOH

$$\frac{0.185}{M/1}\times 1000 = 25\times 0.1$$

$\therefore$ Molar mass of acid $R-\underset{\underset{O}{\|}}{C}-OH = 74\ \text{g mol}^{-1}$

$\therefore$ Molar mass of R = 74 – (Molar mass of COOH)

= 74 – 45 = 29

$\therefore$ Molar mass of R' = 58 – 29 = 29

Thus, $R = R'$, also R may be $C_nH_{2n+1} = 29$

$\therefore$ $n = 2$

i.e., R' and R is C_2H_5

(3) Thus, ester is $CH_3\cdot CH_2COOCH_2\cdot CH_3$

Reaction :

$$\underset{\substack{\text{Ester}\\ \text{(Ethyl propanoate)}}}{CH_3CH_2COOC_2H_5} + H_2O \longrightarrow \underset{\substack{\text{Acid}\\ \text{(Propanoic acid)}}}{CH_3CH_2COOH} + \underset{\substack{\text{Alcohol}\\ \text{(Ethyl alcohol)}}}{C_2H_5OH}$$

183. (i) Since, (X) is hydrolysed to give an acid (Y) and an alcohol (Y) and thus, (X) is ester.

$$\underset{(X)}{R-\underset{\underset{O}{\|}}{C}-OR'} \xrightarrow[H^+]{HOH} \underset{(Y)}{RCOOH} + \underset{(Z)}{R'OH}$$

(ii) Oxidation of alcohol (Z) gives acid (Y), it shows that (Z) is a primary alcohol $R-CH_2OH$.

$$\underset{(Z)}{R'OH} \xrightarrow{\text{Oxidation}} \underset{(Y)}{RCOOH}$$

$\therefore$ $R\cdot CH_2\cdot OH \longrightarrow RCOOH$ ($\because$ R' is $R-CH_2$)

So, (X) is $R-\underset{\underset{O}{\|}}{C}-O\cdot CH_2R$

$\therefore$ (X) is $CH_3\cdot CH_2-\underset{\underset{O}{\|}}{C}-OCH_2\cdot CH_2\cdot CH_3$ (Propylpropanoate)

(Y) is $CH_3\cdot CH_2COOH$ (Propanoic acid)

(Z) is $CH_3\cdot CH_2\cdot CH_2OH$ (Propan-1-ol)

184. (1) (E) C_3H_6O does not give Tollen's test, does not reduce Fehling solution but forms hydrazone and so, (E) is a ketone. A ketone of 3 C-atoms is only acetone.

$$\underset{(E)}{CH_3\cdot CO\cdot CH_3}$$

(2) (E) is formed by heating (B) with $Ca(OH)_2$ thus, (B) is CH_3COOH (acetic acid).

$$\underset{(B)}{2CH_3COOH} + Ca(OH)_2 \xrightarrow{\Delta} (CH_3COO)_2Ca \xrightarrow{\Delta}$$

$$\underset{(E)}{CH_3COCH_3}$$

(3) (B) is formed by the oxidation of (D) and thus, (D) is C_2H_5OH (ethyl alcohol).

$$\underset{(D)}{C_2H_5OH} \xrightarrow{\text{Oxidation}} \underset{(B)}{CH_3COOH}$$

(4) (B) and (D) both are formed by (C) on hydrolysis in acid medium and thus, (C) should be an ester $CH_3COOC_2H_5$ (ethyl acetate)

$$\underset{(C)}{CH_3COOC_2H_5} \xrightarrow[H^+]{HOH} \underset{(B)}{CH_3COOH} + \underset{(D)}{C_2H_5OH}$$

(5) Now (B) and (C) both are formed with action of (A) over C_2H_5OH and so, (A) can be acetic anhydride.

$$\underset{(A)}{(CH_3CO)_2O} + C_2H_5OH \longrightarrow \underset{(C)}{CH_3COOC_2H_5} + \underset{(B)}{CH_3COOH}$$

185. (1) (C) is β-keto acid and thus, it may be

$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{R'}{|}}{CH}-COOH$$

(2) (*C*) on decarboxylation gives 3-pentanone, *i.e.*,

$$R\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{R'}{|}}{CH}\text{—}COOH \xrightarrow{\text{Soda lime}} R\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{R'}{|}}{CH_2}$$

or $CH_3\text{—}CH_2\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{CH_3}{|}}{CH_2}$

3-Pentanone

Thus, R is C_2H_5 and R' is CH_3

$\therefore$ (*C*) is $C_2H_5\cdot CO\cdot \underset{\underset{CH_3}{|}}{CH}\cdot COOH$

(3) (*C*) is formed along with ethanol from (*B*) on acid hydrolysis so (*B*) is a β -keto ester (ethyl ester).

$$\underset{\underset{(B)}{CH_3}}{\underset{|}{C_2H_5CO\cdot CH}}\cdot COOC_2H_5 \xrightarrow{HOH} \underset{\underset{(C)}{CH_3}}{\underset{|}{C_2H_5COCH}}\cdot COOH + C_2H_5OH$$

(2-Methyl-3-ketopentanoic acid)

(4) (*B*) is formed as a condensation of two mole of ester (*A*), since the condensation occurs at 'α' C-atom, *i.e.*, Claisen condensation or Claisen reaction so, the probable structure of (*A*) is

$$\underset{(A)}{CH_3\cdot CH_2\cdot COOC_2H_5}$$

Reaction: α-carbon

$$\underset{(A)}{CH_3\cdot CH_2}\underset{O}{\overset{\|}{C}}OC_2H_5 + \underset{(A)}{CH_3\cdot CH_2\cdot COOC_2H_5} \xrightarrow{C_2H_5ONa}$$

(Ethyl propanoate)

$$CH_3\text{—}CH_2\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{CH_3}{|}}{CH}COOC_2H_5 + C_2H_5OH$$

(*B*)

Ethyl, (2-Methyl, 3-ketopentanoate)

186. (1) Compound (*A*) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ gives two compounds (*B*) and (*C*) and thus, it seems to be an ester $RCOOR'$

(2) $\underset{(A)}{RCOOR'} \xrightarrow{\text{Reduction}} \underset{(B)}{RCH_2OH} + \underset{(C)}{R'OH}$

(3) (*F*) is monobasic acid of molar mass 60 and hence, (*F*) is CH_3COOH.

($\because$ $RCOOH = 60$, $\therefore$ $R = 15$, *i.e.*, CH_3COOH)

(4) (*F*) is obtained by oxidation of (*D*) and (*D*) is obtained by oxidation of (*B*) and thus, (*D*) is CH_3CHO and (*B*) is CH_3CH_2OH

(5) Thus, an ester of six C-atoms giving two alcohols, one of 2 carbon atoms, the other alcohol must be of four carbon atoms. Thus, ester (*A*) is

$$CH_3\cdot CH_2\cdot \overset{(A)}{CH_2}COOCH_2\cdot CH_3$$

Reduction

$$CH_3\cdot CH_2\cdot \underset{(C)}{CH_2CH_2OH} + \underset{(B)}{CH_3\cdot CH_2OH}$$

$\xrightarrow{[O]}$ CH_3CHO (*D*)

$\xrightarrow{[O]}$ CH_3COOH (*F*)

or $CH_3COO\overset{(A)}{CH_2}CH_2CH_2CH_3$

Reduction

$$\underset{(B)}{CH_3\cdot CH_2OH} + \underset{(C)}{CH_3CH_2CH_2CH_2OH}$$

(6) (*D*) on treating with alkali and subsequent heating gives (*E*) which on catalytic hydrogenation gives (*C*)

$$\underset{(D)}{2CH_3CHO} \xrightarrow[\text{Aldol condensation}]{NaOH\,(aq.)} \underset{\text{Aldol}}{CH_3\cdot CH(OH)\cdot CH_2CHO} \xrightarrow{\Delta}$$

$$\underset{\text{Butanol-1}}{\underset{(C)}{CH_3CH_2\cdot CH_2\cdot CH_2OH}} \xleftarrow{\text{Reduction}} \underset{\text{Crotonaldehyde}}{\underset{(E)}{CH_3\cdot CH=CH\cdot CHO}}$$

187. (1) (*A*) $C_5H_8O_2$ liberates CO_2 with $NaHCO_3$ so, (*A*) is acid, *i.e.*, (*A*) is C_4H_7COOH.

(2) (*A*) seems to be unsaturated and thus shows geometrical isomerism.

(3) $\underset{(A)}{C_4H_7COOH} \xrightarrow{H_2} \underset{(B)}{C_5H_{10}O_2}$;

Since, (*B*) is optically active and thus, acid (*B*) may be

(*B*) $CH_3\cdot CH_2\cdot \overset{*}{\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}}\text{—}COOH$ (2-Methylbutanoic acid)

*is asymmetric carbon.

(4) Since, (*B*) is formed by hydrogenation of acid (*A*) having geometrical isomers, thus, (*A*) can only be

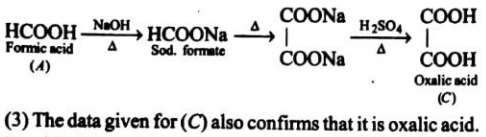
$CH_3\cdot CH=\underset{\underset{CH_3}{|}}{C}\text{—}COOH$ (2-Methylbut-2-enoic acid)

(*A*) $\underset{\text{Cis}}{\overset{CH_3\text{—}C\text{—}COOH}{\underset{CH_3\text{—}C\text{—}H}{\|\quad\|}}}$ $\underset{\text{Trans}}{\overset{CH_3\text{—}C\text{—}COOH}{\underset{H\text{—}C\text{—}CH_3}{\|\quad\|}}}$

188. (1) (*A*) is sodium salt of a carboxylic acid produced by a gas (*B*) on reacting with NaOH at high *P* and *T*. The reaction is a characteristic reaction of CO and NaOH at high *P* and *T*.

$$\underset{(B)}{CO} + NaOH \xrightarrow{P,\,T} HCOONa \xrightarrow{HOH} \underset{(A)}{HCOOH}$$

(2) (*A*) on heating in presence of NaOH followed with H_2SO_4 gives a dibasic acid (*C*)



(3) The data given for (*C*) also confirms that it is oxalic acid.
Empirical formula of (*C*)

Element	%	Relative no. of atoms	Simplest ratio
C	$\frac{12}{44}\times\frac{0.39}{0.40}\times 100 = 26.59$	2.21	1
H	$\frac{2}{18}\times\frac{0.08}{0.40}\times 100 = 2.22$	2.22	1
O	$100-(26.59+2.22)=71.19$	4.44	2

$\therefore$ Empirical formula of (*C*) is CHO_2; Empirical formula mass = 45

Also, molar mass of (*C*)

$$\frac{\text{Mass of Ag}}{\text{Eq. mass of Ag}} = \frac{\text{Mass of Ag salt}}{E+108}$$

where, *E* is Eq. mass of anion of acid

$$\frac{0.71}{108} = \frac{1}{E+108}$$

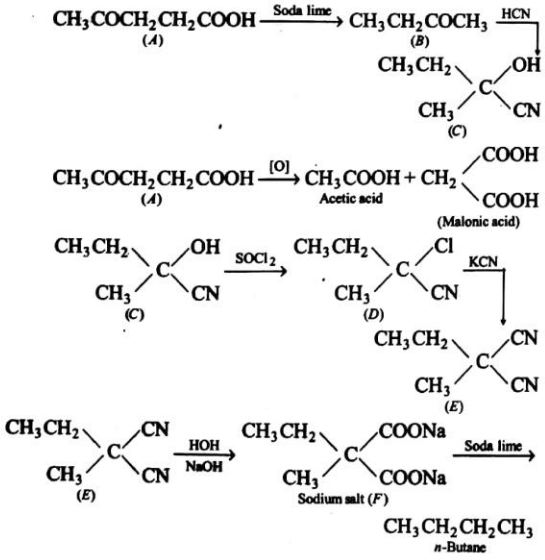
$\therefore \quad E = 44$

$\therefore$ Eq. mass of acid $= 44 + 1 = 45$

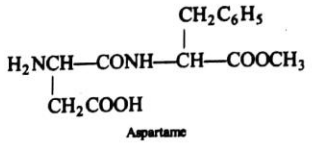
$\therefore$ Molar mass of acid $= 90\ \text{g mol}^{-1}$

$\therefore$ M. formula of $(C) = (CHO_2)_2 = COOH\cdot COOH$

189. The statements given in problem suggest (*A*) to be $CH_3COCH_2CH_2COOH$



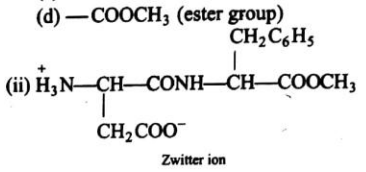
190.



Aspartame

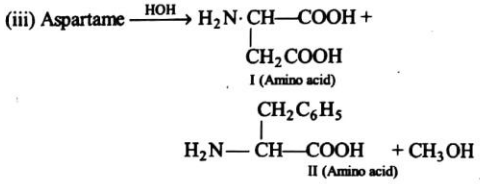
(i) The four functional groups are :
(a) $-NH_2$ (amino group)
(b) $-COOH$ (carboxylic group)
(c) $-CONH-$ (peptide or amide group)
(d) $-COOCH_3$ (ester group)

(ii)



Zwitter ion

(iii)



I (Amino acid)

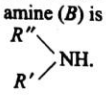
II (Amino acid)

(iv) $H_2N\cdot CH\cdot COOH$ is more hydrophobic as it has one —COOH and one $-NH_2$ group along with more powerful hydrophobic chain $-CH_2C_6H_5$.

191. (1) (*A*) on hydrolysis gives an amine (*B*) and a carboxylic acid (*C*), *i.e.*, amine and *R*COOH.

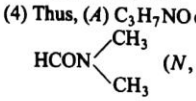
(2) Amine (*B*) reacts with benzene sulphonyl chloride and the product is insoluble in aqueous solution of NaOH and therefore, amine (*B*) is secondary amine,

i.e.,



(3) Acid (*C*) reacts with Tollen's reagent and thus, it may be formic acid HCOOH.

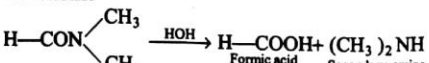
(4) Thus, (*A*) C_3H_7NO can be



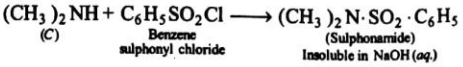
(N, N' – Dimethylformamide)

(5) The structure can be justified by the reactions.

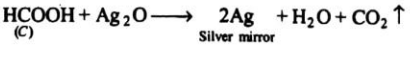
Reactions:



Formic acid (*C*) Secondary amine (*B*)



Benzene sulphonyl chloride (Sulphonamide) Insoluble in NaOH (*aq.*)



Silver mirror

192. (1) Compound gives foul odour with $CHCl_3$ and alcoholic KOH and thus, it is primary amine say $R—NH_2$. The reaction is carbylamine reaction.

(2) $RNH_2 \xrightarrow[0°C]{HCl + NaNO_2} ROH + N_2$

$\because$ 112 mL N_2 is given by 0.295 g

$\therefore$ 22400 mL N_2 is given by $\dfrac{0.295 \times 22400}{112} = 59$

$\therefore$ Molar mass of $RNH_2 = 59$

$\therefore$ $R = 59 - (14 + 2) = 43$

i.e., $C_nH_{2n+1} = 43$

$\therefore$ $n = 3$

(3) Given,

$C_3H_7NH_2 \xrightarrow{HCl + NaNO_2} C_3H_7OH \xrightarrow{I_2 + NaOH}$ yellow precipitate

Since, alcohol gives iodoform test and thus, it is secondary alcohol, *i.e.*,

$CH_3CHOH \cdot CH_3$ (Propan-2-ol)

Thus, original compound should be $CH_3\underset{\underset{NH_2}{|}}{CH}\cdot CH_3$

Propan-2-amine

193. (1) For empirical formula of (*A*)

Element	%	Relative no. of atoms	Simplest ratio
C	49.32	4.11	3
H	9.59	9.59	7
N	19.18	1.37	1
O	21.91	1.37	1

$\therefore$ Empirical formula of (*A*) is $\mathbf{C_3H_7NO}$

and Empirical formula mass of (*A*) = 73

(2) Molar mass of acid (*B*) can be derived as:

$$\frac{\text{Mass of Ag}}{\text{Eq. mass of Ag}} = \frac{\text{Mass of salt}}{\text{Eq. mass of salt}}$$

$$\frac{59.67}{108} = \frac{100}{E + 108}$$

$\therefore$ $E = 73$, *i.e.*, equivalent mass of anion of salt

$\therefore$ Equivalent mass of acid = $E + 1 = 73 + 1 = 74$

$\therefore$ Molar mass of acid = $74 \times 1\,g\,mol^{-1}$ $\quad\because$ Basicity = 1

(3) Acid (*B*) is monobasic and thus (*B*) is $C_nH_{2n+1}COOH$

$\therefore$ $12n + 2n + 1 + 12 + 32 + 1 = 74$

$\therefore$ $n = 2$

So, acid (*B*) is $CH_3 \cdot CH_2COOH$.

(4) Since, (*B*) is obtained by the action of (*A*) with NaOH followed with hydrolysis and so (*A*) is $CH_3CH_2CONH_2$.

$$\underset{\text{(Propanamide) (A)}}{CH_3CH_2CONH_2} \xrightarrow{NaOH} CH_3\cdot CH_2COONa + NH_3$$

$$\xrightarrow{HOH} \underset{(B)}{CH_3CH_2COOH}$$

194. (1) For empirical formula of (*Y*)

Element	%	Relative no. of atoms	Simplest ratio
C	49.31	4.11	3
H	9.59	9.59	7
N	19.18	1.37	1
O	21.91	1.37	1

$\therefore$ Empirical formula of (*Y*) is $\mathbf{C_3H_7NO}$.

(2) (*Y*) reacts with Br_2 and NaOH to give (*Z*) and (*Z*) reacts with HNO_2 to give ethanol and thus, empirical formula of (*Y*) seems to be molecular formula with $—CONH_2$ group.

$$\underset{\substack{(Y)\\\text{(Propanamide)}}}{CH_3CH_2CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{(Z) (Ethanamine) basic}}{CH_3CH_2NH_2}$$

Hofmann's bromamide reaction

$$\downarrow HNO_2$$

$$\underset{\text{Ethanol}}{CH_3\cdot CH_2OH}$$

(3) (*Y*) is formed from (*X*) having Cl on treatment with NH_3 and so (*X*) is CH_3CH_2COCl, *i.e.*, propanoyl chloride.

$$\underset{(X)}{CH_3\cdot CH_2COCl} + NH_3 \longrightarrow \underset{(Y)}{CH_3CH_2CONH_2}$$

195. Alanine is α-amino propionic acid, *i.e.*, $CH_3\underset{\underset{NH_2}{|}}{CH}\cdot COOH$

At pH = 2, $CH_3CHNH_2COOH \xrightarrow{H^+} CH_3\overset{+}{C}HNH_3COOH$

At, pH = 10, $CH_3CHNH_2COOH \xrightarrow{OH^-} CH_3CHNH_2COO^-$

196. The given reactions suggest that

(i)

$$\underset{(A)}{CH_3CH_2CON}\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow{NaOH} \underset{(B)}{(CH_3)_2NH} + \underset{(C)}{CH_3CH_2COONa}$$

(ii) $\underset{(B)}{(CH_3)_2NH} \xrightarrow{HNO_2} \underset{\text{Yellow oil (E)}}{(CH_3)_2N\cdot NO}$

(iii) $\underset{(B)}{(CH_3)_2NH} \xrightarrow{CH_3COCl} \underset{(D)}{(CH_3)_2NCOCH_3}$

197. (1) (*A*) on distillation loses water and forms (*B*) which on further distillation with P_2O_5 gives (*C*)

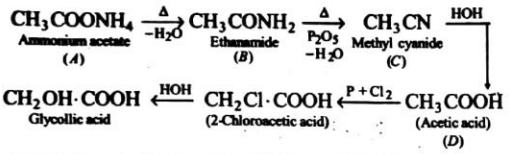
$$\underset{(A)}{C_2H_7NO_2} \xrightarrow[-H_2O]{\Delta} \underset{(B)}{C_2H_5NO} \xrightarrow[P_2O_5]{\Delta} \underset{(C)}{C_2H_3N}$$

(2) (*C*) on hydrolysis gives (*D*) which on treating with $P + Cl_2$ followed with hydrolysis gives glycollic acid.

$$C_2H_3N \xrightarrow{HOH} (D) \xrightarrow[\text{(ii) HOH}]{\text{(i) P + Cl}_2} \underset{\text{Glycollic acid}}{\overset{CH_2OH}{\underset{COOH}{|}}}$$

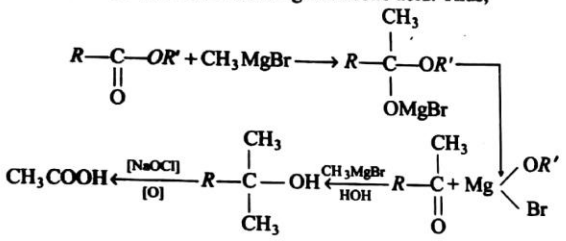
(3) All these facts can be explained if (*A*) is ammonium acetate, *i.e.*, CH_3COONH_4.

Reactions:



198. (i) Let the ester be $R-\underset{\underset{O}{\|}}{C}-OR'$, *i.e.*, $C_4H_8O_2$

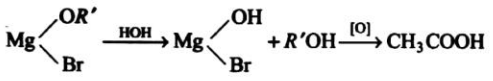
(ii) It reacts with CH_3MgBr; the product (*B*) on acidification gives an alcohol (*B*) which on oxidation with NaOCl followed with acidification gives acetic acid. Thus,



(iii) Thus, *R* should be H because only secondary alcohol can be oxidised by NaOCl and not tertiary. Thus, the ester may be

$H-COOCH_2\cdot CH_2\cdot CH_3$ or $H-COOCH(CH_3)_2$

(iv) Also,



Thus, *R'*OH must be secondary alcohol of three carbon atoms,

i.e. $(CH_3)_2CHOH$. And thus, ester is $H-COOCH(CH_3)_2$

199. Acid anhydride (*A*) reacts with an acid (*B*) to give an acid (*C*) of equivalent mass 74 and an anhydride (*D*). These may be

$$\underset{(A)}{(CH_3\cdot CH_2\cdot CO)_2O} + 2\underset{(B)}{CF_3CH_2COOH} \longrightarrow 2\underset{(C)}{CH_3\cdot CH_2COOH} + \underset{(D)}{(CF_3\cdot CH_2CO)_2O}$$

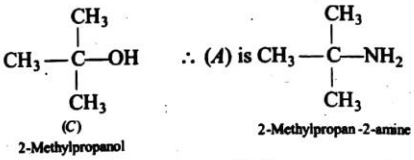
CH_3CH_2COOH has eq. mass = 74

and $CF_3\cdot CH_2COOH$ has eq. mass = 128.

200. (1) Both (*A*) and (*B*) lose N_2 on treating with HNO_2 forming alcohols (*C*) and (*D*) respectively and thus, (*A*) and (*B*) both are primary amines.

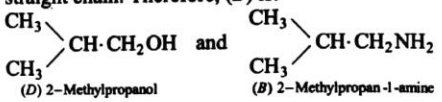
$$\underset{(A) \text{ or } (B)}{C_4H_9NH_2} \xrightarrow{HNO_2} \underset{(C) \text{ or } (D)}{C_4H_9OH}$$

(2) (*C*) reacts with Lucas reagent immediately and thus, (*C*) is tertiary alcohol. The tertiary alcohol of formula C_4H_9OH is :



(*C*) 2-Methylpropanol — ∴ (*A*) is 2-Methylpropan-2-amine

(3) (*D*) does not react with Lucas reagent and is easily oxidised and thus, it is primary alcohol ($-CH_2OH$). Complete methylation of (*B*) does not give on decomposition butene-1. Thus, (*B*) and (*D*) do not have straight chain. Therefore, (*B*) is:



(*D*) 2-Methylpropanol and (*B*) 2-Methylpropan-1-amine

201. (i) Molecular formula of (*A*) suggests that it is

either $C_2H_5N\langle^{O}_{O}$ Nitroethane

or $C_2H_5O-N=O$ Ethyl nitrite

(ii) Since, (*A*) undergoes hydrolysis to give an alcohol (*B*) and an acid, it is ethyl nitrite $C_2H_5O-N=O$.

Reactions :

$$\underset{\text{Ethyl nitrite}}{\underset{(A)}{C_2H_5O-N=O}} \xrightarrow[H^+]{H_2O} \underset{(B)}{C_2H_5OH} + HNO_2$$

Molar mass of (*B*) is = 46

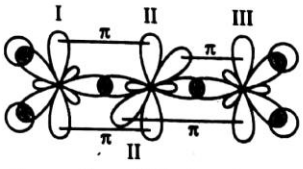
$$C_2H_5O-N=O \xrightarrow{\text{Reduction}} C_2H_5OH + NH_3$$

202. (a)

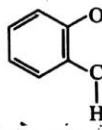
$$CH_3CH_2C\equiv CH \xrightarrow{Na} CH_3CH_2C\equiv CNa \xrightarrow{CH_3X} (A)$$

$$(A) \text{ or } CH_3CH_2C\equiv CCH_3 \xrightarrow[H_2SO_4]{HgSO_4^{\ddagger}} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$$

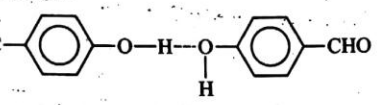
(b) Allene is $\overset{I}{\underset{sp^2}{CH_2}}=\overset{II}{\underset{sp}{C}}=\overset{III}{\underset{sp^2}{CH_2}}$



(c) *o*-hydroxy benzaldehyde shows intramolecular H-bonding, (chelation) a weaker H-bonding than intermolecular H-bonding noticed in *p*-hydroxy benzaldehyde.

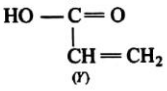


o-Hydroxy benzaldehyde

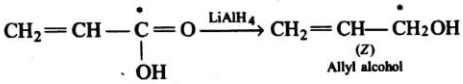
and OHC—  —CHO

p-Hydroxy benzaldehyde

203. (a) $BaCO_3 + H_2SO_4 \longrightarrow \underset{\text{gas }(X)}{CO_2} + BaSO_4 + H_2O$

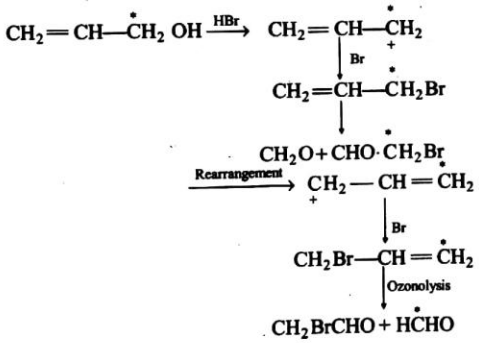
$CH_2=CHBr \xrightarrow{\text{(i) Mg / Ether}} CH_2=CHMgBr \xrightarrow[\text{(iii) HOH}]{\text{(ii) } CO_2}$ 

(Y)

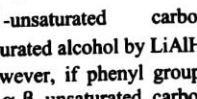


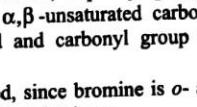
(Z) Allyl alcohol

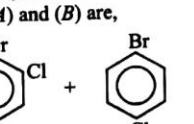
Acrylic acid



(Rearrangement)



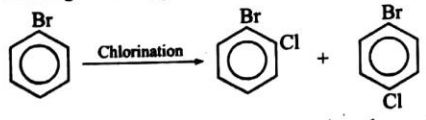




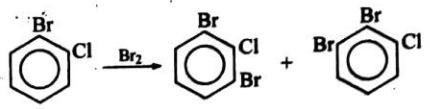
$CH_2BrCHO + HCHO$

204. (a) $CH_2=CHCH_2OH$; α,β-unsaturated carbonyl compounds are reduced to unsaturated alcohol by $LiAlH_4$.
(b) $C_6H_5CH_2CH_2CH_2OH$; However, if phenyl group is attached to β-carbon atom of α,β-unsaturated carbonyl compounds, both double bond and carbonyl group are reduced by $LiAlH_4$.

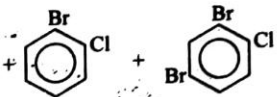
205. (1) Bromobenzene is chlorinated, since bromine is *o*- and *p*-directing and thus, products (*A*) and (*B*) are,



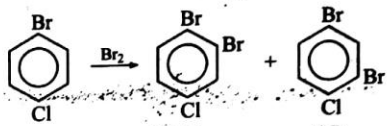
(2) Monobromination of (*A*) gives several products whereas (*B*) gives only two isomers and thus, (*A*) and (*B*) are,



(*A*) (I) (II)

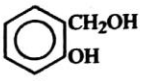


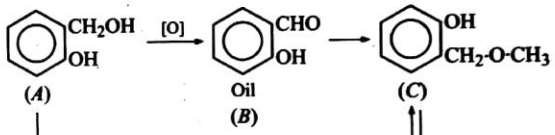
(III) (IV)



(*B*) (*D*) (*C*)

(3) (*C*) is identical to (IV) but (*D*) does not resemble with (I) to (IV).

206. The given reactions suggest that (*A*) is 

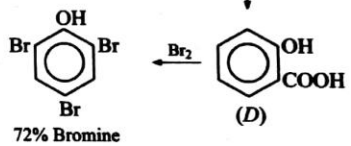


(*A*) Oil (*B*) (*C*)

Volatile due to intramolecular H-bonding

$(CH_3)_2SO_4$; NaOH

[O]



72% Bromine (*D*)

207. (1) For empirical formula of (*A*), a hydrocarbon (*i.e.*, C and H only)

Element	%	Relative no. of atoms	Simplest ratio
C	90.56	7.55	1 or 4
H	9.44	9.44	1.25 or 5

∴ Empirical formula of (*A*) = C_4H_5

Empirical formula mass = 53

Given, Molar mass = $53 \times 2 = 106$ g mol^{-1}

∴ Molecular formula of (*A*) = $(C_4H_5) = C_8H_{10}$

(2) $(A) \xrightarrow[\text{oxidation}]{\text{Vigorous}} (B)$ Dibasic acid, $R\begin{matrix}COOH\\COOH\end{matrix}$

Meq. of dibasic acid = Meq. of NaOH

$$\frac{0.1}{E} \times 1000 = 24.1 \times 0.05$$

∴ Equivalent mass of dibasic acid = 83

∴ Molar mass of dibasic acid = 166

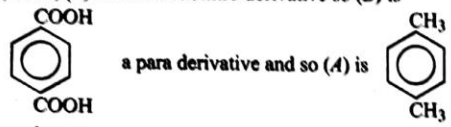
∴ Molar mass of $R = 166 - 2\times45 = 76$

This also suggests R to be C_6H_4.

(3) (B) on heating with soda lime gives benzene and thus, (B) is

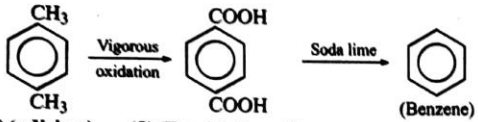
$C_6H_4(COOH)_2$ and so (A) is $C_6H_4(CH_3)_2$

(4) Also, (B) shows mononitro derivative so (B) is

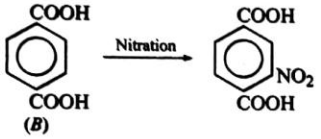


a para derivative and so (A) is

Reactions :



(A) (p-Xylene) (B) (Terephthalic acid) (Benzene)



(B)

208. (i) Both (B) and (C) $C_8H_8O_2$ are monobasic acids, (B) on chlorination gives a compounds having 3 Cl-atoms whereas (C) on chlorination gives a compounds having 2 Cl-atoms. Thus,

(B) is $C_6H_4(CH_3)(COOH) \xrightarrow[h\nu]{Cl_2} C_6H_4(CCl_3)(COOH)$

(o-, m- and p- (B)) (o-, m- and p- (I))

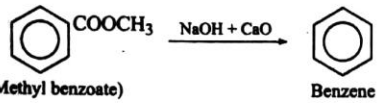
(C) is $\underset{(C)}{C_6H_5CH_2COOH} \xrightarrow[h\nu]{Cl_2} \underset{(II)}{C_6H_5\cdot CCl_2\cdot COOH}$

(ii) Acid (I) formed by (B) on hydrolysis gives dibasic acid (D), which gives benzene with soda lime.

$C_6H_4(CCl_3)(COOH) \xrightarrow{HOH} C_6H_4(COOH)_2 \xrightarrow[+CaO]{NaOH} C_6H_6$

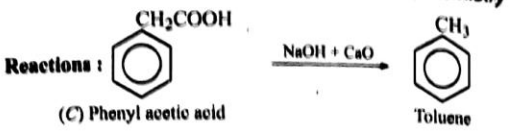
(o-, m- and p- (I)) (o-, m- and p-dibasic acid)

(iii) Compound (A) being neutral but gives C_6H_6 with soda lime and thus, (A) is

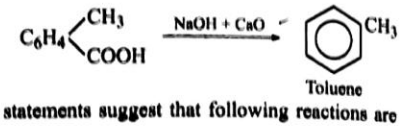


(A) (Methyl benzoate) Benzene

Reactions :

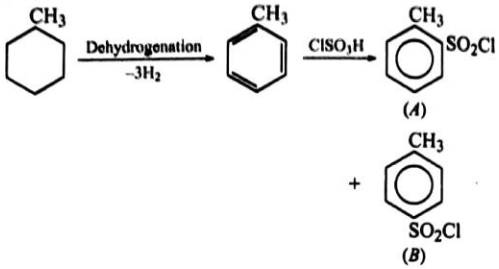


(C) Phenyl acetic acid Toluene

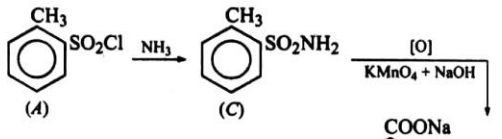


Toluene

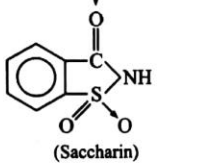
209. The given statements suggest that following reactions are possible:



(A) (B)



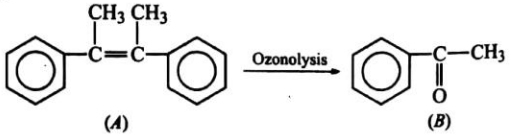
(A) (C) (D)



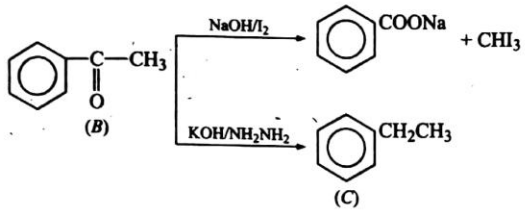
(Saccharin)

(B) (Chloramine-T antiseptic)

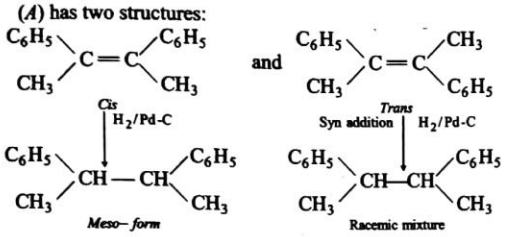
210.



(A) (B)

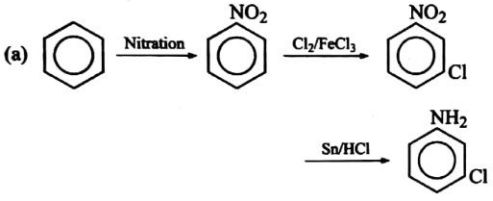


(*A*) has two structures:



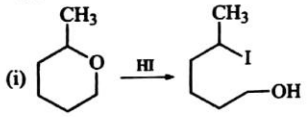
211.

(a)



(b)

(i)

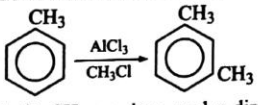


This is acid catalysed cleavage of ether where nucleophile attacks the most substituted carbon.

(ii) $CH_3-\underset{\underset{O}{\diagdown\diagup}}{C}(CH_3)-CH_2 \xrightarrow[CH_3ONa]{CH_3OH} (CH_3)_2C(OH)-CH_2OCH_3$;

This is base catalysed cleavage of ether where nucleophile attacks least substituted carbon.

(iii)

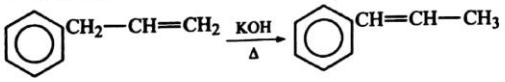


Major product;

No doubt CH_3 gp. is *o*- and *p*-directing and thus *o*- and *p*-xylenes are formed along with little *m*-xylene. But at 80°C *o*- and *p*-xylenes are readily dealkylated whereas *m*-xylene is stable product.

Also, presence of HCl favours dealkylation.

(iv)



212. Given,

$C_7H_8 \xrightarrow[h\nu]{Cl_2}$ Chlorinated product $\xrightarrow[(B)]{H_2O}(C)$

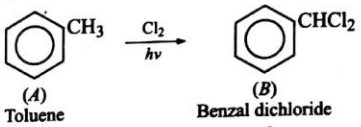
(i) (*C*) gives positive test with Tollen's reagent and thus, (*C*) is aldehyde.

(ii) (*C*) is obtained by hydrolysis of (*B*) and thus, (*B*) is terminal gem dihalide, $-CHCl_2$ group.

(iii) (*B*) is obtained by chlorination of (*A*) thus, (*A*) is $C_6H_5CH_3$.

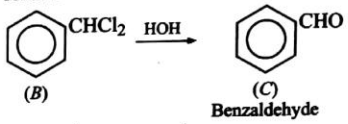
Reactions :

(i)



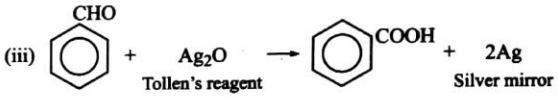
(*A*) Toluene — (*B*) Benzal dichloride

(ii)

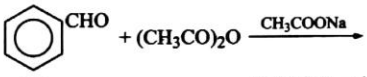


(*B*) — (*C*) Benzaldehyde

(iii)



(iv)

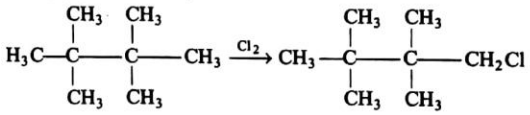


(*C*) — $C_6H_5CH{=}CH{\cdot}COOH$ Cinnamic acid

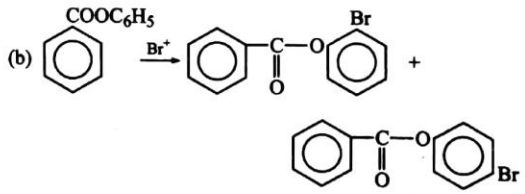
This is Perkins reaction, (*D*) has molar mass 148.15 g mol^{-1}.

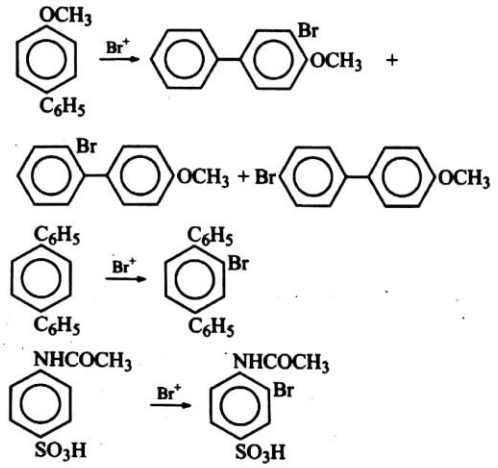
∵ Monobasic acid ∴ E. mass = 148.15

213. (a) The alkane having C_8H_{18} structure gives only single monochloride on substitution and thus, it should be 2,2,3,3-tetra methyl butane.

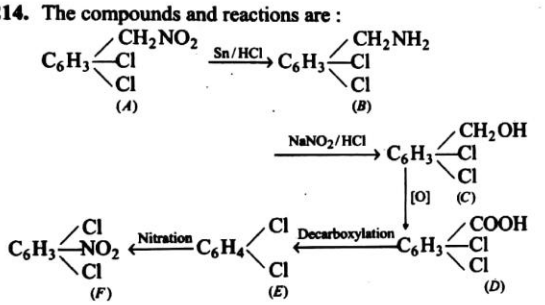


(b)





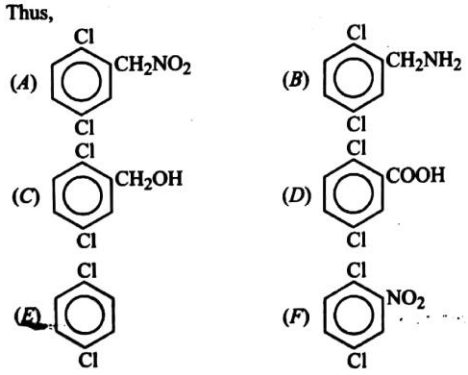
214. The compounds and reactions are :



only one product

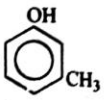
Since, (*F*) is only one product and thus, (*E*) is para derivative.

Thus,

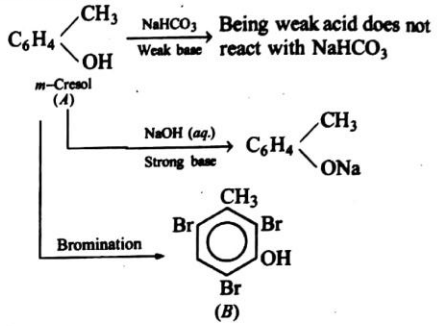


215. (i) (*A*) gives characteristic colour with aqueous $FeCl_3$ and so it has phenolic group.

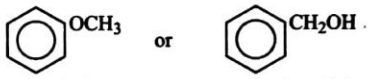
(ii) (*A*) on treatment with Br_2 gives $C_7H_5OBr_3$ and thus, taking an account of molecular formula of (*A*); (*A*) seems to be a methyl substituted phenol, *i.e.*, cresol.

(iii) On the basis of bromination, (*A*) can be  because meta position can form tribromo derivative.

Reactions :

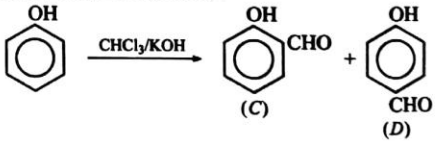


(iv) If (*A*) neither dissolves in aqueous NaOH, nor it gives characteristic colour with $FeCl_3$, it is neutral compound, *i.e.*, either

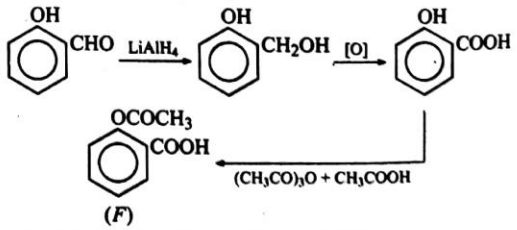


Anisole Benzyl alcohol

216. (i) The organic compound (*A*) is phenol as it undergoes Reimer-Tiemann reaction.



(ii) (*C*) does not reduce Schiff's reagent due to intramolecular H-bonding and is also steam volatile.

(iii) 

Acetyl salicylic acid or aspirin, a pain killer.

217. (i)

Element	%	Relative no. of atoms	Simplest ratio
C	68.32	5.59	8
H	6.4	6.40	9
Cl	25.26	0.71	1

Hence, Empirical formula of (*A*) = C_8H_9Cl

Empirical formula mass = 140.5

$\because$ Molar mass = 140.5 g mol^{-1}

∴ Molecular formula = C_8H_9Cl

(2) Given, $\underset{(A)}{C_8H_9Cl} \xrightarrow{HOH} \underset{(B)}{C_8H_9OH} \xrightarrow{Oxidation} \underset{(C)}{C_8H_8O}$

(3) (*C*) reacts with phenyl hydrazine and thus, a carbonyl compound.

(4) (*C*) gives positive iodoform test and thus, has CH_3CO- unit. Thus, (*C*) is $C_6H_5COCH_3$ (Acetophenone)

(5) Since, (*C*) is formed by the oxidation of (*B*) and thus, (*B*) is $C_6H_5CHOHCH_3$ (1-Phenylethanol)

(6) Since, (*B*) is obtained by hydrolysis of (*A*) so, (*A*) is $C_6H_5CHClCH_3$ (1-Chloro-1-phenylethane)

Reactions : $\underset{(A)}{C_6H_5CHCl\cdot CH_3} \xrightarrow[H^+]{HOH} \underset{(B)}{C_6H_5CHOH\cdot CH_3}$

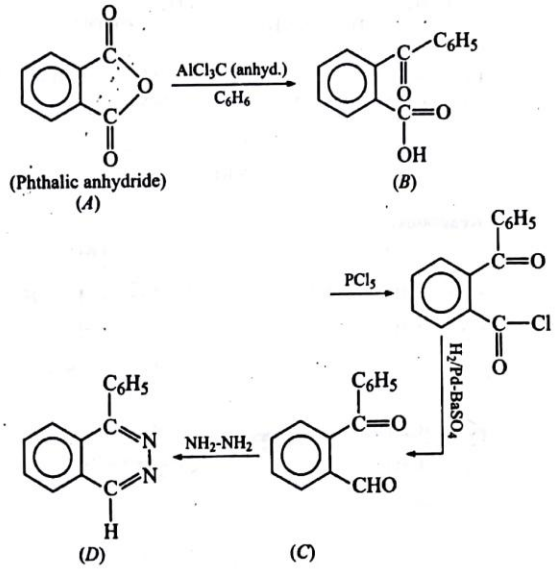
$\xrightarrow{Oxidation} \underset{(C)}{C_6H_5COCH_3}$

$C_6H_5COCH_3 + H_2N\cdot NHPh \longrightarrow C_6H_5-\overset{\overset{NNHph}{\|}}{C}-CH_3$

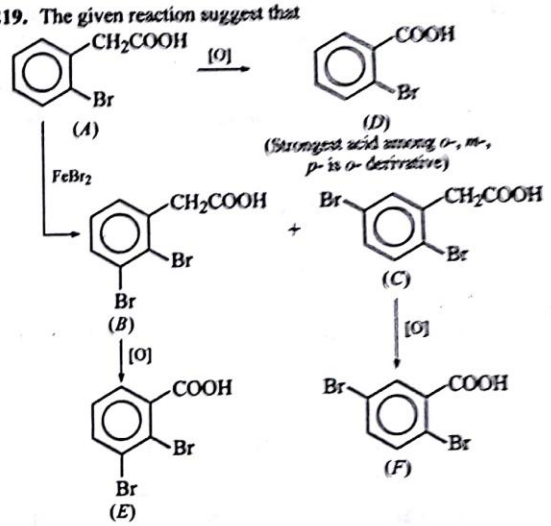
Phenyl hydrazone

$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow \underset{\text{Yellow ppt.}}{C_6H_5COONa} + CHI_3 + 3NaI + 3H_2O$

218.



219. The given reaction suggest that



220. (*X*) is $C_6H_5CH_2MgX$ and (*Y*) is CH_3MgX

$C_6H_5CH_2MgX + \underset{(P)}{(CH_3)_2C=O} \longrightarrow C_6H_5CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

$CH_3MgX + (C_6H_5CH_2)(CH_3)C=O \longrightarrow C_6H_5CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

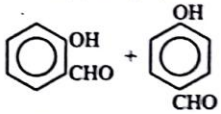
221. (1) Given, mixture of (*A*) and (*B*)

$\xrightarrow[+KOH\,(aq.)]{CHCl_3}$ Organic layer + Alkaline aqueous layer
(*A*) (*B*)

(2) Organic layer on treating with KOH(alc.) produces (*C*) of unpleasant odour (C_7H_5N) and thus, (*C*) is C_6H_5NC. This is carbylamine reaction. Therefore, (*A*) is $C_6H_5NH_2$.

$\underset{\text{(Aniline) (A)}}{C_6H_5NH_2} + CHCl_3 + 3KOH(alc.) \longrightarrow \underset{\text{Phenyl isocyanide (C)}}{C_6H_5NC} + 3KCl + 3H_2O$

(3) Alkaline layer on treating with $CHCl_3$ followed with acidification gives two isomers (*D*) and (*E*) ($C_7H_6O_2$). This is Reimer-Tiemann reaction and thus, (*B*) is C_6H_5OH.

$\underset{\text{Phenol (B)}}{C_6H_5OH} + CHCl_3 + KOH \xrightarrow{H^+}$  +

(*D*) Ortho — (*E*) Para

Hydroxybenzaldehydes

222. Since, % of chlorine is fix in each hydrochloride and thus all amines are isomers. Also amine hydrochloride is $C_nH_{2n+3}N \cdot HCl$.

$\because$ 32.42 is chlorine then amine = (100 – 32.42 – 1) = 66.58

$\therefore$ 35.5 is chlorine then amine = $\frac{66.58 \times 35.5}{32.42} = 72.90$

$\therefore \quad 12n + 2n + 3 = 72.90$

$\therefore \quad n = 4$

Thus, amine is $C_4H_{11}N$.

The possible amines are :

$$\underset{(A)}{CH_3CH_2CH_2CH_2NH_2} \xrightarrow{HNO_2} N_2 + CH_3CH_2CH_2CH_2OH$$

$$\underset{(B)}{CH_3\underset{CH_3}{\underset{|}{CH}}\cdot CH_2NH_2} \xrightarrow{HNO_2} N_2 + (CH_3)_2CHCH_2OH$$

$$\underset{(C)}{(CH_3)_3C\cdot NH_2} \xrightarrow{HNO_2} N_2 + (CH_3)_3C\cdot OH$$

$$\underset{(D)}{CH_3\cdot\underset{NH_2}{\underset{|}{CH}}\cdot CH_2\cdot CH_3} \xrightarrow{HNO_2} N_2 + \underset{C_2H_5}{\overset{CH_3}{\diagdown\!\!\diagup}}C\cdot HOH$$

All primary amines give N_2 with HNO_2.

Others are $\underset{(E)}{CH_3CH_2CH\cdot NH\cdot CH_3}$

or $CH_3\underset{CH_3}{\underset{|}{CH}}\cdot NHCH_3$

$\underset{(F)}{CH_3CH_2NHCH_2CH_3}$

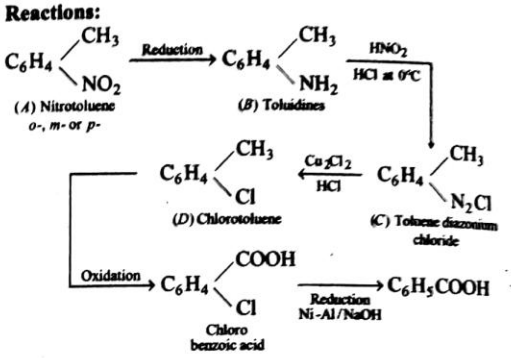
or $CH_3N\overset{CH_3}{\underset{CH_2CH_3}{\diagdown\!\!\diagup}}$ (G)

223. (i) (*A*) $C_7H_7NO_2$ on reduction gives a solid (*B*) and thus, (*A*) contains $-NO_2$ group which is reduced to $-NH_2$ group.

(ii) (*B*) undergoes diazotization (since $-NH_2$ group in it) to give (*C*) which on treating with Cu_2Cl_2/HCl gives (*D*) and (*D*) on reduction with Ni-Al/NaOH gives benzoic acid. This suggests that Cl is present at another position in C_6H_6 ring in (*D*).

(iii) Keeping these facts into account (*A*) is $C_6H_4\overset{CH_3}{\underset{NO_2}{\diagdown\!\!\diagup}}$

Reactions:



224. (i) (*A*) releases N_2 with HNO_2 and thus, (*A*) is primary amine, *i.e.*,

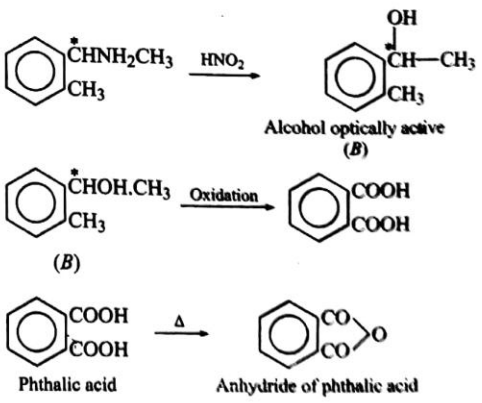
$$\underset{(A)}{C_9H_{11}NH_2} \xrightarrow{HNO_2} \underset{(B)}{C_9H_{11}OH}$$

(ii) (*A*) forms alcohol (*B*) with HNO_2 which is optically active and thus, keeping in view of molecular formula of (*A*) and (*B*) as well as the fact that (*B*) on oxidation gives dicarboxylic acid (*i.e.*, two side chains on C_6H_6 ring), (*B*) can be

$$C_6H_4\overset{CH_3}{\underset{\underset{(B)}{CH\cdot OH\cdot CH_3}}{\diagdown\!\!\diagup}} \xrightarrow{[O]} C_6H_4\overset{COOH}{\underset{COOH}{\diagdown\!\!\diagup}}$$

(iii) Since, acid formed on oxidation of (*B*) forms anhydride and thus, two side chains are at ortho positions, *i.e.*,

Reactions:



*is asymmetric carbon.

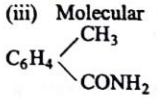
225.

C = 71.11%	$\frac{71.11}{12}$	5.92	8
H = 6.67%	$\frac{6.67}{1}$	6.67	9
N = 10.37%	$\frac{10.37}{14}$	0.74	1
O = 11.85%	$\frac{11.85}{16}$	0.74	1

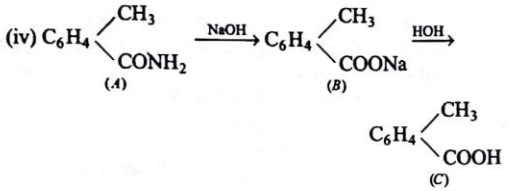
(i) Empirical formula of (A) $\mathbf{C_8H_9NO}$; (A) contains only one N-atom in its molecule and thus, molecular formula of (A) is C_8H_9NO.

(ii) (A) gives NH_3 with NaOH and thus has $CONH_2$ group.

(iii) Molecular formula of (A) suggests it to be

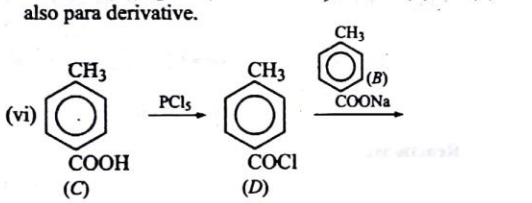


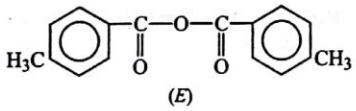
(iv)



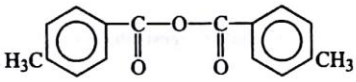
(v) Electrophilic substitution on (C) gives only one product and thus, (C) is para derivative and therefore (A) and (B) are also para derivative.

(vi)





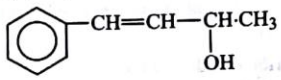
Thus, (A) : ; (B) : ; (C) : ;

(D) : ; (E) : 

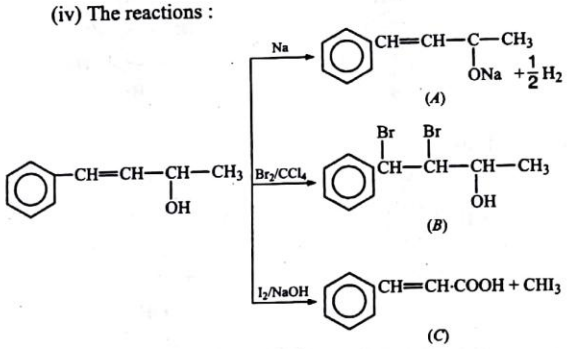
226. (i) Compound (A) has —OH gp. along with unsaturation as it reacts with Na and decolourises Br_2/CCl_4.

(ii) (A) gives iodoform test and thus, it should have structure.

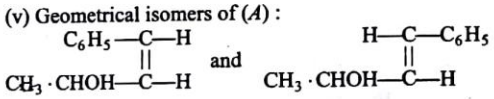
(iii) Thus, (A) may be



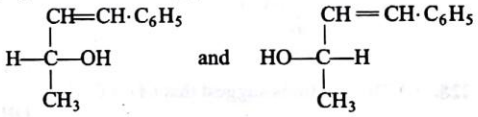
(iv) The reactions :



(v) Geometrical isomers of (A) :



(vi) Optical isomers of (A) :



227. (1) For empirical formula of (A)

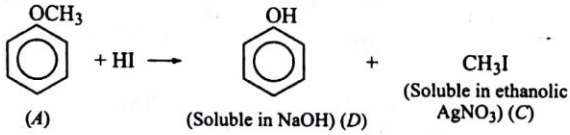
Element	%	Relative No. of atoms	Simplest ratio
C	$\frac{12}{44} \times \frac{0.308}{0.108} \times 100 = 77.77$	6.46	7
H	$\frac{2}{18} \times \frac{0.072}{0.108} \times 100 = 7.40$	7.40	8
O	$100 - (77.77) + 7.40 = 14.83$	0.93	1

$\therefore$ Empirical formula of $(A) = \mathbf{C_7H_8O}$

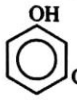
(2) Since, (B) gives $C_7H_5OBr_3$ and (B) is isomer to (A). Thus, molecular formula of (A) and (B) is C_7H_8O.

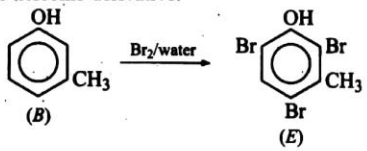
(3) (A) is insoluble in NaOH and $NaHCO_3$ so (A) is

(4) (A) is also confirmed by action with HI

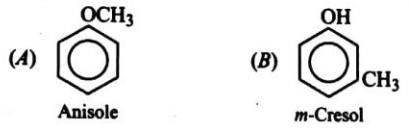


(5) (B) is soluble in NaOH and gives (E) $C_7H_5OBr_3$ with Br_2 water and so (B) is

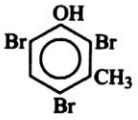

i.e., *m*-cresol since only meta position can provide tribromo derivative.



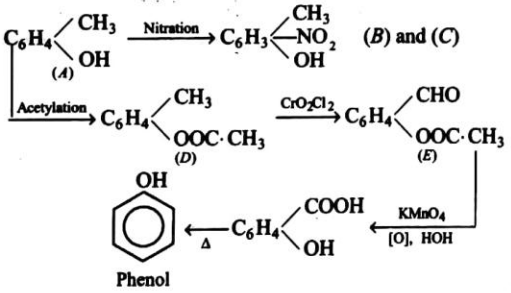
Thus,



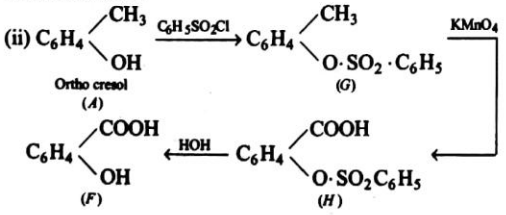
(*C*) CH_3I (Methyl iodide) (*D*)


(*E*) (2,4,6-Tribromo *m*-cresol)

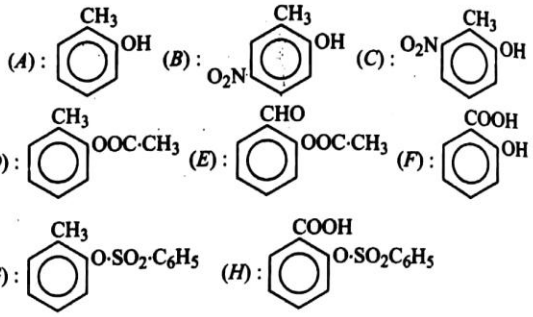
228. (i) The reactions suggest that (*A*) is $C_6H_4(CH_3)(OH)$



Since, (*F*) on heating gives phenol and thus (*F*) is ortho derivative, *i.e.*, salicylic acid. Thus, (*A*), (*D*) and (*E*) are also ortho derivative.



Thus,

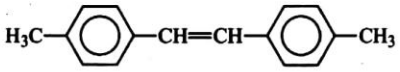


229. (i) (*A*) decolourises bromine solution and adds up one H_2 molecule and thus, (*A*) has one double bond.

(ii) Oxidation of (*A*) gives (*B*) which forms only one mono substitution product. The molecular formula of (*B*) $C_6H_4(COOH)_2$ suggests that (*B*) is,

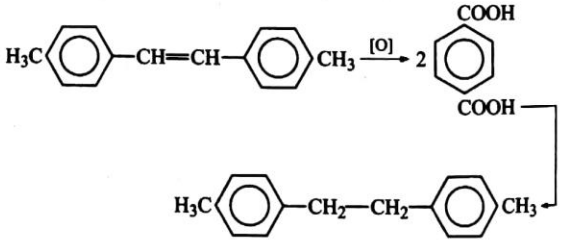
(*P*-isomer)

(iii) Keeping in view of the above facts (*A*) seems to be



1,2-Ditolyl ethene

Reactions:

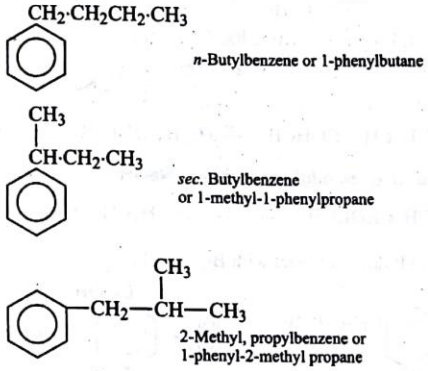


230. (1) (*A*) has mono substituted alkyl group and thus, molecular formula suggests that (*A*) is where, *R* is $-C_4H_9$.

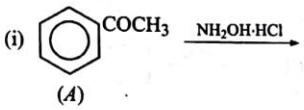
(2) The alkyl group attached on benzene ring is oxidised only if it has at least one benzylic hydrogen atom. Since, the alkyl group shows resistance to oxidation and thus, it should not have benzylic carbon atom, *i.e.*, *R* is $-C(CH_3)_3$.

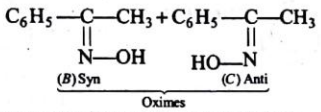
(3) Thus, (*A*) is

(4) Other (mono substituted) isomers of (*A*) are

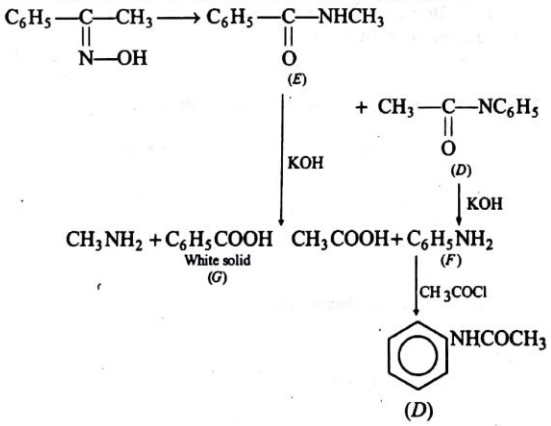


231.

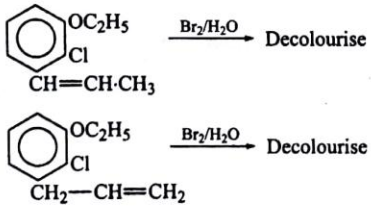




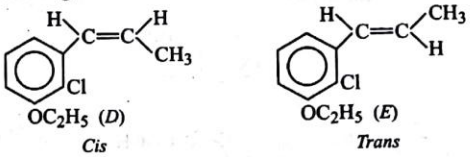
(ii) Oximes undergo Beckmann rearrangement as:

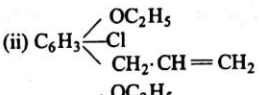


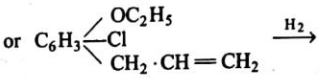
232. The properties suggests that (*A*) is,

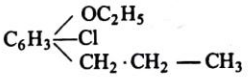


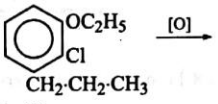
(i) Shows geometrical isomerism while (ii) does not,

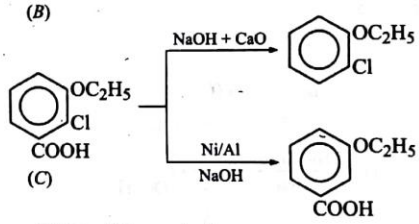


(ii) 

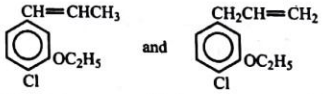
or 



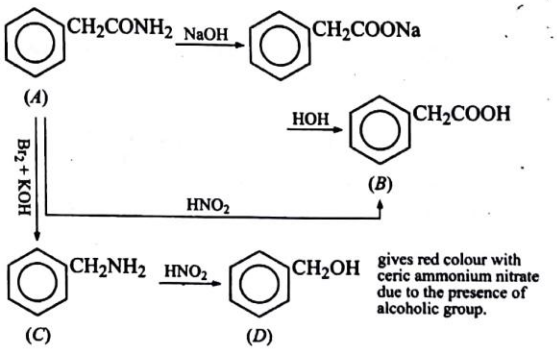




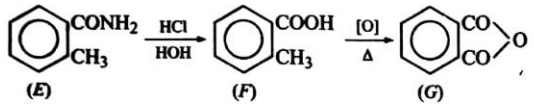
Note : (*A*) may also be



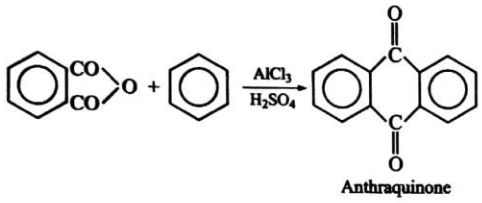
233. The statements provided suggest (*A*) to be $C_6H_5CH_2CONH_2$ having molar mass = 135 g mol^{-1}.



The reaction are



(E) (F) (G)



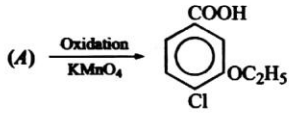
Anthraquinone

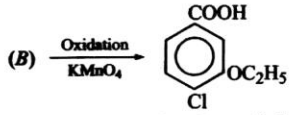
An isomer (E) of (A) is

234. (i) (A) and (B) ($C_{11}H_{13}OCl$) both are isomers and unsaturated.

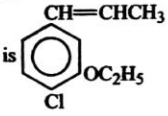
(ii) $(A) \xrightarrow{H_2} (C)$

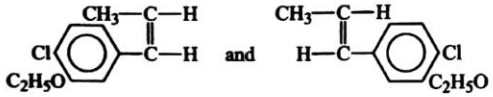
$(B) \xrightarrow{H_2} (C)$

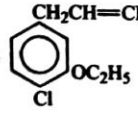
(iii) (A) 

(B) 

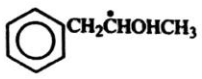
(iv) The side chain at I carbon of ring is oxidised to —COOH

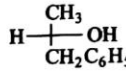
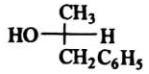
∴ (A) is  with two geometrical isomers



(B) is 

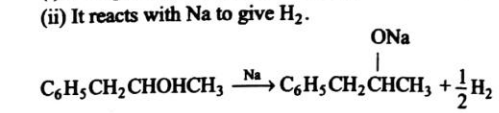
235. The statements given from (i) to (iv) suggest (A) to be:



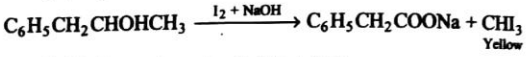
or  and 

(i) It is optically active has C* centre.

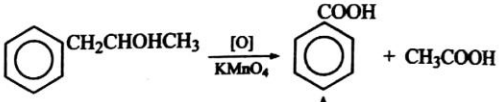
(ii) It reacts with Na to give H_2.

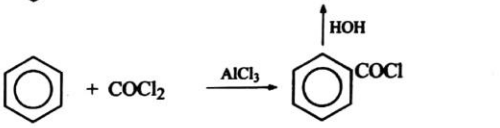


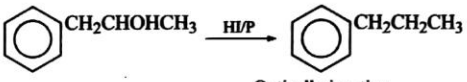
(iii) It gives iodoform with I_2 + NaOH.



(iv) It does not react with $Br_2 + CCl_4$.

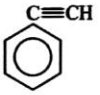
(v) 

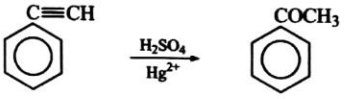


(vi) 

Optically inactive
(1-phenyl propane)

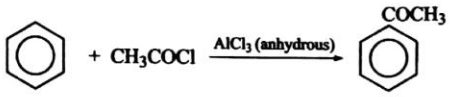
(vii) Being secondary alcohol, it gives test with Lucas reagent in about 5 minute.

236. (i) The molecular formula suggests that (A) is 

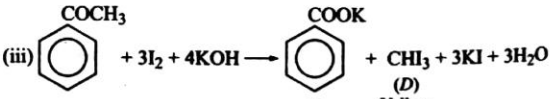
(ii) 

(A) (B)
Acetophenone

(B) can also be obtained as,



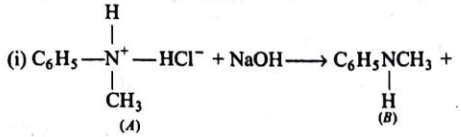
(B)

(iii) 

(D)
Yellow

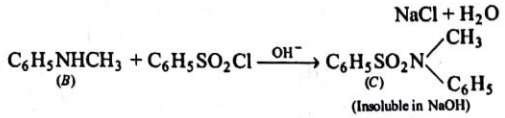
(C)

237. The given statements suggests that,



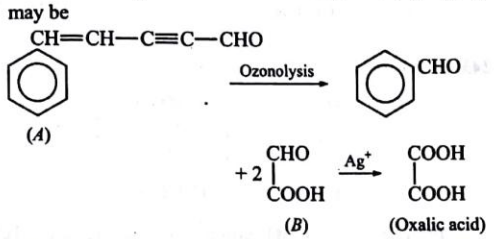
(i) $C_6H_5-\overset{H}{\underset{CH_3}{N^+}}-HCl^- + NaOH \longrightarrow \underset{H}{C_6H_5NCH_3} +$ $NaCl + H_2O$

(A) (B)



(ii) $\underset{(B)}{C_6H_5NHCH_3} + C_6H_5SO_2Cl \xrightarrow{OH^-} \underset{(C)}{C_6H_5SO_2N\begin{matrix}CH_3\\C_6H_5\end{matrix}}$ (Insoluble in NaOH)

238. The statement provides that the compound (*A*), $C_{11}H_8O$ may be

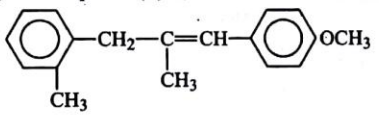


$CH{=}CH-C{\equiv}C-CHO$ —Ozonolysis→ CHO (*A*)

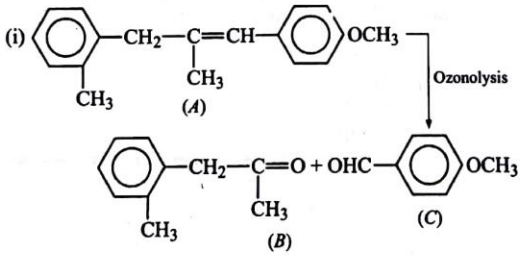
$+2$ $\underset{COOH}{\overset{CHO}{|}}$ $\xrightarrow{Ag^+}$ $\underset{COOH}{\overset{COOH}{|}}$

(*B*) (Oxalic acid)

239. The given compound (*A*) is,

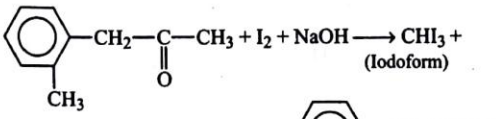


This is proved by following ahead steps.

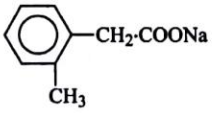


(i) $-CH_2-\underset{CH_3}{\overset{}{C}}=CH-OCH_3$ (*A*) —Ozonolysis→ $-CH_2-\underset{CH_3}{\overset{}{C}}=O + OHC-OCH_3$ (*B*) (*C*)

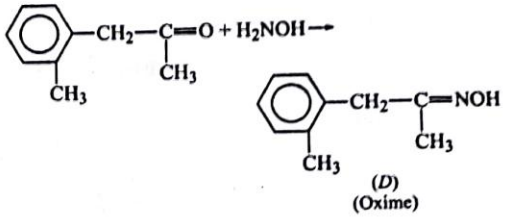
(ii) (*B*) gives iodoform test as it has $CH_3-\underset{O}{\overset{}{C}}-$ unit and produces oxime with NH_2OH.



$-CH_2-\underset{O}{\overset{}{C}}-CH_3 + I_2 + NaOH \longrightarrow CHI_3 +$ (Iodoform)



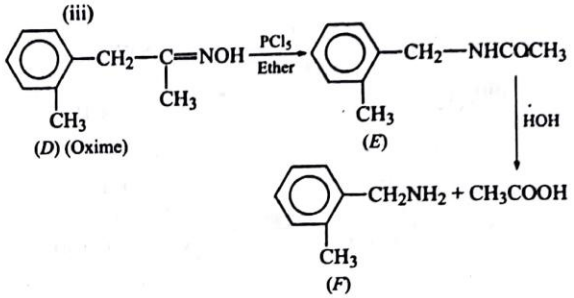
$-CH_2\cdot COONa$



$-CH_2-C=O + H_2NOH \rightarrow$ $-CH_2-C=NOH$

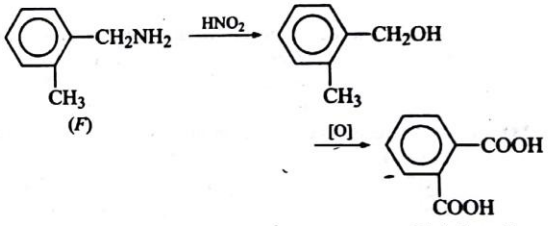
(*D*) (Oxime)

(iii)



$-CH_2-C=NOH \xrightarrow[Ether]{PCl_5}$ $-CH_2-NHCOCH_3$ —HOH→ $-CH_2NH_2 + CH_3COOH$

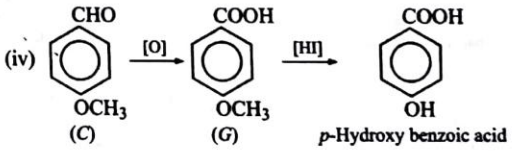
(*D*) (Oxime) (*E*) (*F*)



$-CH_2NH_2 \xrightarrow{HNO_2}$ $-CH_2OH$ —[O]→ $-COOH$ $COOH$

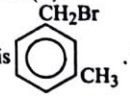
(*F*) Phthalic acid

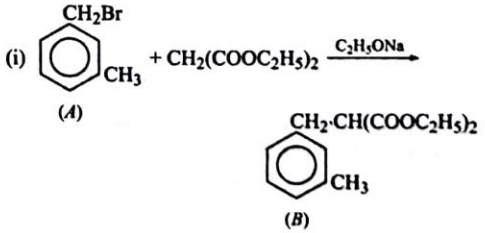
This confirms ortho position of CH_3 in ring.



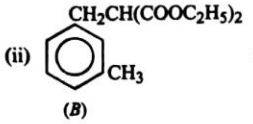
(iv) $\underset{OCH_3}{\overset{CHO}{|}}$ (*C*) $\xrightarrow{[O]}$ $\underset{OCH_3}{\overset{COOH}{|}}$ (*G*) $\xrightarrow{[HI]}$ $\underset{OH}{\overset{COOH}{|}}$ *p*-Hydroxy benzoic acid

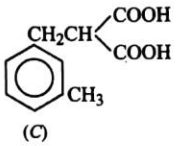
Formation of *p*-hydroxy benzoic acid confirms that two groups are at para position in (*C*).

240. The given compound (*A*) is  CH_2Br, CH_3. This is confirmed by the following findings.

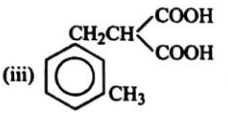


(i) $\underset{CH_3}{\overset{CH_2Br}{|}}$ (*A*) $+ CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa}$ $\underset{CH_3}{\overset{CH_2\cdot CH(COOC_2H_5)_2}{|}}$ (*B*)

(ii) 

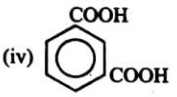
(B) + HOH $\xrightarrow{H_2SO_4}$ 

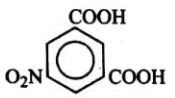
(C)

(iii) 

(C) $\xrightarrow{[O]}$

(D)

(iv) 

(D) $\xrightarrow{\text{Nitration}}$ 

(E)

The compound (*E*) a mononitro derivative in which each group is at same distance in benzene nucleus means that it is symmetrical trisubstituted (1,3,5) product and thus, two groups in (*A*), (*B*), (*C*) and (*D*) are at meta positions.

241. The statements given in the problem suggest the following compounds.

(i)

(*A*) $\xrightarrow[HOH]{H^+}$

(*B*) $\xrightarrow{CHCl_3/KOH}$

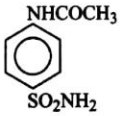
(*C*)

(*A*) Acetanilide (sparingly soluble in H_2O)

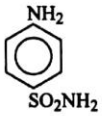
(*C*) (Carbylamine, unpleasant odour)

(ii)

(*A*) $\xrightarrow{ClSO_3H}$

(*D*) $\xrightarrow{NH_3}$ 

(*E*)

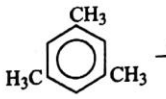
(*E*) $\xrightarrow[HOH]{H^+}$ 

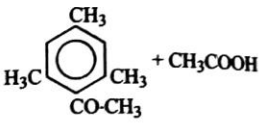
Sulphanilamide (a drug)

242. The statements given in problem suggest that (*A*) is acetic acid. The reactions are given below:

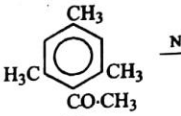
(i) $\underset{(A)}{CH_3COOH} \xrightarrow[700°C]{AlPO_4} \underset{(B)\ \text{Ketene}}{CH_2=C=O}$

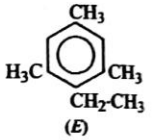
(ii) $\underset{(B)}{CH_2=C=O} + \underset{(A)}{CH_3COOH} \longrightarrow \underset{(C)}{(CH_3CO)_2O}$

(iii) $(CH_3CO)_2O$ + 

$\xrightarrow{AlCl_3}$ 

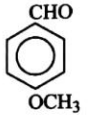
+ CH_3COOH

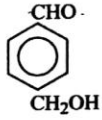
(iv) 

(*D*) $\xrightarrow{Na/Hg.HCl}$ 

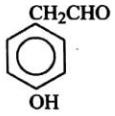
(*E*)

243. The isomers are :

(*A*) 

or 

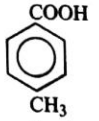
Presence of —CHO group and thus reduces Tollen's reagent.

(*B*) 

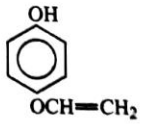
Presence of —CHO group and thus reduces Tollen's reagent. Phenolic group gives positive test with $FeCl_3(aq.)$.

(*C*)

Presence of methyl ketone group and thus gives positive iodoform test.

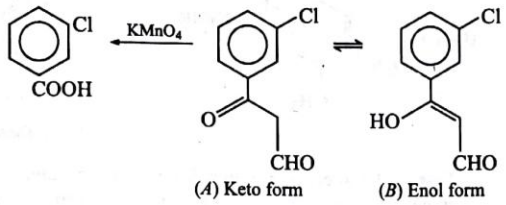
(*D*) 

Presence of carboxylic group and thus forms sodium salt of acid.

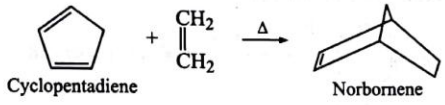
(*E*) 

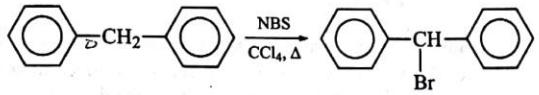
On acid hydrolysis gives 1,4-dihydroxy benzene.

244.



245.

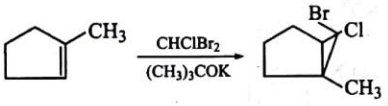
(i) 

(ii) 

246. (a) $CH_3CH_2CHClCOOH \xrightarrow{KOH\ (alc.)} CH_3CH{=}CHCOOH$

$\xrightarrow{H^+} CH_3CH^+CH_2COOH \xrightarrow{Cl^-} P$

(b) $(CH_3)_3CH \xrightarrow[h\nu]{Br_2} (CH_3)_3C{\cdot}Br \xrightarrow[2.\ D_2O]{1.\ Mg/ether} (CH_3)_3C{\cdot}D$

(c) 

(d) $CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{=}CH_2 + HC(CH_3)_3 \xrightarrow[0°C]{HF}$

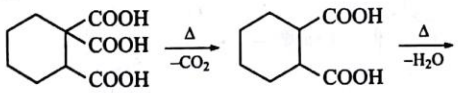
$(CH_3)_2CH{-}CH_2{\cdot}C(CH_3)_3$

(e) $RCH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} RCH_2CH_2CHO$

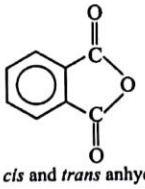
(f) $CH_3COCH_3 \xrightarrow{700°C} CH_2{=}C{=}O + CH_4$

(g) $CH_3COOH \xrightarrow{\Delta} CH_2{=}C{=}O + H_2O$

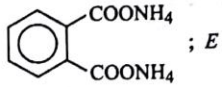
247. (a)

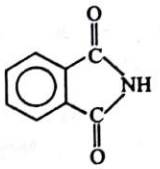


cis and *trans* cyclohexane 1,2-dicarboxylic acid



cis and *trans* anhydrides

(b) *D*: 

; *E* 

(c) A: $H_2C{=}CH{\cdot}CH_2COPh$

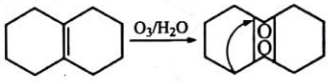
(d) $CH_2{=}CH_2$; Less substituted alkene is formed.

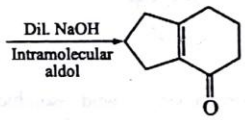
(e) $H_2C{=}CH{-}\underset{\displaystyle Ph}{\overset{|}{\underset{|}{CH}}}{-}CH_3 \xrightarrow{H^+}$

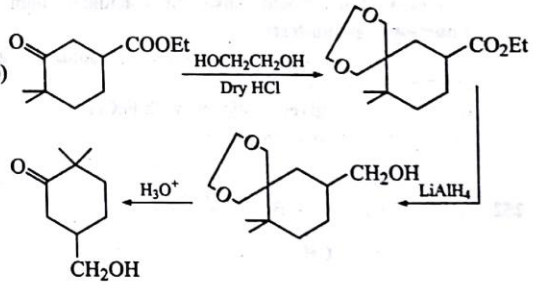
$H_3C{-}\overset{+}{C}H{-}\underset{\displaystyle Ph}{\overset{|}{\underset{|}{CH}}}{-}CH_3 \longrightarrow$

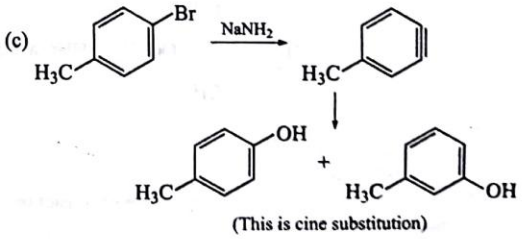
$H_3C{-}CH_2{-}\underset{\displaystyle Ph}{\overset{|}{\overset{+}{\underset{|}{C}}}}{-}CH_3 \xrightarrow[-H^+]{H_2O} CH_3{-}CH_2{-}\underset{\displaystyle Ph}{\overset{|}{\overset{OH}{\underset{|}{C}}}}{-}CH_3$

248.

(a) 

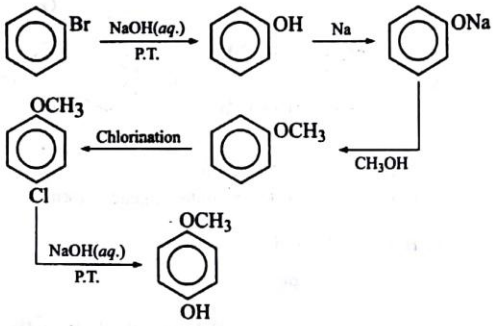


(b) 

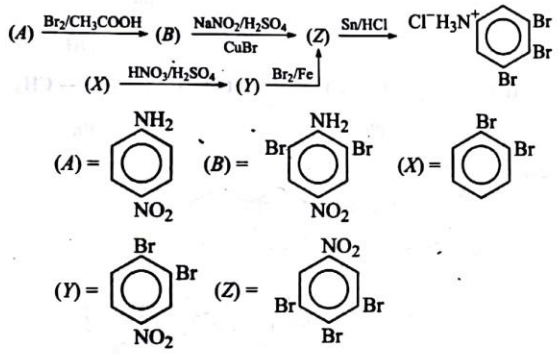
(c) 

(This is cine substitution)

249.

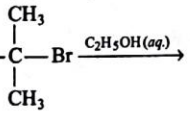


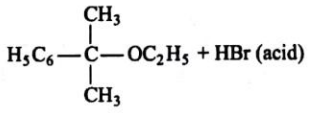
250.



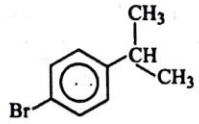
251. *p*-Amino benzoic acid—soluble in acidic medium
p-Hydroxy benzoic acid—insoluble in acidic medium.
Functional group tests:
(i) —COOH group with $NaHCO_3$ solution gives effervescences of CO_2.
(ii) —OH group gives enolic test with $FeCl_3$.
(iii) —NH_2 group gives dye test.

252. (a) (i)



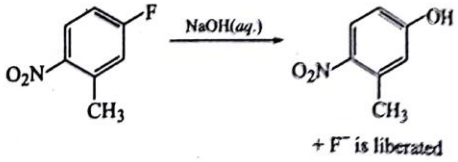


(ii)



$C_2H_5OH(aq.)$ → No reaction

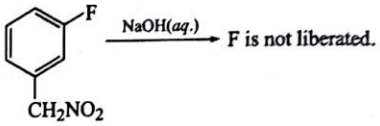
(b) (i)



+ F^- is liberated

This is a bimolecular reaction. Rate of this reaction is being enhanced by presence of electron withdrawing groups at ortho and para positions.

(ii)

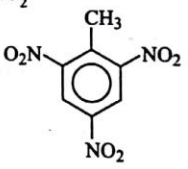


F is not liberated.

Bimolecular mechanism is not possible in this case.
(c) (i) Due to presence of lone pair on nitrogen atom NO group is electron donating and ortho, para directing.
(ii) NO_2 group is electron withdrawing and meta directing.
(d) Due to reduction of central ring, three four membered antiaromatic rings become stable while on reduction of terminal ring only one antiaromatic ring can be stabilized.

253. (*A*) H_2SO_4
(*B*) Br_2
(*C*) $NO_2^{\oplus}$

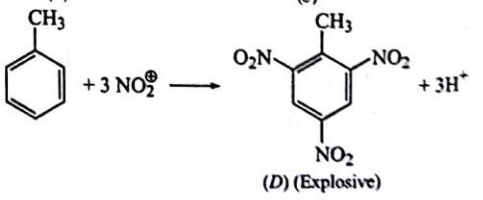
(D)



Reactions involved are:

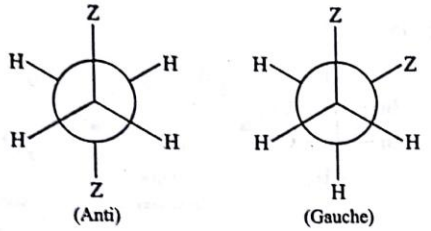
$$\underset{(A)}{2H_2SO_4} + 2NaBr + MnO_2 \longrightarrow \underset{(B)\text{ (Brown fumes)}}{Br_2} + Na_2SO_4 + MnSO_4 + 2H_2O$$

$$\underset{(A)}{H_2SO_4} + HNO_3 \longrightarrow HSO_4^- + \underset{(C)}{NO_2^{\oplus}} + H_2O$$



(*D*) (Explosive)

254. (a)



Mole fraction of anti form = 0.82
Mole fraction of Gauche form = 0.18

$$\mu_{obs} = 1$$

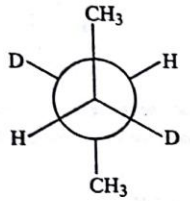
$$1 = \mu_{(anti)} \times 0.82 + \mu_{(Gauche)} \times 0.18$$

$$\mu_{(anti)} = 0$$

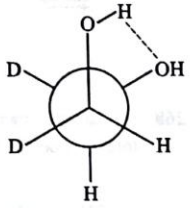
$$\therefore \quad 1 = \mu_{(Gauche)} \times 0.18$$

$$\mu_{Gauche} = \frac{1}{0.18} = 5.55\,D$$

(b) (i)



(ii)



255. 1.93, 1.97 and 2.0 respectively.

256. $H_2C{=}CH{-}\underset{[A]}{C(=O){-}H} \longleftrightarrow \overset{+}{C}H_2{-}CH{=}C(-\ddot{O}:^-){-}H \longleftrightarrow :\bar{C}H_2{-}CH{=}C(-\ddot{O}:^+){-}H$ $[B]$ $[C]$

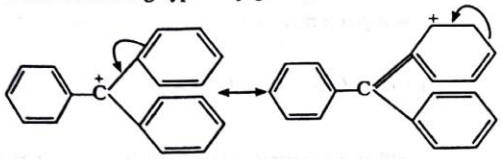
Stability order : $[A] > [B] > [C]$

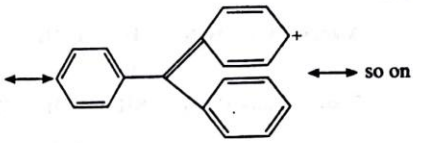
$[A]$ is more stable as it has no formal charge and have more covalent bonds with complete octet. $[B]$ has negative charge on more electronegative atom 'O' whereas $[C]$ has negative charge on less electronegative atom 'C' thus $[C]$ is less stable than $[B]$.

257. Stability order $\underset{9\,\alpha\text{-H atom}}{(CH_3)_3\overset{+}{C}} > \underset{3\,\alpha\text{-H atoms}}{CH_3\overset{+}{C}H_2} > \underset{\text{no }\alpha\text{-H atom}}{\overset{+}{C}H_3}$

The stability can be explained in terms of hypercojugation of carbocations. More is the number of α-H atoms in molecule showing hyperconjugation, more is its stability.

258.

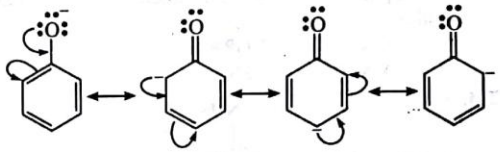




Due to the presence of three benzene rings, triphenyl methyl cation forms nine canonical structures showing exhaustive resonance stabilization.

259. $:\bar{C}{\equiv}N$ and $:\bar{N}{\rightleftharpoons}C$ are two tautomeric forms of cyanide ion $:\bar{C}N$ is less stable than $\bar{N}C$ because negative charge is present on less electronegative atoms.

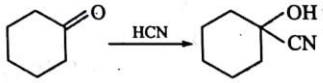
260. Phenoxide ion :

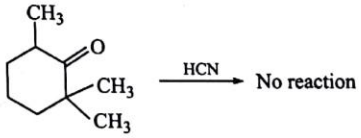


Carboxylate ion :

Carboxylate ion is more stabilized due to the presence of negative charge on more electronegative atom in both the canonical forms, whereas in phenoxide ion, negative charge also exist in less electronegative atom in all but except one canonical form.

261.





due to steric hindrance of three methyl gps at α-carbon of $>C{=}O$ gp

262. $H_2\ddot{N}{-}\overset{\ddot{O}:}{\overset{\|}{C}}{-}\ddot{N}H{-}\ddot{N}H_2 \longleftrightarrow H_2\overset{+}{N}{=}\overset{O^-}{\overset{|}{C}}{-}\ddot{N}H\ddot{N}H_2$

As a result of resonance in semicarbazide only NH_2 gp directly attached to CO gp shows a decrease in electron density (see N acquires + ve charge) and thus does not act as nucleophile. The other NH_2 gp is not involved and retains its nucleophile nature.

263. (4)

Tetrapeptide contains 3 peptide linkage and gives 4 amino acid on hydrolysis

Glycine (Gly) $H_2N{-}CH_2{-}COOH$

Alanine (Ala) $H_2N-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

Phenyl alanine (Phe) $NH_2-\underset{\displaystyle CH_2-Ph}{\underset{|}{CH}}-COOH$

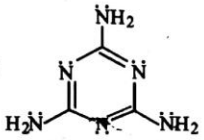
Valine (Val) $H_2N-\underset{\displaystyle CH-CH_3}{\underset{|}{CH}}-COOH$ (CH_3 below CH)

Since tetrapeptide contains free COOH at alanine so that alanine is last unit of tetrapeptide. Glycine does not contain chiral carbon so that Glycine cannot be at first position in tetrapeptide. Hence possible structure of this tetrapeptide will be 4

PVGA VGPA

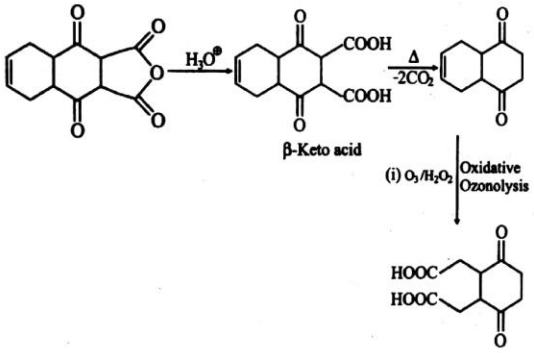
PGVA VPGA

264. (6)

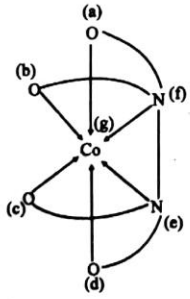
Melamine is 

Number of lone pairs on melamine = 6

265. (2)



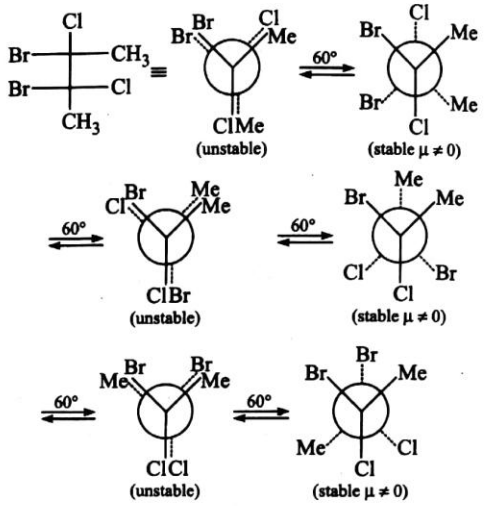
266. (8)

EDTA is 

N—Co—O bond angles are

agf, bgf, egf, dgf, age, bge, cge, dge

267. (3)



268. (5) Stereoisomers also react separately with $NaBH_4$. The total number of ketones that give a racemic product(s) are :

(a) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

will not give a racemic mixture on reduction with $NaBH_4$

(b) $CH_3-CH_2-CH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

(c) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

(d) $H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

(e) $CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

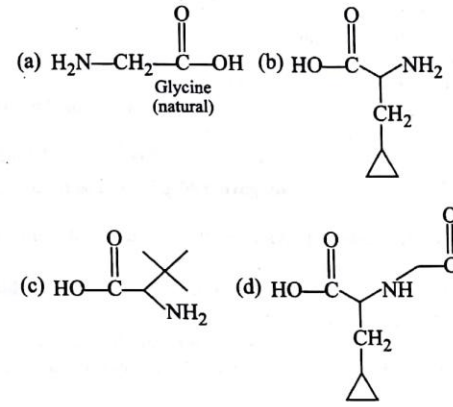
will give a racemic mixture on reduction with $NaBH_4$

(f) $CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

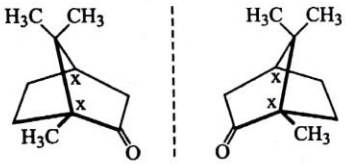
269. (1)

This peptide on complete hydrolysis produced 4 distinct amino acids which are given below :



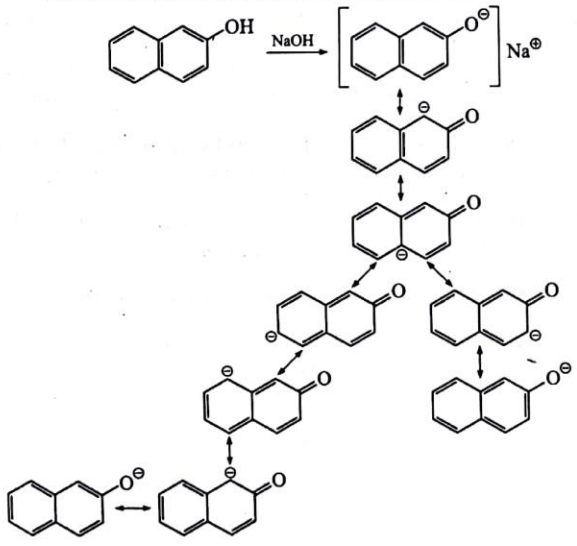
Only glycine is naturally occurring amino acid

270. (2) *M* is an organic compound known as camphor. It contains two **rigid** chiral centre so it can exist only in **two** enantiomeric forms.

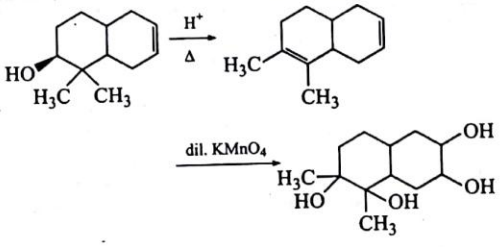


271. (9)

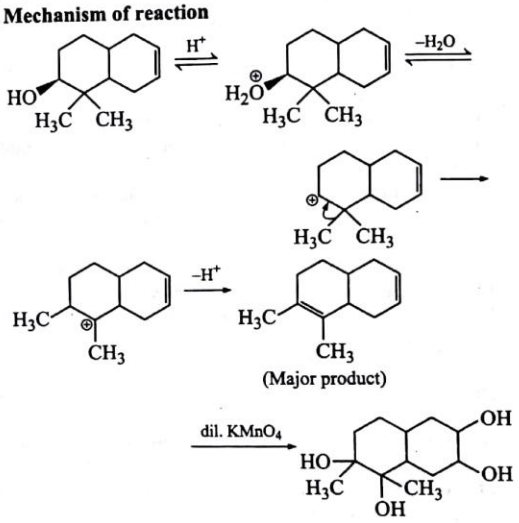
Reaction of β-naphthol gives sodium salt. Given below are resonance structure of anion of sodium salt formed.



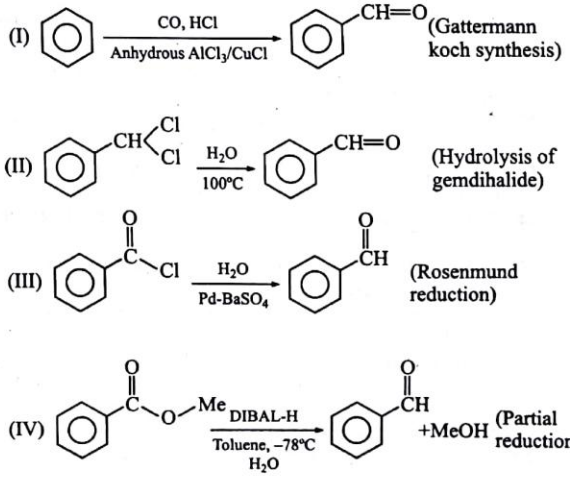
272. (4)



Mechanism of reaction

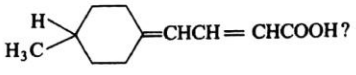


273. (4)

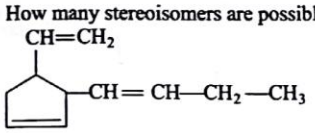


• SINGLE INTEGER ANSWER PROBLEMS •

1. Volume ratio of gases evolved (at NTP) at cathode and anode during the electrolysis of $HCOONa_{(aq.)}$ is .....
2. Volume ratio of gases evolved (at same P and T) at cathode and anode during the electrolysis of $CH_3COONa_{(aq.)}$.
3. Mole ratio of gases evolved at cathode and anode during the electrolysis of $CH_3(CH_2)_2COONa_{(aq.)}$:
4. The number of α-H atoms in 2-methyl but-2-ene is .....
5. The maximum number of tautomers of a compound can be .....
6. The compound shows metamerism. It must possess a functional group which has valence equal to or greater than .....
7. A molecule having formula C_7H_8O can show maximum number of aromatic isomers :
8. The number of α-H atoms in but-2-ene is .....
9. Number of acidic hydrogen, in the molecule $CH_3CO{\cdot}CHI{\cdot}CO{\cdot}CH_3$:
10. The number of possible structural and stereo isomers that can be produced during monochlorination of 2-methyl butane are .....
11. The degree of unsaturation in cyclobutanone is .....
12. The degree of unsaturation in benzene is .....
13. The maximum number of acidic hydrogen in a molecule of C_6H_{10} is :
14. The number of C=O bonds in Ninhydrin is :
15. The number optical isomers of cyclic alcohol having molecular formula C_4H_7OH.
16. Alkaline solution of glucose shows an equilibrium. The number of molecules involved in equilibrium are .....
17. A polyene has four double bonds. Maximum no. of products that can be formed on ozonolysis are :
18. Number of π-bonds in allyl cyanide is .....
19. Number of H-atoms in glycine is .....
20. Number of pairs of *cis-trans* isomers for the compound having molecular formula $C_2IBrClF$:
21. Number of enantiomeric pairs obtained on monochlorination of 2-methyl butane :
22. Total number of molecules having disubstitution nature for the molecular formula C_6H_{14} :
23. The number of enantiomeric pairs formed on monochlorination of 2-methyl butane :
24. The number of 2° carbon atoms in 2,2,4-trimethyl hexane are .....
25. The number of diastereoisomeric pair of the compound $CH_3CHOH{\cdot}CHBr{\cdot}CH_3$ are .....
26. Total enantiomeric pairs of compound sorbitol $CH_2OH(CHOH)_4CH_2OH$ are .....
27. Total number of meso isomers of sorbitol are .....
28. Number of *p*-orbitals left unused in *sp*-hybridized carbon atom .....
29. Number of asymmetric carbon atoms in glucose is .....
30. Number of 4° carbon atoms in 2,2,4,4-tetramethyl pentane is .....
31. An alkane forms monosubstitution products. The minimum number of carbon atoms in it should be .....
32. The ratio of asymmetric carbon atoms and number of enantiomeric pairs of butan-2,3-diol is .....
33. Number of π-bonds in tetra cyanomethane is .....
34. *d*-2-iodobutane on treatment with NaI in acetone produces how much optically active forms .....
35. 0.22 g of organic compound C_xH_yO occupied 112 mL at NTP and on combustion gave 0.44 g CO_2. The ratio of $y:x$ is .....
36. Possible number of alkanes with molecular formula C_7H_{16} are .....
37. Which ratio of CH_4 and O_2 on heating in presence of Cu or Fe at high pressure yields CH_3OH?
38. The molar mass of an organic compound is 64 g mol^{-1}. If it is assumed that vapour density of CH_4 is one, the vapour density of compound will be .....
39. Number of molecules of alkene required for the reaction of one molecules of B_2H_6 to carry out hydroboration .....
40. 11.43 g of Br_2 reacts with how much pent-1-ene?
41. 1.60 g Br_2 reacts with 1.12 g alkene. The number of carbon atoms in alkene is .....
42. The silver salt of an unknown alkyne contains 67.08% Ag. Assuming no other functional gp, the number of carbon atoms in alkyne is .....
43. Number of ethyl alcohol molecules absorbed by one molecule of $MgCl_2$:
44. One mole of glycerol is completely acylated. The number of moles of acetyl chloride needed are .....
45. The ratio of number of carbon atom to number of oxygen atoms in [18]-crown-6-molecules are .....
46. 0.037 g of an alcohol *R*—OH on treatment with CH_3MgI gives 11.2 cm^3 gas at STP. The number of carbon atoms in alcohol are .....
47. A straight chain organic compound $C_3H_8O_3$ yields $C_9H_{14}O_6$ on complete acetylation. The number of hydroxyl groups in $C_3H_8O_3$ are .....
48. A polyhydric alcohol having molecular formula $C_5H_{12}O_5$ is changed to $C_{13}H_{20}O_9$ on treatment with acetic anhydride. No. of OH gp in alcohol is .....
49. Benzil (PhCOCOPh) is completely reduced by $LiAlH_4$. Number of possible stereomers of molecule obtained after reduction is .....
50. The ratio of carbon and oxygen atoms in 2-methyl benzoic acid is .....
51. Maximum number of stereo isomers of the compound 2,3,5,6-tetrachloroheptane are .....
52. How many isomers are possible for



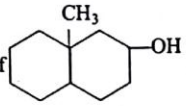
53. How many stereoisomers are possible for



54. How many isomers are possible for C_3H_6DCl?

55. Number of basic nitrogen atoms in purine is .....

56. The number of stereo isomers of



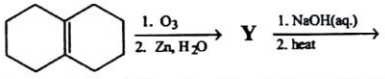
.....

57. How many structural isomers are possible when one of the hydrogen in diphenyl methane is replaced by a halogen.

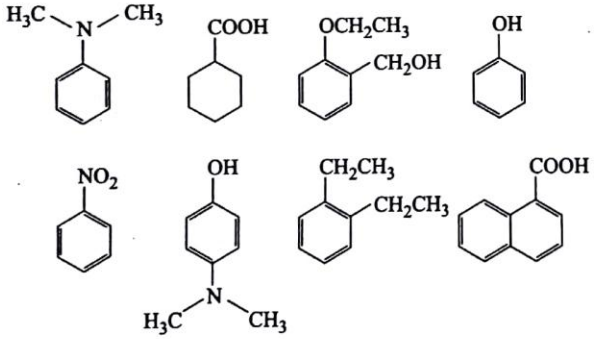
58. The number to chiral centres present in 3,4-dibromo-2-pentanol is .....

59. The total number of cyclic as well as stereoisomers possible for a compound with the molecular formula C_5H_{10} is : **(IIT 2009)**

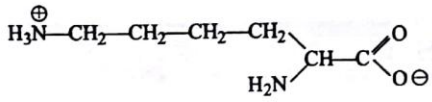
60. In the scheme given below, the total number of intramolecular aldol condensation products formed from **'Y'** is : **(IIT 2010)**



61. Amongst the following, the total number of compounds soluble in aqueous NaOH is : **(IIT 2010)**



62. The total number of basic groups in the following form of lysine is : **(IIT 2010)**

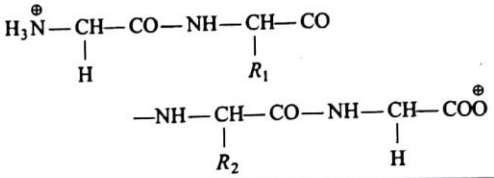


63. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is : **(IIT 2010)**

64. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclo pentyl hexane using alcoholic KOH is : **(IIT 2011)**

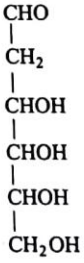
65. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the compound $CH_3CH_2CH(CH_3)CH_2CH_3$: **(IIT 2011)**

66. The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0? **(IIT 2012)**

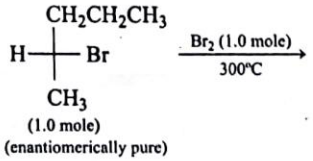


Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H
IV	CH_2CONH_2	$(CH_2)_4NH_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

67. When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form is: **(IIT 2012)**



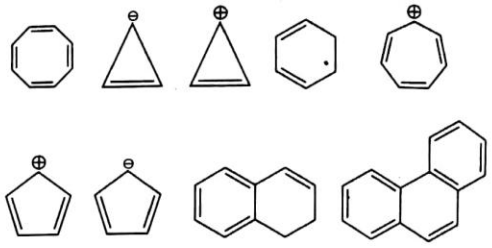
68. In the following monobromination reaction, the number of possible chiral products is :



(1.0 mole)
(enantiomerically pure)

[JEE (Advanced) I 2016]

69. Among the following, the number of aromatic compound(s) is: **[JEE (Advanced) I 2017]**

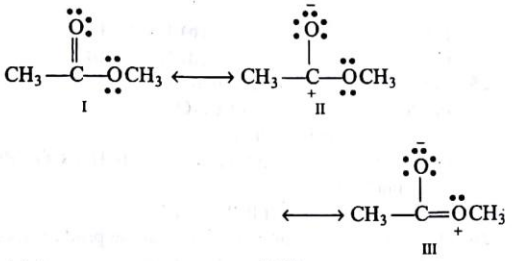


ANSWERS

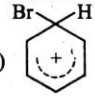
1. Three	**2.** Three	**3.** Two	**4.** Nine	**5.** Two	**6.** Two	**7.** Five	**8.** Six	**9.** One	**10.** Six	**11.** Two	**12.** Four
13. One	**14.** Three	**15.** Two	**16.** Three	**17.** Five	**18.** Three	**19.** Five	**20.** Three	**21.** Two	**22.** Two	**23.** Two	**24.** Two
25. Four	**26.** Four	**27.** Two	**28.** Two	**29.** Four	**30.** Two	**31.** Three	**32.** Two	**33.** Eight	**34.** Two	**35.** Two	**36.** Nine
37. Nine	**38.** Four	**39.** Six	**40.** Five	**41.** Eight	**42.** Four	**43.** Six	**44.** Three	**45.** Three	**46.** Four	**47.** Three	**48.** Four
49. Three	**50.** Four	**51.** Eight	**52.** Four	**53.** Eight	**54.** Eight	**55.** Three	**56.** Eight	**57.** Four	**58.** Three	**59.** Seven	**60.** One
61. Four	**62.** Two	**63.** Six (4+2)		**64.** Five	**65.** Eight	**66.** Eight	**67.** Eight	**68.** Five	**69.** Five		

OBJECTIVE PROBLEMS (One Answer Correct)

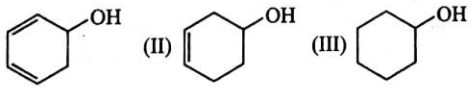
1. Which are ambiphiles or ambidents?
   (a) CH_3CN (b) HCHO
   (c) HF (d) All of these
2. Which of the following canonical structure is more contributor to real structure?



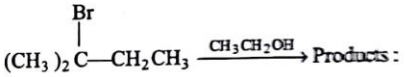
   (a) I (b) II
   (c) III (d) All of these
3. The intermediate formed in bromination of benzene is :



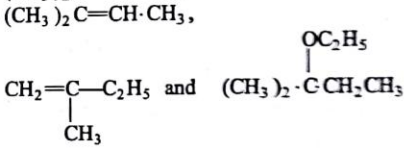
   (a) Br^+ (b)
   (c) Br^- (d) $C_6H_5Br^-$
4. The order of ease of dehydration for given alcohols :



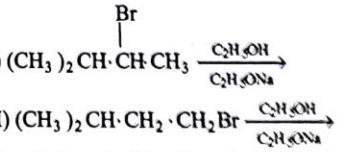
   (a) III < II < I (b) I < II < III
   (c) II < I < III (d) I < III < II
5. The IUPAC name of $CH_3CH(OH)\cdot CH_2\cdot C(C_2H_5)(OH)\cdot CH_3$ is :
   (a) 2-methyl-2,4-pentanediol
   (b) 4-methyl-2,4-hexanediol
   (c) 3-methyl-3,5-hexanediol
   (d) none of the above
6. The Hitler army sign, *i.e.*, reverse of 'Swastik' represents which compound :
   (a) 2,2-dimethyl butane (b) 3,3-dimethyl hexane
   (c) 2,3-dimethyl pentane (d) 3,3-diethyl pentane
7. Which of the following is correct about ionisation energy and electron affinity of methyl free radical ($\dot{C}H_3$)?
   (a) $IE = EA$ (b) $IE > EA$
   (c) $IE < EA$ (d) Nothing can be said
8. The correct decreasing order of nucleophilicity of the following is :
   (a) $RCOO^- > HO^- > RO^-$ (b) $RO^- > OH^- > RCOO^-$
   (c) $RO^- > RCOO^- > OH^-$ (d) $H^-O > RO^- > RCOO^-$
9. Which of the following shows heterovalent resonance ?
   (a) CO_3^{2-} (b) C_6H_6
   (c) CO_2 (d) $CH_2=CH-CH=CH_2$
10. Which of the following hydrate will be more stable ?
    (a) $Br_2CHCH(OH)_2$ (b) $Br_2CH\cdot CH_2CH(OH)_2$
    (c) $CH_3CH(OH)_2$ (d) $BrCH_2CH(OH)_2$
11. Which of the following carbonyl compound will show addition of HCN?
    (a) $(CH_3)_2CH\cdot COCH(CH_3)_2$
    (b) $C_6H_5CO\cdot C_6H_5$
    (c) CH_3COCH_3
    (d) All of the above
12. Predict the products formed in the reaction



    (a) $(CH_3)_2C=CH\cdot CH_3$
    (b) $(CH_3)_2C=CH\cdot CH_3$,



    (c) $CH_2=C(CH_3)-C_2H_5$ only
    (d) $(CH_3)_2C=CH\cdot CH_3$ and $CH_2=C(CH_3)-C_2H_5$ only
13. The product formed during β-elimination in the reaction is :



    (a) only 2-methyl but-2-ene in I and II
    (b) 3-methyl but-1-ene in II and 2-methyl but-2-ene and 3-methyl but-1-ene in I
    (c) 2-methyl but-2-ene and 3-methyl but-1-ene in II and 2-methyl but-2-ene in I
    (d) all the three enes in I and II
14. S_N1 reactions take place fastest in the medium :
    (a) H_2O (b) CH_3OH
    (c) C_6H_6 (d) acetone
15. 1-bromo-3-chloropropane on treating with aq. NaCN gives :
    (a) $Cl\cdot CH_2CH_2CN$ (b) $Br\cdot CH_2\cdot CH_2CN$
    (c) $Cl\cdot CH_2\cdot CH_2CH_2CN$ (d) $Br\cdot CH_2\cdot CH_2\cdot CH_2CN$
16. An optically active compound is 50% optically pure then for 100 g sample of this means :
    (a) one enantiomer is 50% and the other enantiomer is absent

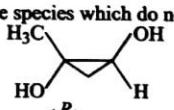
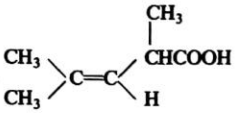
(b) one enantiomer is 50% and the other enantiomer is also 50%
(c) one enantiomer is 75% and the other enantiomer is 25%
(d) the compound has no optical activity

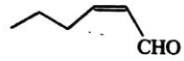
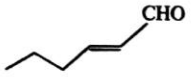
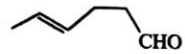
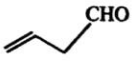
17. The simplest chiral alkanes have molar mass ..... and the number is .....
(a) 100, 2 (b) 86, 1
(c) 100, 1 (d) 114, 1

18. The molecule $CH_3CH{=}CH{\cdot}CH(CH_3)OH$ can show :
(a) Geometrical isomerism only
(b) Optical isomerism only
(c) Structural isomerism only
(d) Structural and stereoisomerism including geometrical and optical both

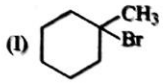
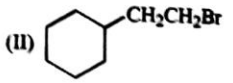
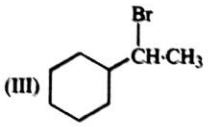
19. 2-methyl-1-chloro butane an optically active alkane on subjecting for Wurtz reaction gives :
(a) Optically inactive 3,6-dimethyl octane
(b) Optically active 2,6-dimethyl octane
(c) Optically active 3,6-dimethyl octane
(d) Optically inactive 2,6-dimethyl octane

20. Select the correct statement :
(a) $R_1C^{\oplus}$ in a carbocation is chiral carbon
(b) $R_2C^{\bullet}$ in a free radical is chiral carbon
(c) R_3C^{-} in a carbanion is a chiral carbon
(d) sp^2 carbon in oximes and imines are chiral

21. The species which do not possess chirality :
(a) 
(b)
(c) 
(d) CH_3CDHCl

22. The correct structure of *trans*-2-hexenal is :
(a) 
(b) 
(c) 
(d) 

23. One of the chain termination step in the halogenation of alkanes other than methane is :
(a) Addition reaction
(b) Neutralisation reaction
(c) Elimination reaction
(d) Disproportionation reaction

24. The correct decreasing order for dehydrohalogenation for the given halides is :
(I) 
(II) 
(III) 
(a) I > III > II (b) I > II > III
(c) III > I > II (d) II > I > III

25. Which one is not correctly matched ?
(a) Adkin's catalyst ($CuO{\cdot}Cr_2O_4$)
(b) Adam's catalyst (PtO_2)
(c) Lindlar's catalyst Pd on $CaCO_3 + (CH_3COO)_2Pb$ and quinolene
(d) Wilkinson catalyst $P(Ph_3)_2Cl_2$

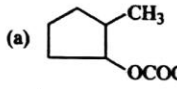
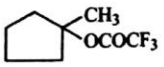
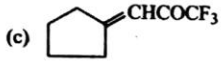
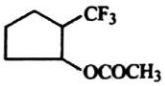
26. Which of the reactant does not form the product according to peroxide effect on 2-methyl propene ?
(a) CH_3SH (b) $CBrCl_3$
(c) $CHCl_3$ (d) None of these

27. Which of the following can be used for hydroxylation of alkene ?
(a) OsO_4/pyridine followed by hydrolysis by $Na_2SO_3 + NaHSO_3$
(b) Baeyer's reagent at room temperature
(c) HCOOH followed by hydrolysis
(d) All of the above

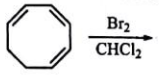
28. The degree or element of unsaturation (DU) is given by the formula $DU = \frac{2n_1 + 2 - n_2}{2}$; where n_1 and n_2 are number of C and H or Cl-atoms respectively. Which can be said about degree of unsaturation :
(a) DU = 1 mean on olefinic bond or one ring
(b) DU = 2 means two olefinic bond or one triple (C≡C) bond, two C=C or two rings or one ring with C=O bond
(c) DU = 0 mean no unsaturation
(d) All of the above

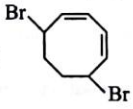
29. The number of optical isomers of alkyne C_6H_{10} are :
(a) 2 (b) 4
(c) 6 (d) 8

30. Which one represents the product of the reaction given below ?

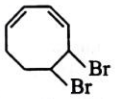
(a) 
(b) 
(c) 
(d) 

31. The product formed in the reaction is :



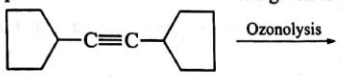
(a) 

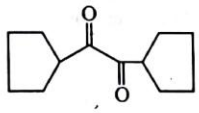
(b) $C_8H_{10}Br_6$

(c) 

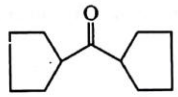
(d) none of these

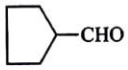
32. The product formed in the reaction given is :



(a) 

(b)

(c) 

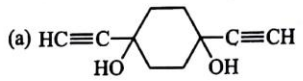
(d) 

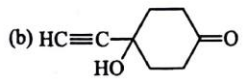
33. Which of the following does not react with propynide ion ?
(a) H_2O (b) CH_3OH
(c) $NH_3(l)$ (d) 1-hexene

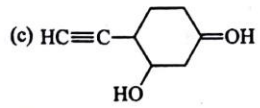
34. Which of the following is not dissolved in conc. H_2SO_4 :
(a) Acetylene (b) Ethane
(c) But-2-yne (d) Propene

35. How many terminal alkynes isomers are possible for the formula C_6H_{10} :
(a) 2 (b) 3
(c) 4 (d) 5

36. The product of the reaction of cyclohexa-1,4-dione with acetylene in acidic medium is :

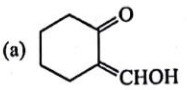
(a) 

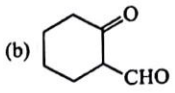
(b) 

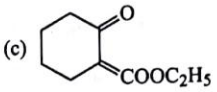
(c) 

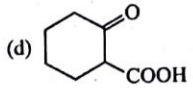
(d) No reaction

37. The major reaction product of combination of cyclohexanone with ethyl formate in presence of C_2H_5ONa is :

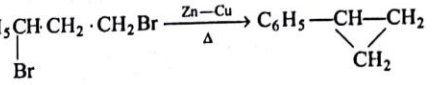
(a) 

(b) 

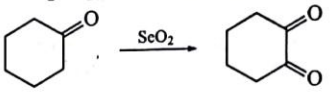
(c) 

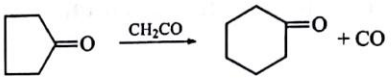
(d) 

38. Which of the following reaction is not correct ?

(a) 

(b) $ClCH_2CH_2CH_2CN \xrightarrow{\text{Conc.NaOH}} HO\cdot CH_2\cdot CH_2\cdot CH_2CN$

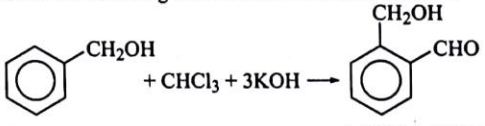
(c) 

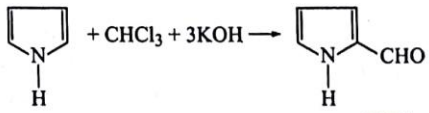
(d) 

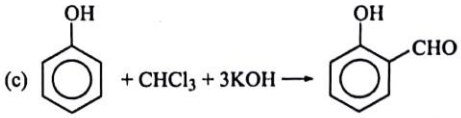
39. 1,2-dibromo cyclohexane on treatment with base yields 1,3-cyclohexadiene and not cyclohexyne. The reason is :
(a) H-atoms are not available at 1,2-positions
(b) elimination of HBr takes place
(c) a triple bond in a small ring is not favourable
(d) all of the above

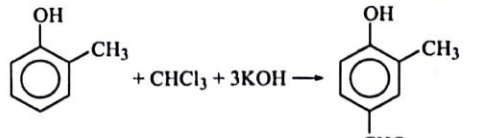
40. Carbocations do not gain stability by :
(a) Hydride shift (b) Methyl shift
(c) Phenyl shift (d) Ethyl shift

41. Which of the following is not Reimer-Tiemann reaction :

(a) 
$+ 3KCl + 2H_2O$

(b) 
$+ 3KCl + 2H_2O$

(c) 
$+ 3KCl + 2H_2O$

(d) 
$+ 3KCl + 2H_2O$

42. Which of the following statement is wrong ?
(a) H_2O is a poor nucleophile and good leaving group
(b) OH^- is a good nucleophile and good leaving group
(c) F^- is a good nucleophile but poor leaving group
(d) I^- is a poor nucleophile but good leaving group

43. Select the wrong statement :
(a) Nucleophilicity of nucleophile is its ability to donate electron pair to metal ion
(b) Basic nature of a base is its ability to donate electron pair to a proton
(c) Nucleophilicity of a nucleophile is its ability to donate electron pair to a carbocation (or an electrophile)
(d) Nucleophiles may or may not carry –ve charge

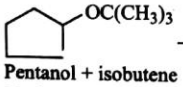
44. Which of the following compound on reacting with Mg will give Grignard reagent ?
(a) $HOCH_2CH_2CH_2Br$ (b) $CH_3C{\equiv}CCH_2CH_2I$
(c) $Br{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OH$ (d) $CH_3\underset{\underset{NH_2}{|}}{CH}{-}CH_2\cdot CH_2Br$

45. Select the wrong statement :
(a) Al isopropoxide is a specific reducing agent for aldehydes and ketones having some other reducible groups like $>C{=}C<$, $-C{\equiv}C-$, $-NO_2$, etc.
(b) Al terbutoxide oxidises 1° and 2° alcohols into aldehydes and ketones respectively
(c) Nucleophilicity is increased with the number of electron repelling group R irrespective of the nature of R
(d) $CH_2\cdot CH_2Cl$ is a weaker base than $CH_3CH_2O^-$

46. Which of the following will not give iodoform test?
(a) Pyruvic acid (b) Benzophenone
(c) Lactic acid (d) Acetophenone

47. Which fact does not support about the use of $ZnCl_2$ with HCl in Lucas reagent test for the test of alcohols ?
(a) $ZnCl_2$ is a Lewis acid
(b) It forms H_2ZnCl_4 with HCl which is stronger acid than HCl
(c) H_2ZnCl_4 reacts with alcohols to form $R^{\oplus}$ readily
(d) $ZnCl_2$ reacts with alcohol to form R^+ readily

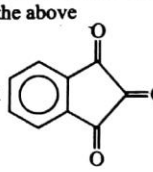
48. Ethoxy ethanol and methyl isopropyl ether can be distinguished by :
(a) conc. HI (b) iodoform test
(c) Amm. $AgNO_3$ (d) $ZnCl_2$

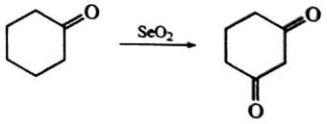
49. In,  ; the products are :
(a) Pentanol + isobutene
(b) Cyclopentanol + isobutene
(c) Cyclopentene + isobutanol
(d) Cyclopentanol + propene

50. The product formed in the reaction :
$$Ph\cdot CH_2CH_2COCl + H_2 \xrightarrow[S \text{ or quinoline}]{Pd/C} \text{is :}$$
(a) $Ph\cdot CH_2CHO$ (b) $PhCH_2CH_2CH_2OH$
(c) $Ph\cdot CH_2\cdot CH_2CHO$ (d) $PhCH_2CH_2CH_3$

51. Which of the following statement about carbonyl compounds is correct ?
(a) α-H atom is acidic
(b) The anion left after removal of H^+ is stabilised enolate anion
(c) The base, catalysed aldol condensation is due to the acidic nature of α-H-atom
(d) All of the above

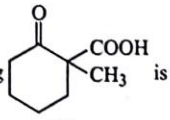
52. Conversion of carbonyl group of a molecule to methylene group cannot be done successfully if substrate :
(a) contains alkali sensitive group, in case of Wolff Kishner reduction
(b) contains acid sensitive group, in case of Clemmensen reduction
(c) is sterically hindered ketone, in case of Clemmensen reduction or Wolff Kishner reduction
(d) all of the above

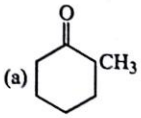
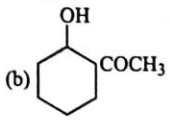
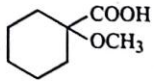
53. Ninhydrin  , exists as a hydrate. Which C=O is hydrated :
(a) Top one (b) Middle one
(c) Bottom one (d) All of these

54. Which one does not correctly represents the oxidation by SeO_2?
(a) 
(b) $C_6H_5\cdot CH_2\cdot \underset{\underset{O}{\|}}{C}\cdot C_6H_5 \xrightarrow{SeO_2} C_6H_5\cdot \underset{\underset{O}{\|}}{C}\cdot \underset{\underset{O}{\|}}{C}\cdot C_6H_5$
(c) $CH_3COCH_2CH_3 \xrightarrow{SeO_2} CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}\cdot CH_3$
(d) $C_6H_5COCH_3 \xrightarrow{SeO_2} C_6H_5\,\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{CH}$

55. Benzaldehyde do not respond test for —CHO group by Fehling's solution or Benedicts solution because :
(a) it does not contain α-H-atom
(b) it is aromatic aldehyde
(c) it undergoes Cannizzaro reaction due to alkaline nature of these reagent
(d) all of the above

56. $C_nH_{2n}O_2$, a saturated monocarboxylic acid formula does not represent its isomerism with :
(a) esters
(b) hydroxy carbonyl compounds
(c) hydroxy oxiranes
(d) anhydrides

57. The product formed on heating  is :

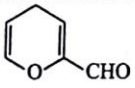
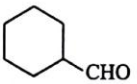
(a) 
(b) 
(c) 
(d) $C_6H_{11}OCH_3$

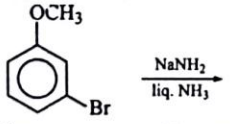
58. Which is not correct about fumaric and maleic acid?
(a) K_2 of fumaric acid is more than maleic acid
(b) Maleiate ion shows H-bonding
(c) Fumarate ion shows H-bonding
(d) Maleiate ion is less stable than fumarate ion

59. The correct order for increasing stability is :
(a) $C_6H_{11}\overset{+}{C}H_2 < C_6\overset{+}{H}_{11} < C_6H_{11}\overset{+}{C}(CH_3)_3$
(b) $C_6\overset{+}{H}_{11} < C_6H_{11}\overset{+}{C}H_2 < C_6H_{11}\overset{+}{C}(CH_3)_3$
(c) $C_6H_{11}\overset{+}{C}(CH_3)_3 < C_6H_{11}\overset{+}{C}H_2 < C_6\overset{+}{H}_{11}$
(d) $C_6H_{11}\overset{+}{C}H_2 < C_6H_{11}\overset{+}{C}(CH_3)_3 < C_6\overset{+}{H}_{11}$

60. Which type of nitroalkanes do not show tautomerism ?
(a) *p*-nitro alkanes (b) *s*-nitro alkanes
(c) *t*-nitro alkanes (d) None of these

61. Which alkyl halide cannot be used for alkylation of amines ?
(a) 3° halide (b) Allyl and vinyl halide
(c) β-alkyl halide (d) All of these

62. Which will not show Cannizzaro reaction ?
(a)  (b) $C_6H_5COCHCl_2$
(c) $(CH_3)_3CCHO$ (d) 

63. The product formed in the reaction are :

(a) *o*-anisidine (b) *m*-anisidine
(c) *p*-anisidine (d) all of these

64. Total structural isomers of C_4H_8 are :
(a) 2 (b) 3
(c) 4 (d) 5

65. Cyclic isomers of C_5H_{10} are :
(a) 1 (b) 3
(c) 4 (d) 5

66. Which cycloalkane does not exhibit geometrical isomerism?
(a) 1,2-dimethyl cyclo propane
(b) 1,1,2-trimethyl cyclo propane
(c) 1,3,5-trimethyl cyclo hexane
(d) 1,2-dimethyl cyclo butane

67. *Cis*-but-2-ene on heating with I_2 gives :
(a) *trans*-but-2-ene (b) 1,2-di iodo butane
(c) 1,1-di iodo butane (d) no reaction

68. How many isomers of C_6H_{12} can be hydrogenated to give 2-methyl pent-1-ene?
(a) 2 (b) 3
(c) 4 (d) 5

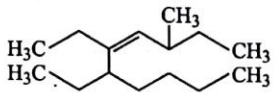
69. Which represents the increasing stability order at room temperature for :
(I) *n*-pentane; (II) iso pentane; (III) neo pentane?
(a) I < II < III (b) III < II < I
(c) II < III < I (d) I < III < II

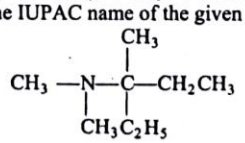
70. The total cyclic alcoholic isomers of C_4H_7OH and the number of chiral molecules respectively are :
(a) 5, 2 (b) 5, 3
(c) 4, 2 (d) 4, 3

71. Which one is not correctly matched ?
(a) Carbocation-sp^2-trigonal planar
(b) Carbanion-sp^3-pyramidal
(c) Me^+-sp^2-trigonal planar
(d) Singlet carbene-sp^2-coplanar

72. Which is not a characteristic of triplet carbene ?
(a) *sp*-linear
(b) Two bond pair of electron and no lone pair of electron
(c) Two electrons with same spin in different orbitals
(d) Two electrons with opposite spin in one orbital

73. Which of the following nitroalkanes is insoluble in alkalies :
(a) *p*- (b) *s*-
(c) *t*- (d) all of these

74. The IUPAC name of the following compound is :

(a) 5,6-diethyl-3-methyl dec-4-ene
(b) 7-methyl-2,4,6-trien
(c) 6-methyl heptene
(d) 3,3-diethyl-5-ethyl-4-decane

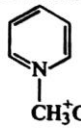
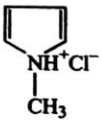
75. The IUPAC name of the given compound is :

(a) 3-methyl-3-*N*,*N*-dimethyl pentane

(b) 3-ethyl-3-*N*,*N*-dimethyl pentane
(c) 3-methyl-3-*N*,*N*-dimethyl butane
(d) none of these

76. Which of the following reaction is not reversible ?
(a) Esterification
(b) Hydrolysis of ester by acids
(c) Hydrolysis of ester by alkalies
(d) None of the above

77. Which of the following has shorter $>C=O$ bond?
(a) $(RCO)_2O$ (b) $RCOOR'$
(c) $RCOCl$ (d) $RCONH_2$

78. $CH_3NHCH_2 \cdot CH_2 \cdot CH_3$ and $CH_3NHCHCH_3$ (CH_3 branch) are :
(a) Chain isomers (b) Position isomers
(c) Metamers (d) Functional isomers

79. Which one is a quaternary salt?
(a)  (b) $(CH_3)_3\overset{+}{N}HCl^-$
(c)  (d) $(CH_3)_4N^+Cl^-$

80. Of the following amine the lowest b.pt. amine is :
(a) *n*-butyl amine (b) *n*-pentyl amine
(c) *N*,*N'*-dimethyl ethanamine
(d) *N*-methyl propanamine

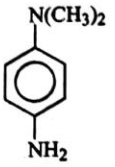
81. Which type of amines are obtained by Ritter reaction ?
(a) R_3CNH_2 (b) $R-\underset{\displaystyle R}{\overset{\displaystyle R}{N}}$
(c) R_2—NH (d) R—NH_2

82. Glucose reacts wtih phenyl hydrazine to yield an glucosazone. Which is not correct about this reaction :
(a) In all three molecule of phenyl hydrazine are used for one molecule of glucose
(b) Phenyl hydrazine acts as reducing agent as well as condensating agent
(c) Fructose also gives same osazone
(d) Only one molecule is used as condensating agent

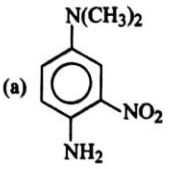
83. Fructose or glucose or mannose with dil. NaOH solution gives an equilibrium mixture of ..... sugars :
(a) 2 (b) 3
(c) 4 (d) 5

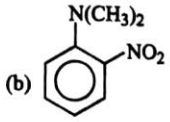
84. Halogen atoms although *o*- and *p*- directing group but it deactivates rings for further S_E reactions. The deactivating effect is due to :
(a) + *E* effect (b) + *M* (or + *T* effect)
(c) – *I* effect (d) + *I* effect

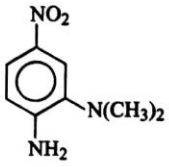
85. The product obtained in the reaction :



Nitration , is

(a) 

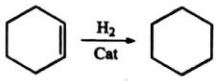
(b) 

(c) 

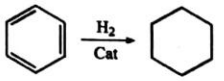
(d) Nitration is not possible

86. The correct order for increasing rate of nitration is :
(a) $C_6H_5NO_2 < C_6H_5Cl < C_6H_6 < C_6D_6$
(b) $C_6H_5NO_2 < C_6H_5Cl < C_6H_6 = C_6D_6$
(c) $C_6H_5NO_2 < C_6H_6 < C_6H_5Cl < C_6D_6$
(d) $C_6H_5Cl < C_6H_5NO_2 < C_6D_6 < C_6H_6$

87. If



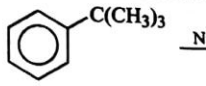
; $\Delta H = -29$ kcal mol^{-1} and



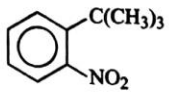
; $\Delta H = -51$ kcal mol^{-1}

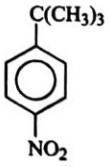
The resonance energy of C_6H_6 is :
(a) – 36 kcal mol^{-1} (b) + 36 kcal mol^{-1}
(c) – 22 kcal mol^{-1} (d) + 22 kcal mol^{-1}

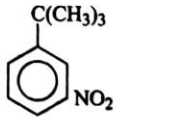
88. The product obtained in the reaction is :



Nitration mixture

(a) 

(b) 

(c) 

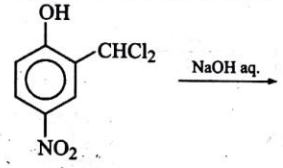
(d) All of these

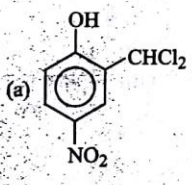
89. $C_6H_5CH_2CH_3$ and $C_6H_5CHClCH_3$ can be distinguished by :
(a) Alcoholic KOH (b) Alcoholic $AgNO_3$
(c) Acidified $KMnO_4$ (d) None of these

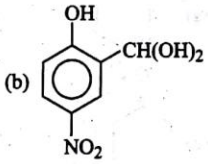
90. Toluene reacts with Br_2/Fe gives *p*-bromo toluene as major product because $-CH_3$ group :
(a) activates the ring by hyperconjugation
(b) causes steric hindrance
(c) deactivates the ring
(d) only *p*-directing

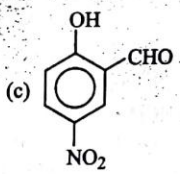
91. Tetraphenyl methane can be obtained by the reaction of :
(a) $C_6H_6 + CCl_4 \xrightarrow{AlCl_3}$
(b) $C_6H_5Cl + (C_6H_5)_3\overset{-}{C}\overset{+}{K} \xrightarrow[\text{liq. } NH_3]{KNH_2}$
(c) $C_6H_6 + CHCl_3 \xrightarrow{AlCl_3}$
(d) $C_6H_5Cl + CH_4 \xrightarrow{AlCl_3}$

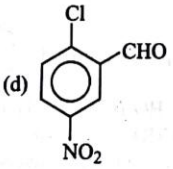
92. The product formed in the reaction is :



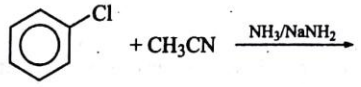
(a) 

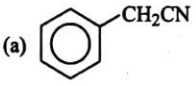
(b) 

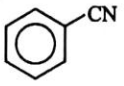
(c) 

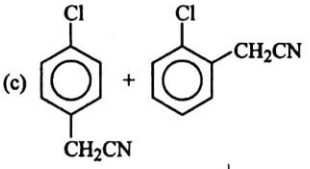
(d) 

93. The product formed in the reaction is :



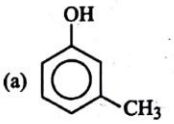
(a) 

(b) 

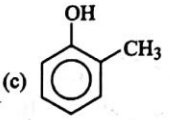
(c) 

(d)

94. Which of the following cresols can produce tribromo derivative on dissolution in Br_2 water ?

(a) 

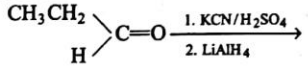
(b)

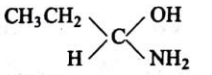
(c) 

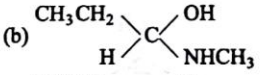
(d) All of these

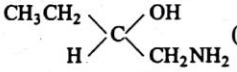
95. *p*-aminobenzoic acid and *p*-hydroxy benzoic acid in a solution can be separated by :
(a) acids (b) alkalies
(c) ether (d) alcohol

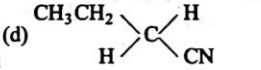
96. The product formed in the reaction is :



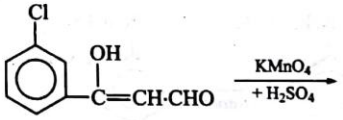
(a) 

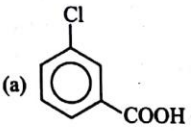
(b) 

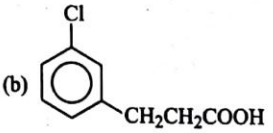
(c) 

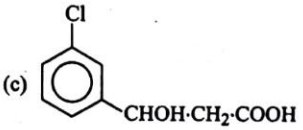
(d) 

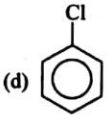
97. The product formed in the reaction is :



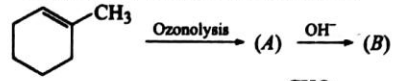
(a) 

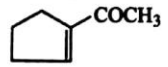
(b) 

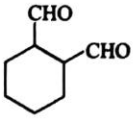
(c) 

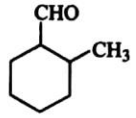
(d) 

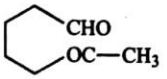
98. The final product (*B*) formed in the reaction :



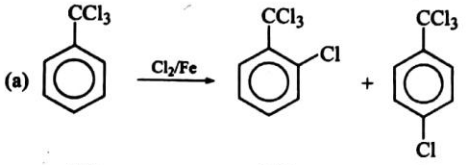
(a) 

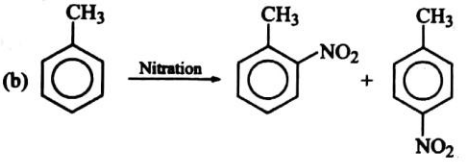
(b) 

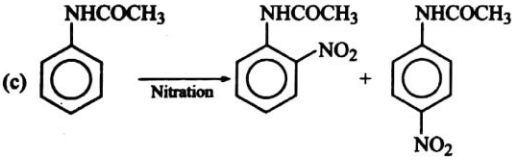
(c) 

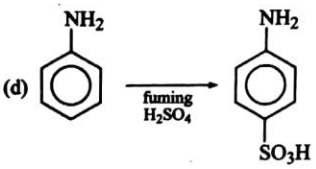
(d) 

99. The product formed in the reaction is not correctly given in :

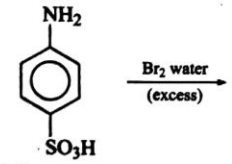
(a) 

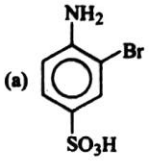
(b) 

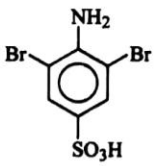
(c) 

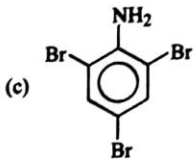
(d) 

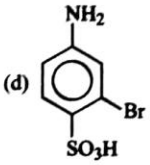
100. The product formed in the reaction :



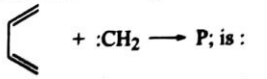
(a) 

(b) 

(c) 

(d) 

101. The product formed during the reaction :



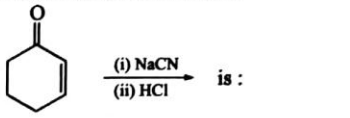
(a)

(b)

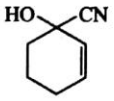
(c)

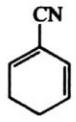
(d) none of these

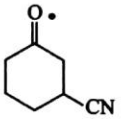
102. The product formed in the reaction

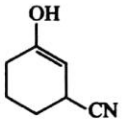


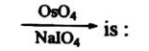
is :

(a) 

(b) 

(c) 

(d) 

103. The product formed in  is :

(a) $CHO\cdot(CH_2)_4\cdot CHO$ (b) $CHO(CH)_4COOH$

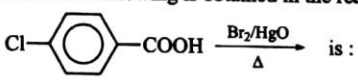
(c) $CHO(CH)_4\cdot CHO$ (d) $COOH(CH)_4COOH$

104. The number of products of ozonolysis of polyenes (if n is number of double bonds) are :

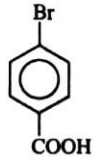
(a) n (b) $n+1$

(c) $n+2$ (d) $n+3$

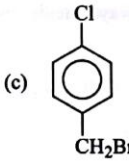
105. Which of the following is obtained in the reaction :



is :

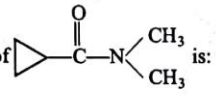
(a) 

(b)

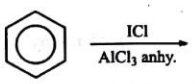
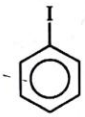
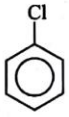
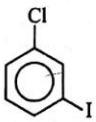
(c)  (d)

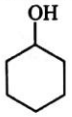
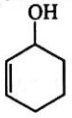
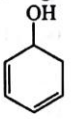
106. Dihydroxy acetone on treatment with HIO_4 gives :
(a) HCOOH (b) HCHO
(c) HCHO and HCOOH (d) HCHO and CO_2

107. Which of the following is not reducing sugar :
(a) Fructose (b) Glucose
(c) Lactose (d) Sucrose

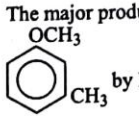
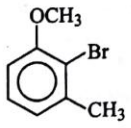
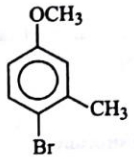
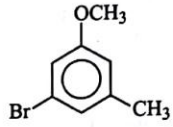
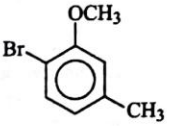
108. The IUPAC name of  is:
(a) *N*,*N*-dimethyl cyclopropanone
(b) *N*,*N*-dimethyl cyclopropanamine
(c) *N*,*N*-dimethyl cyclopropanamide
(d) cyclopropanone dimethyl amine

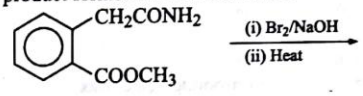
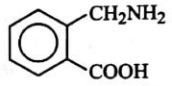
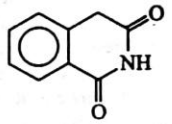
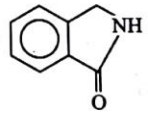
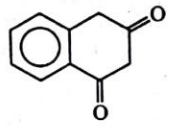
109. Urea has :
(a) Chain isomer (b) Position isomer
(c) Geometrical isomer (d) Tautomer

110. The product formed in the reaction :
 is :
(a)  (b) 
(c) (d) 

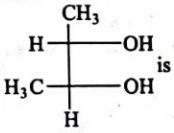
111. The correct order for dehydration for the following is :
(I)  , (II)  , (III) 
(a) I > II > III (b) III > II > I
(c) I > III > II (d) II > III > I

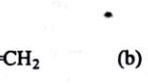
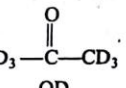
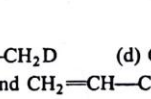
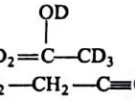
112. The decreasing order of the stability of carbocations is :
$CH_3 \cdot \overset{+}{C}H \cdot CH_3$ (I); $CH_3 \cdot \overset{+}{C}H \cdot OCH_3$ (II); $CH_3 \cdot \overset{+}{C}H \cdot COCH_3$ (III)
(a) I > II > III (b) III > II > I
(c) III > I > II (d) II > I > III

113. The major product formed on monobromination of  by $FeBr_3/Br_2$:
(a)  (b) 
(c)  (d) 

114. The product formed in the reaction is :

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

115. Which of the following is not an intermediate in Hofmann bromamide reaction ?
(a) *R*NCO (b) *R*CON
(c) *R*CONHBr (d) *R*NC

116. Correct configuration of molecule  is :
(a) 1*S*, 2*S* (b) 1*S*, 2*R*
(c) 1*R*, 2*S* (d) 1*R*, 2*R*

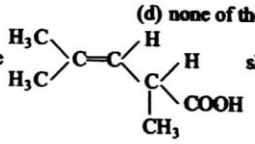
117. The enol form of acetone after treatment with D_2O gives :
(a)  (b) 
(c)  (d) 

118. In the compound $CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$, the $C_2{-}C_3$ bond is of the type :

(a) $sp-sp^2$ (b) sp^3-sp^3
(c) $sp-sp^3$ (d) sp^2-sp^3

119. Hybridization of carbon in singlet carbene is :
(a) sp (b) sp^2
(c) sp^3 (d) none of these

120. Hybridization of carbon in triplet carbene is :
(a) sp (b) sp^2
(c) sp^3 (d) none of these

121. The structure  shows :
(a) geometrical isomerism
(b) optical isomerism
(c) geometrical and optical isomerisms
(d) tautomerism

122. Allyl isocyanide has :
(a) 9σ and 4π bonds
(b) 8σ and 5π bonds
(c) 9σ, 3π and 3 non-bonded electrons
(d) 8σ, 3π and 4 non-bonded electrons

123. Which is not correct about the stability of carbocation :
(a) Presence of electron attracting gp shows destabilization
(b) Presences of electron repelling gp shows stabilization
(c) Presence of Resonance shows stabilization
(d) Presence of Resonance shows destabilization

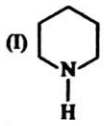
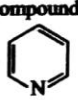
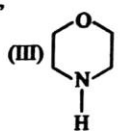
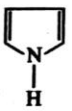
124. In the following groups,

$\underset{I}{-OAc}$ $\underset{II}{-OMe}$ $\underset{III}{-OSO_2Me}$ $\underset{IV}{-OSO_2CF_3}$

the order of leaving group ability is :
(a) I > II > III > IV (b) IV > III > I > II
(c) III > II > I > IV (d) II > III > IV > I

125. Which of the following always stabilizes both carbocation and carbanion if present :
(a) Electron attracting gp (b) Electron repelling gp
(c) Resonance (d) All of these

126. In the following compounds,

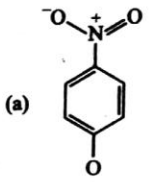
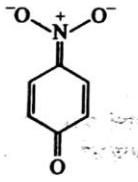
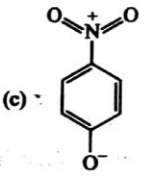
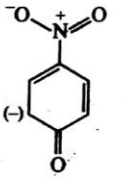
(I)  (II)  (III)  (IV) 

the order of basic nature is :
(a) IV > I > III > II (b) III > I > IV > II
(c) II > I > III > IV (d) I > III > II > IV

127. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane is :
(a) 2 (b) 3
(c) 4 (d) 1

128. Which of the following is/are correct :
(a) Quartz is an optically active substance
(b) Banzil shows optical activity
(c) Optically in active substance always yields optically inactive substance
(d) All of these

129. The intermediate during the addition of HCl to propene in the presence of peroxide is :
(a) $CH_3\dot{C}HCH_2Cl$ (b) $CH_2\overset{\oplus}{C}HCH_3$
(c) $CH_3CH_2\dot{C}H_2$ (d) $CH_3CH_2\overset{+}{C}H_2$

130. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is :
(a)  (b) 
(c)  (d) 

131. The correct basic character of methyi amines in gaseous phase is :
(a) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$
(b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
(c) $(CH_3)NH_2 > (CH_3)_2NH > (CH_3)_3N > NH_3$
(d) $(CH_3)_2NH > CH_3NH_2 > NH_3 > (CH_3)_3N$

132. IUPAC name of :
$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(CH_3)CH_2{\cdot}CH_2CH_2CH_2CH(CH_3)CH_3$
(a) 3, 4, 9-trimethyl decane
(b) 2, 7, 8-trimethyl decane
(c) Isopropyl heptane
(d) 2, 4, 9-trimethyl decane

133. The most reactive cycloalkane is :
(a) Cyclopropane (b) Cyclobutane
(c) Cyclopentane (d) Cycloheptane

134. $(CH_3)_3C{\cdot}MgCl$ on reaction with D_2O gives :
(a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$
(c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$

135. The strongest acid among the following is :
(a) $CH{\equiv}CH$ (b) C_6H_6
(c) C_2H_6 (d) CH_3OH

136. Buna-N rubber is a copolymer of :
(a) Propadiene + Vinyl chloride
(b) Butadiene + Vinyl cyanide
(c) Propadiene + Butadiene
(d) None of the above

137. Which of the following will not decolorize Baeyer's reagent:
(a) 1, 1, 2-trimethyl ethene
(b) 1, 1-dimethyl ethene
(c) 1, 2-dimethyl ethene
(d) 1, 1, 2, 2-tetramethyl ethene

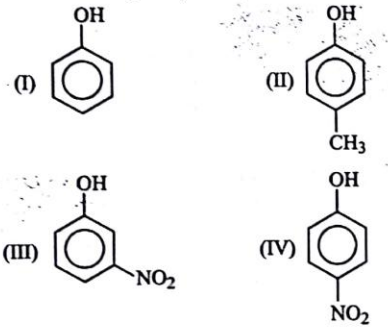
138. Which of the following gives iodoform test :
(a) *m*-and *p*-hydroxy phenol
(b) Ethyl acetoacetate
(c) Pentan-3-one
(d) diethyl malonate

139. Electrolysis of 2% NaCl solution with C_2H_5OH gives :
(a) CH_3CHO (b) $CHCl_3$
(c) CH_3COCH_3 (d) CCl_4

140. $CHCl_3$ and CCl_4 can be identified by :
(a) Iodoform test (b) Wurtz reaction
(c) Carbylamine reaction (d) Wolf-Kishner reaction

141. Select the correct statement
(a) S_N1 reactions are sterospecific and stereo selective
(b) S_N2 reaction are stereospecific but not stereoselective
(c) S_N2 reactions are stereo selective but not stereospecific
(d) S_N2 reactions are stereoselective as well as stereospecific

142. In the following compounds,



the order of acidic nature is :
(a) III > IV > I > II (b) I > IV > III > II
(c) II > I > III > IV (d) IV > III > I > II

143. $CH_3CHO + H_2NOH \longrightarrow CH_3—CH=N—OH$
The above reaction occurs at :
(a) pH = 1 (b) pH = 3.5
(c) any value of pH (d) pH = 12

144. $CH_3CH_2COOH \xrightarrow[\text{Red P}]{Br_2} A \xrightarrow{NH_3\ alc.} B$, *B* in the reaction is :
(a) Lactic acid (b) Ethyl amine
(c) Propyl amine (d) Alanine

145. Which of the following carboxylic acids undergoes decarboxylation easily ? Explain briefly.
(a) $C_6H_5—CO—CH_2—COOH$
(b) $C_6H_5—CO—COOH$
(c) $C_6H_5—\underset{\displaystyle OH}{\underset{|}{CH}}—COOH$
(d) $C_6H_5—\underset{\displaystyle NH_2}{\underset{|}{CH}}—COOH$

146. The acid *D* obtained through the following sequence of reactions is :

$$C_2H_5Br \xrightarrow{\text{Alc. KOH}} A \xrightarrow[CCl_4]{Br_2} B \xrightarrow[\text{(excess)}]{KCN} C \xrightarrow{H_3O^+} D$$

(a) Succinic acid (b) Malonic acid
(c) Maleic acid (d) Oxalic acid

147. Which of the following acids on heating loses a molecule of H_2O to form an α,β-unsaturated acid?
(a) $CH_3CHOHCOOH$ (b) $HOCH_2COOH$
(c) $CH_3CHOHCH_2COOH$ (d) $HOCH_2CH_2CH_2COOH$

148. The molecule does not contain :
(a) Allylic H-atom
(b) Vinylic H-atom
(c) H-atom attached on *sp*-hybridized carbon
(d) H-atom attached on sp^3-hybridized carbon

149. Presence of which increases the solubility of alkenes in water :
(a) Ag^+ (b) Ag
(c) Cl_2 (d) Br_2

150. Among the following statements on the nitration of aromatic compounds, the false one is :
(a) The rate of nitration of benzene is almost the same as that of hexadeuterobenzene
(b) The rate of nitration of toluene is greater than that of benzene
(c) The rate of nitration of benzene is greater than that of hexadeuterobenzene
(d) Nitration is an electrophilic substitution reaction

151. Which of the following decolorizes few drops of dilute $KMnO_4$ and gives brown mass :
(a) *n*-butanol (b) *s*-butanol
(c) *t*-butanol (d) none of these

152. Which aldehyde gives positive test with Tollens reagent but not with Benedicts solution :
(a) HCHO (b) C_6H_5CHO
(c) CH_3CHO (d) $CH_2=CH\cdot CHO$

153. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with :
(a) SO_2Cl_2 (b) $SOCl_2$
(c) Cl_2 (d) NaOCl

154. The bond order of individual C—C bond in benzene is :
(a) one (b) two
(c) between one and two (d) one and two alternately

155. Molecule in which the distance between the two adjacent carbon atoms is largest in :
(a) Ethane (b) Ethene
(c) Ethyne (d) Benzene

156. Which of the following is correct about alanine ?
(a) It is α-amino propanoic acid

$$CH_3-\underset{\displaystyle \overset{+}{N}H_3}{\underset{|}{CH}}-COOH$$

(b) It exists as $CH_3CH\cdot COOH$ in solution of pH = 2

$$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COO^-$$

(c) It exists as in solution of pH = 10
(d) All of the above

157. Among the following the compound that can be most readily sulphonated is :
(a) Benzene (b) Nitrobenzene
(c) Toluene (d) Chlorobenzene

158. The maximum number of isomers for an alkene with the molecular formula C_4H_8 is :
(a) 2 (b) 3
(c) 4 (d) 5

159. The compound with no dipole moment is :
(a) Methylchoride (b) Carbon tetrachloride
(c) Methylene chloride (d) Chloroform

160. The compound 1, 2-butadiene has :
(a) Only *sp* hybridized carbon atoms
(b) Only sp^2 hybridized carbon atoms
(c) Only *sp* and sp^2 hybridized carbon atoms
(d) *sp*, sp^2 and sp^3 hybridized carbon atoms

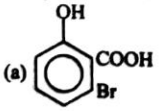
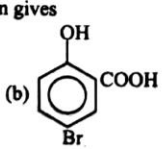
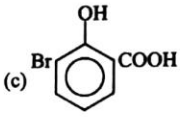
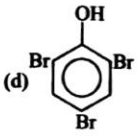
161. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism ?
(a) 2-butene (b) 2-butyne
(c) 2-butanol (d) butanal

162. The IUPAC name of the compound having the formula is :

$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH=CH_2$$

(a) 3, 3, 3-trimethyl-1-propene
(b) 1, 1, 1-trimethyl-2-propene
(c) 3, 3-dimethyl-1-butene
(d) 2, 2-dimethyl-3-butene

163. The compound that is most reactive towards electrophilic nitration is :
(a) toluene (b) benzene
(c) benzoic acid (d) nitrobenzene

164. Salicylic acid on bromination gives
(a) 
(b) 
(c) 
(d) 

165. The bond between carbon atom (1) and carbon atom (2) in compound $N\equiv \underset{1}{C}-\underset{2}{CH}=CH_2$ involves the hybridization as :
(a) sp^2 and sp^2 (b) sp^3 and *sp*
(c) *sp* and sp^2 (d) *sp* and *sp*

166. The IUPAC name of the compound $CH_2=CH-CH(CH_3)_2$ is :
(a) 1, 1-dimethyl-2-propene (b) 3-methyl-1-butene
(c) 2-vinyl propane (d) none of these

167. Which of the following will have least hindered rotation about carbon-carbon bond ?
(a) Ethane (b) Ethylene
(c) Acetylene (d) Hexachloroethane

168. If two compounds have the same empirical formula but different molecular formulae, they must have :
(a) different percentage composition
(b) different molecular weight
(c) same velocity
(d) same vapour density

169. The number of isomers of C_6H_{14} is :
(a) 4 (b) 5
(c) 6 (d) 7

170. Out of the following compounds which will have a zero dipole moment ?
(a) 1,1-dichloro ethylene
(b) *cis*-1, 2-dichloro ethylene
(c) *trans*-1, 2-dichloroethylene
(d) None of these compounds

171. Polarisation of electrons in acrolein may be written as :
(a) $\overset{-\delta}{CH_2}=CH-\overset{+\delta}{C}=O$
(b) $\overset{-\delta}{CH_2}=CH-CH=\overset{+\delta}{O}$
(c) $\overset{-\delta}{CH_2}=\overset{+\delta}{CH_2}-CH=O$
(d) $\overset{+\delta}{CH_2}=CH-CH=\overset{-\delta}{O}$

172. What is the decreasing order of strength of the bases OH^-, NH_2^-, $HC\equiv C^-$ and $CH_3CH_2^-$?
(a) $CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$
(b) $H-C\equiv C^- > CH_3-CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > H-C\equiv C^- > CH_3-CH_2^-$
(d) $NH_2^- > H-C\equiv C^- > OH^- > CH_3-CH_2^-$

173. The Cl—C—Cl in 1, 1, 2, 2, tetrachloroethene and tetrachloromethane respectively will be about :
(a) 120° and 109° 5' (b) 90° and 109.5°
(c) 109.5° and 90° (d) 109.5° and 120°

174. In CH_3CH_2OH the bond that undergoes heterolytic cleavage most readily is :
(a) C—C (b) C—O
(c) C—H (d) O—H

175. The compound which gives the most stable carbonium ion on dehydration is :
(a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$
(b) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$
(c) $CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}}-CH_2-CH_2OH$
(d) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$

176. The number of sigma and pi bonds in 1-butene 3-yne are :
(a) 5 sigma and 5 pi (b) 7 sigma and 3 pi
(c) 8 sigma and 2 pi (d) 6 sigma and 4 pi

177. The compound which has one isopropyl group is :
(a) 2, 2, 3, 3-tetramethyl pentane
(b) 2, 2-dimethyl pentane
(c) 2, 2, 3-trimethyl pentane
(d) 2-methyl pentane

178. The C—H bond distance is the longest in :
(a) C_2H_2 (b) C_2H_4
(c) C_2H_6 (d) $C_2H_2Br_2$

179. Amongst the following, the most basic compound is :
(a) benzylamine (b) aniline
(c) acetanilide (d) *p*-nitroaniline

180. The formation of cyanohydrin from ketone is an example of :
(a) electrophilic addition (b) nucleophilic addition
(c) nucleophilic substitution (d) electrophilic substitution

181. The enolic form of acetone contains :
(a) 9 sigma bonds, 1 pi bond and 2 lone pairs
(b) 8 sigma bonds, 2 pi bonds and 2 lone pairs
(c) 10 sigma bonds, 1 pi bond and 1 lone pair
(d) 9 sigma bonds, 2 pi bonds and 1 lone pair

182. The hybridisation of carbon atoms in C—C single bond of $H-C\equiv C-CH=CH_2$.
(a) sp^3-sp^3 (b) sp^2-sp^3
(c) $sp-sp^2$ (d) sp^3-sp

183. Isomers which can be interconverted through rotation around a single bond are :
(a) conformers (b) diastereomers
(c) enantiomers (d) positional isomers

184. Which statement is not correct ?
(a) Phenoxide ion has more number of canonical forms than benzoate ion
(b) Only one canonical form of phenoxide ion has –ve charge on more electronegative O-atom
(c) Phenoxide ion is more stable than benzoate ion
(d) Two canonical form of benzoate ion have –ve charge an more electronegative O-atom

185. Which of the following are oxidised by Fehling solution :
(a) Glucose (b) Phenyl hydrazine
(c) HCOOH (d) C_6H_5CHO

186. Arrange in order of decreasing trend towords S_E reactions :
(I) Chlorobenzene, (II) benzene
(III) Anilinium chloride, (IV) Toluene
(a) II > I > III > IV (b) III > I > II > IV
(c) IV > II > I > III (d) I > II > III > IV

187. Malonic acid and succinic acid can be identified by :
(a) Heating followed with addition of $NaHCO_3$
(b) Fehling solution
(c) Iodoform test
(d) Litmus

188. Arrange the following compounds in order of increasing dipole moment :
(I) Toluene (II) *m*-dichlorobenzene
(III) *o*-dichlorobenzene (IV) *p*-dichlorobenzene
(a) I < IV < II < III (b) IV < I < II < III
(c) IV < I < III < II (d) IV < II < I < III

189. Ammonium formate on heating gives :
(a) HCOOH (b) NH_3
(c) $HCONH_2$ (d) N_2H_4

190. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is :
(a) MeCOCl (b) MeCHO
(c) MeCOOMe (d) MeCOOCOMe

191. How many optically active stereoisomers are possible for butane-2, 3-diol ?
(a) 1 (b) 2
(c) 3 (d) 4

192. The optically active tartaric acid is named as D (+) tartaric acid because it has a positive :
(a) Optical rotation and is derived from D glucose
(b) pH in organic solvent
(c) Optical rotation and is derived from D (+) glyceraldehyde
(d) Optical rotation when substituted by deuterium

193. The conversion of 3,3-dimethyl but-1-ene into 3,3-dimethyl butanol can be made by :
(a) acid catalysed hydration
(b) oxymercuration-demercuration
(c) hydroboration-oxidation
(d) acidified $KMnO_4$ oxidation

194. Marsh gas mainly contains :
(a) C_2H_2 (b) CH_4
(c) H_2S (d) CO

195. Which of the following decolourises alkaline $KMnO_4$ solution :
(a) C_3H_8 (b) C_2H_4
(c) CH_4 (d) CCl_4

196. The compound with the highest boiling point is :
(a) *n* - hexane (b) *n* - pentane
(c) 2, 2 - dimethylpropane (d) 2 - methylbutane

197. When propyne is treated with aqueous H_2SO_4 in presence of $HgSO_4$ the major product is :
(a) propanal (b) propyl hydrogen sulphate
(c) acetone (d) propanol

198. Which of the following compounds does not dissolve in conc. H_2SO_4 even on warning ?
(a) ethylene (b) benzene
(c) hexane (d) aniline

199. Baeyer's reagent is :
(a) alkaline permanganate solution
(b) acidified permanganate solution
(c) neutral permanganate solution
(d) aqueous bromine solution

200. Acidic hydrogen in present in :
(a) ethyne (b) ethane
(c) benzene (d) ethene

201. Anti-Markovnikoff addition of HBr is not observed in :
(a) Propene (b) but-1-ene
(c) but-2-ene (d) pent-2-ene

202. The highest boiling point is expected for :
(a) iso-octane
(b) *n* - octane
(c) 2, 2, 3, 3-tetramethyl butane
(d) *n* - butane

203. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are :
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

204. In the addition of HBr to propene in the absence of peroxides the first step involves the addition of :
(a) H^+ (b) Br^-
(c) $H^\bullet$ (d) Br

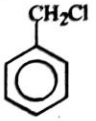
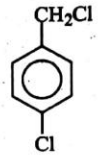
205. The chief reaction product of reaction between *n* - butane and bromine at 130° C is :
(a) $CH_3CH_2CH_2CH_2Br$ (b) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HBr$
(c) $CH_3-\underset{\displaystyle CH_2Br}{\underset{|}{CH_2}}-CHBr$ (d) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CBr_2}}$

206. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives :
(a) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$ and CH_3MgBr
(b) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ and $MgBr(OC_2H_5)$
(c) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H=CH_2$ and $Mg(OH)Br$
(d) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ and CH_3CH_2OMgBr

207. During debromination of *meso*-2, 3 dibromobutane, the major compound formed is :
(a) *n* - butane (b) 1-butene
(c) *cis* - 2 - butene (d) *trans* - 2 - butene

208. When cyclohexane is poured on water, it floats, because :
(a) Cyclohexane is in boat form
(b) Cyclohexane is in chair form
(c) Cyclohexane is in crown from
(d) Cyclohexane is less dense than water

209. Which is not correct for aspirin ?
(a) It contains acetyl gp
(b) It contains hydroxy gp
(c) It contains carboxylic gp
(d) It is acetylation product of *o*-hydroxy benzoic acid

210. Which of the following is most reactive for S_N2 reaction ?
(a)
(b) 
(c) 
(d)

211. Bakelite is a condensation polymer of phenol and :
(a) HCOOH (b) HCHO
(c) $HCOOCH_3$ (d) But-1-ene

212. The reaction $CH_3CH=CH-$ $-OH$ with HBr gives :
(a) $CH_3CHBrCH_2-$$-OH$
(b) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{CH}}-$ $-OH$
(c) $CH_3CHBrCH_2-$ $-Br$
(d) CH_3CH_2CHBr- $-Br$

213. The product (s) obtained via oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be :
(a) $CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$
(b) $CH_3-CH_2-CH_2-CHO$
(c) $CH_3-CH_2-CHO + HCHO$
(d) $CH_3CH_2COOH + HCOOH$

214. CCl_4, has no net dipole moment because of :
(a) Its planar structure
(b) Its regular tetrahedral structure
(c) Similar sizes of C and Cl atom
(d) Similar electron affinities of C and Cl atom

215. Chlorobenzene can be prepared by reacting aniline with :
(a) Hydrochloric acid :
(b) Cuprous chloride
(c) Chlorine in presence of anhydrous a aluminium chloirde
(d) Nitrous acid followed by heating with cuprous chloride

216. HBr reacts fastest with :
(a) 2-methyl propan-2-ol (b) Propan-1-ol
(c) Propan-2-ol (d) 2-methyl propan-1-ol

217. The reaction conditions leading to the best yield of C_2H_5Cl are :
(a) C_2H_6 (excess) + $Cl_2 \xrightarrow{\text{light}}$
(b) $C_2H_6 + Cl_2$ (excess) $\xrightarrow[\text{room temp.}]{\text{dark}}$
(c) $C_2H_6 + Cl_2$ (excess) $\xrightarrow{\text{UV light}}$
(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$

218. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly :
(a) Benzoyl chloride (b) *m*-chloro toluene
(c) Benzyl chloride (d) *o* and *p*-chloro toluene

219. *n*-propylbromide on treatment with ethanolic potassium hydroxide produces :
(a) Propane (b) Propene
(c) Propyne (d) Propanol

220. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives :
(a) *o*-cresol (b) *p*-cresol
(c) 2, 4-dihydroxy toluene (d) benzyl alcohol

221. 1-chlorobutane on reaction with alcoholic potash gives :
(a) 1-butene (b) 1-butanol
(c) 2-butene (d) 2-butanol

222. In the reaction of *p*-chlorotoluene with KNH_2 in liq. NH_3 the major product is :
(a) *o*-toluidine (b) *m*-toluidine
(c) *p*-toluidine (d) *p*-chloro aniline

223. Benzyl chloride can be prepared from toluene by chlorination with :
(a) SO_2Cl_2 (b) $SOCl_2$
(c) Cl_2 (d) NaOCl

224. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to the formation of :
(a) Carbanion (b) Carbene
(c) Free radical (d) Carbocation

225. Ethyl alcohol is heated with conc. H_2SO_4 the product formed is :
(a) $H_3C-\overset{\overset{O}{\|}}{C}-OC_2H_5$ (b) C_2H_6
(c) C_2H_4 (d) C_2H_2

226. Which of the following is basic ?
(a) CH_3-CH_2-OH
(b) $OH-CH_2-CH_2-OH$
(c) $H-O-O-H$
(d) $H_3C-\overset{\overset{O}{\|}}{C}-OH$

227. The compound which is not isomeric with diethyl ether is :
(a) *n*-propyl methyl ether (b) butan-1-ol
(c) 2-methyl propan-2-ol (d) butanone

228. The compound which reacts fastest with Lucas reagent at room temperature is :
(a) butan-1-ol (b) butan-2-ol
(c) 2-methylpropan-1-ol (d) 2-methylpropan-2-ol

229. Diethyl ether on heating with conc. HI gives two moles of :
(a) ethanol (b) iodoform
(c) ethyl iodide (d) methyl iodide

230. An industrial method of preparation of methanol is :
(a) catalytic reduction of carbon monoxide in presence of $ZnO-Cr_2O_3$
(b) by reacting methane with steam at 900°C with a nickel catalyst
(c) by reducing formaldehyde with $LiAlH_4$
(d) by reacting formaldehyde with aqueous sodium hydroxide solution

231. When phenol is treated with excess bromine water, it gives :
(a) *m*-bromophenol (b) *o*-and *p*-bromophenol
(c) 2, 4-dibromophenol (d) 2, 4, 6-tribromophenol

232. The compound that will not give iodoform on treatment with alkali and iodine is :
(a) acetone (b) ethanol
(c) diethyl ketone (d) isopropyl alcohol

233. Which of the following is *o*-, *p*-directing gp :
(a) $-CH=CH_2$ (b) $-CCl_3$
(c) $-NH_3^+$ (d) COCl

234. Which of the following compounds is oxidised to prepare methyl ethyl ketone ?
(a) 2-propanol (b) 1-Butanol
(c) 2-Butanol (d) *t*-Butyl alcohol

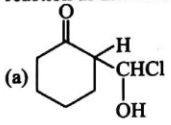
235. Hydrogen bonding is maximum in :
(a) ethanol (b) diethyl ether
(c) ethyl chloride (d) triethyl amine

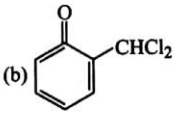
236. Phenol reacts with bromine in carbon disulphide at low temperature to give :
(a) *m*-bromophenol (b) *o*-and *p*-bromophenol
(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol

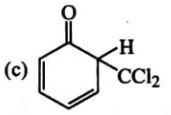
237. The products of combination of an aliphatic thiol (RSH) at 298 K are :
(a) $CO_2(g)$, $H_2O(g)$ and $SO_2(g)$
(b) $CO_2(g)$, $H_2O(l)$ and $SO_2(g)$
(c) $CO_2(l)$, $H_2O(l)$ and $SO_2(l)$
(d) $CO_2(g)$, $H_2O(l)$ and $SO_2(l)$

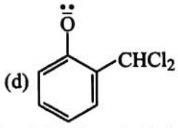
238. The reaction products of $C_6H_5OCH_3 + HI \xrightarrow{\Delta}$ is :
(a) $C_6H_5OH + CH_3I$ (b) $C_6H_5I + CH_3OH$
(c) $C_6H_5CH_3 + HIO$ (d) $C_6H_6 + CH_3OI$

239. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicyldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate ?

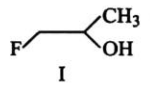
(a) 

(b) 

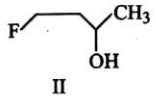
(c) 

(d) 

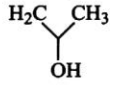
240. The order of reactivity of the following alcohols towards conc. HCl is :



I



II



III

IV

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

241. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives :
(a) diphenyl ether (b) *p*-hydroxy azobenzene
(c) chlorobenzene (d) benzene

242. Among the following compounds, the strongest acid is :
(a) $HC \equiv CH$ (b) C_6H_6
(c) C_2H_6 (d) CH_3OH

243. The reagent with which both acetaldehyde and acetone react easily is :
(a) Fehling's reagent (b) Grignard reagent
(c) Schiff's ragent (d) Tollen's reagent

244. A compound that gives a positive iodoform test is :
(a) 1-pentanol (b) 2-pentanone
(c) 3-pentanone (d) pentanal

245. When acetaldehyde is heated with Fehling's solution it gives a precipitate of :
(a) Cu (b) CuO
(c) Cu_2O (d) $Cu + Cu_2O + CuO$

246. The Cannizzaro reaction is not given by :
(a) trimethylacetaldehyde (b) acetaldehyde
(c) benzaldehyde (d) formaldehyde

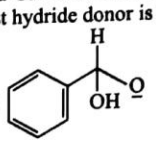
247. *m*-Chlorobenzaldehyde on reaction with conc. KOH at room temperature gives :
(a) potassium *m*-chlorobenzoate and *m*-hydroxybenzaldehyde
(b) *m*-hydroxybenzaldehyde and *m*-chlorobenzyl alcohol
(c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol
(d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol

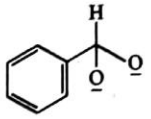
248. In the Cannizzaro reaction given below,

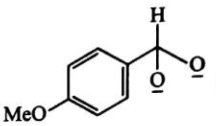
$2PhCHO \xrightarrow{OH^-} PhCH_2OH + PhCO_2^-$ the slowest step is :

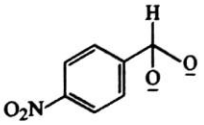
(a) the attack of ^-OH at the carbonyl group,
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic acid
(d) the deprotonation of $PhCH_2OH$

249. In a Cannizzaro reaction, the intermediate that will be the best hydride donor is :

(a) 

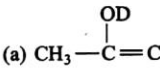
(b) 

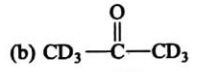
(c) 

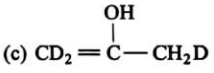
(d) 

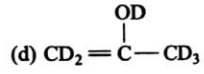
250. Which of the following will react with water :
(a) $CHCl_3$ (b) $Cl_3C \cdot CHO$
(c) CCl_4 (d) $ClCH_4 \cdot CH_2Cl$

251. The enol form of acetone after treatment with D_2O, gives :

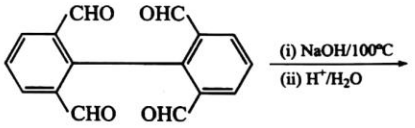
(a) 

(b) 

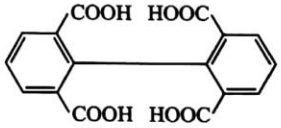
(c) 

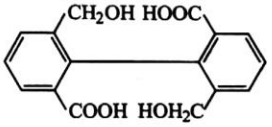
(d) 

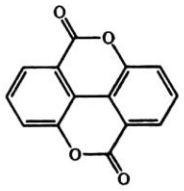
252.

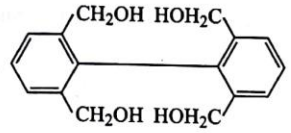


Major product is :

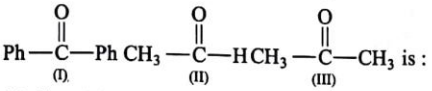
(a) 

(b) 

(c) 

(d)  **(IIT 2003)**

253. The correct order of reactivity of PhMgBr with



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

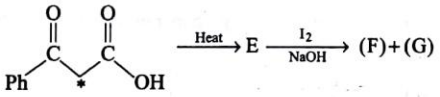
254. How will you convert butan-2-one to propanoic acid ?
(a) Tollen's reagent (b) Fehling's solution
(c) $NaOH/I_2/H^+$ (d) $NaOH/NaI/H^-$

255. $C_6H_5CHO + (X)$

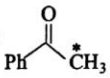
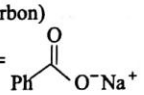
$$\xrightarrow[H_3O^+]{CH_3COONa} C_6H_5CH{=}CHCOOH + Y$$

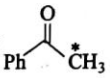
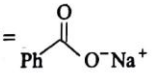
The compound (X) is :
(a) CH_3COOH (b) $BrCH_2—COOH$
(c) $(CH_3CO)_2O$ (d) CHO—COOH

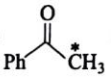
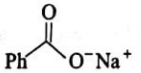
256. In the following reaction sequence, the correct structures of E, F and G are :

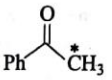
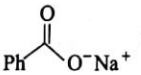


(* implies C labelled carbon)

(a) E =  F =  $G = \dot{C}H_3I^-$

(b) E =  F =  $G = CHI_3$

(c) E =  F =  $G = \dot{C}HI_3$

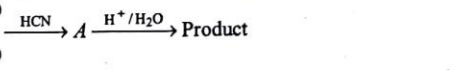
(d) E =  F =  $G = \dot{C}H_3I$

257. Acetamide is treated separately with the following reagents. Which one of the these would give methyl amine ?
(a) PCl_5 (b) $KOH + Br_2$
(c) Sodalime (d) Hot conc. H_2SO_4

258. Hydrogenation of benzyl chloride in the presence of Pd on $BaSO_4$ gives :
(a) Benzylalcohol (b) Benzaldehyde
(c) Benzoic acid (d) Phenol

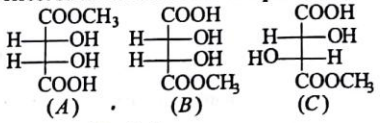
259. The organic product formed in the reaction $C_6H_5COOH \xrightarrow[H_3O^+]{LiAlH_4}$
(a) $C_6H_5CH_2OH$ (b) $C_6H_5COOH + CH_4$
(c) $C_6H_5CH_3 + CH_3OH$ (d) $C_6H_5CH_3 + CH_4$

260. The products formed in the reaction :



(a) *d*-tartaric acid (b) *l*-tartaric acid
(c) *meso* tartaric acid (d) *d*, *l*-and mesotartaric acid

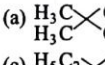
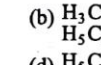
261. The correct statement about the compounds *A*, *B* and *C* is :

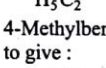
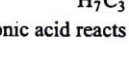


(a) *A* and *B* are identical
(b) *A* and *B* are diastereomers
(c) *A* and *C* are enantiomers
(d) *A* and *B* are enantiomers

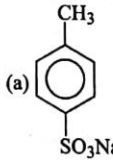
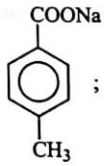
262. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from.
(a) methyl group (b) carboxylic acid group
(c) methylene group (d) bicarbonate

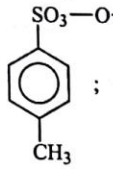
263. Ethyl ester $\xrightarrow[(excess)]{CH_3MgBr} P$, The product '*P*' will be :

(a)  (b) 

(c)  (d) 

264. 4-Methylbenzenesulphonic acid reacts with sodium acetate to give :

(a)  ; CH_3COOH (b)  ; SO_3

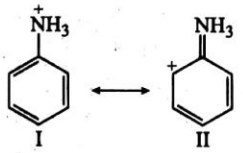
(c) ; SO_3 (d)  ; NaOH

265. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine is :
(a) methylamine (b) ethylamine
(c) diethylamine (d) triethylamine

266. Carbylamine test is performed in alcoholic KOH by heating a mixture of :
(a) chloroform and silver powder
(b) trihalogenated methane and primary amine
(c) an alkyl halide and a primary amine
(d) an alkyl cyanide and a primary amine

267. Butanenitrile may be prepared by heating :
(a) Propyl alcohol with KCN
(b) Butyl alcohol with KCN
(c) Butyl chloride with KCN
(d) Propyl chloride with KCN

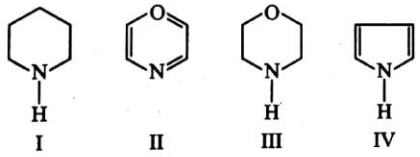
268. Examine the following two structure for the anilinium ion and choose the correct statement from the ones given below :



(a) It is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
(b) It is not an acceptable canonical structure because it is not-aromatic
(c) It is not an acceptable canonical structure because the nitrogen has 10 valence electrons.
(d) It is an acceptable canonical structure.

269. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture HNO_3 acts as a :
(a) base (b) acid
(c) reducing agent (d) catalyst

270. In the following compounds :



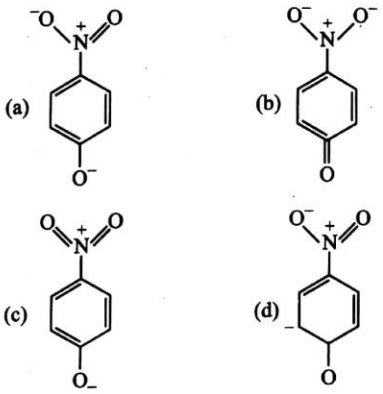
the order of basic nature is :
(a) IV > I > III > II (b) III > I > IV > II
(c) II > I > III > IV (d) I > III > II > IV

271. Among the following statements on the nitration of aromatic compounds, the false one is :
(a) that rate of nitration of benzene is almost the same as that of hexadeutereobenzene.
(b) the rate of nitration of toluene is greater than that of benzene
(c) the rate of nitration of benzene is greater than that of hexadeutereobenzene
(d) nitration is an electrophilic substitution reaction.

272. Which of the following undergoes decarboxylation on heating :

(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2\cdot COOH$
(b) CH_3COOH
(c) $CH_3\cdot\overset{O}{\overset{\|}{C}}-CH_2\cdot CH_2\cdot COOH$
(d) $CH_3-\overset{O}{\overset{\|}{C}}\cdot COOH$

273. The most unlikely representation of resonance structures of *p* -nitrophenoxide ion is :



274. The pair of compounds in which both the compounds give positive test with Tollen's reagent is :
(a) Glucose and Sucrose
(b) Fructose and Sucrose
(c) Acetophenone and Hexanal
(d) Glucose and Fructose

275. The two forms of *D*-glucopyranose obtained from the solution of *D*-glucose are called :
(a) Isomers (b) Anomers
(c) Epimers (d) Enantiomers

276. Identify the correct order of boiling points of the following compounds :

$\underset{(1)}{CH_3CH_2CH_2CH_2OH}$, $\underset{(2)}{CH_3CH_2CH_2CHO}$, $\underset{(3)}{CH_3CH_2CH_2COOH}$

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

277. The product of acid catalysed hydration of 2-phenylpropene is :
(a) 3-phenyl-2-propanol (b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol (d) 2-phenyl-1-propanol

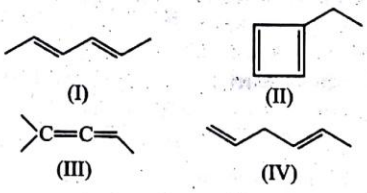
278. The best method to prepare cyclohexene from cyclohexanol is by using :
(a) Conc. HCl + $ZnCl_2$ (b) Conc. H_3PO_4
(c) HBr (d) Conc. HCl

279. In the reaction :

$C_6H_5COOH + NaH\overset{14}{C}O_3 \rightarrow C_6H_5COONa + CO_2 + H_2O$;

C^{14} appears in :
(a) CO_2 (b) C_6H_5COONa
(c) In both (d) All are correct

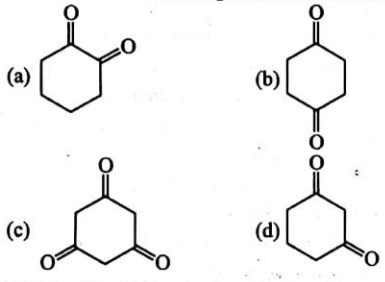
280. The correct order of stability of the following is :



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

281. Which of the following has non polar nature :
(a) *p*-dicyanobenzene (b) *p*-dimethoxy benzene
(c) *p*-dihydroxy benzene (d) *p*-dimercapto benzene

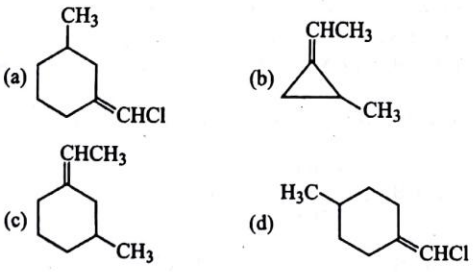
282. In which of the following enolic form is more :

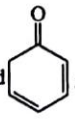


283. Which of the following is optically active :
(a) 1, 1-dibromo-1-chloropropane
(b) 1 , 3-dibromo-1-chloropropane
(c) 1, 1-dibromo-3-chloropropane
(d) 1, 3-dibromo-2-chloropropane

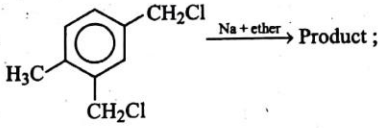
284. Which of the following pair belong to metamers :
(a) 3-methyl butan-2 one and pentane-2-one
(b) Pentane-2-one and Pentane-3-one
(c) *o*-and *m*-methoxytoluene
(d) all of the above

285. Which of the following will not show geometrical isomerism :

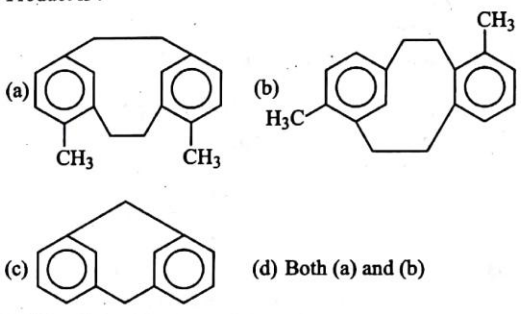


286. Compound  gives identification test with :
(a) $NaHSO_3$ (b) Br_2 water
(c) Fehling solution (d) $FeCl_3$ (*aq.*)

287. Calcium carbide on reacting with heavy water will give :
(a) $Ca(OD)_2 + C_2H_2$ (b) $Ca(OD)_2 + C_2D_2$
(c) $CaD_2 + C_2D_2$ (d) $Ca(OD)_2 + CD_4$

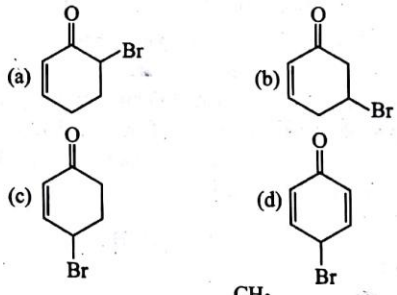
288. In the reaction  Product ;

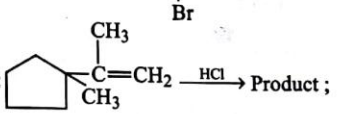
Product is :



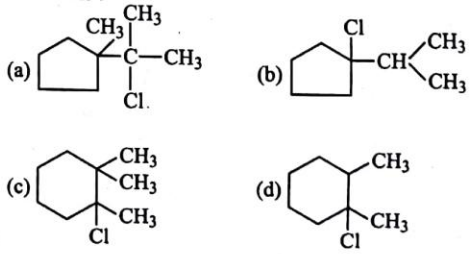
(d) Both (a) and (b)

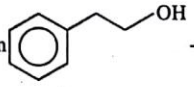
289. Which of the following will not give phenol on treatment with alc. KOH :



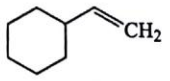
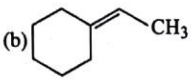
290. In the reaction :  Product ;

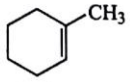
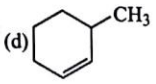
Product is :



291. In the reaction  $\xrightarrow[\Delta]{H^+}$ Major product

(A) ; Thus A is :

(a)  (b) 

(c)  (d) 

292. Predominating product of the reaction :

$$CH_2(Br)-CH=CH-CH_2(Br) \xrightarrow[CH_3OH]{Zn} P \text{ is :}$$

(a) (b)

(c) $CH_2=C=C=CH_2$ (d) $CH_2=CH-CH=CH_2$

293. Clemmensen reduction of the compound $(CH_3)_3C\cdot COCH_3$ gives main product as :

(a) $(CH_3)_2CH\cdot CH(CH_3)_2$ (b) $(CH_3)_3\cdot \overset{OH}{\overset{|}{C}}H\cdot CH_3$

(c) $(CH_3)_3C\cdot CH_2\cdot CH_3$ (d) None of these

294. Carbon mono oxide is passed over heated sodium hydroxide till complete conversion of NaOH to product. The product obtained is dissolved in water and the solution reduces Tollen's reagent as well as reduces mercuric chloride to black precipitate. The product was :

(a) $\begin{matrix}COOH\\|\\COOH\end{matrix}$ (b) HCOOH

(c) HCOONa (d) $\begin{matrix}COONa\\|\\COONa\end{matrix}$

295. Which of the following does not posses acidic hydrogen :

(a) Pentan-2, 4-diane (b) 2, 4, 6-trinitrophenol

(c) DMF (d) Hexane-2, 4-diane

296. Dehydrochlorination allyl chloride gives :

(a) Propadiene (b) Allyl alcohol

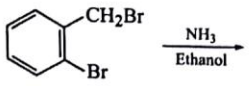
(c) Acetone (d) Propene

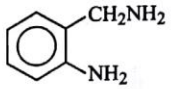
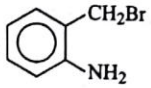
297. Iodoform test is given by :

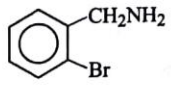
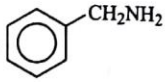
(a) Pyruvic acid (b) Methyl acetate

(c) Methyl benzoate (d) Phenyl acetate

298. The major product obtained in the reaction :



(a)  (b) 

(c)  (d) 

299. Select the wrong statement :

(a) S_N2 reactions are stereospecific as well as stereo selective

(b) S_N1 reactions are neither stereospecific nor stereo selective

(c) Free radicals posses less tendency for rearrangement than carbocation

(d) Nucleophilicity of RS^- is lesser than RO^-

300. Select the wrong statement :

(a) $LiAlH_4$ is stronger reducing agent than $NaBH_4$

(b) $LiAlH_4$ acts as reducing agent in ether medium but $NaBH_4$ in presence of protic solvent.

(c) Carboxylic gp is reduced to 1° alcohol by $LiAlH_4$ in ether or B_2H_6 in THF or H_2 / Pd

(d) Unsaturated carbonyls on reduction with $LiAlH_4$ in ether gives saturated alcohols.

301. The products formed on the reaction :

$$\begin{matrix}CH_3\\C_3H_7\end{matrix}\!\!>\!C=O \xrightarrow{[O]} \text{.... are}$$

(a) $CH_3COOH+C_3H_7COOH$

(b) $CH_3COOH+C_2H_5COOH$

(c) $C_3H_7COOH+HCOOH$

(d) $CH_3COCH_3+CH_3COOH$

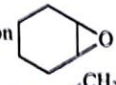
302. Which of the following reaction is wrongly reported :

(a) $RONa+R'Cl \longrightarrow ROR+NaCl$

(b) $RONa+(CH_3)_3\cdot C\cdot Cl \longrightarrow (CH_3)_3\cdot C\cdot O\cdot R+NaCl$

(c) $RONa+(CH_3)_3\cdot C\cdot Cl \longrightarrow R_2C=CH_2+HCl$

(d) $(CH_3)_3CONa+CH_3Cl \longrightarrow (CH_3)_3\cdot C\cdot OCH_3+NaCl$

303. The product formed in the reaction  $\xrightarrow{HIO_4}$ ...

(a) $(CH_2)_4\!\!<\!\!\begin{matrix}CHO\\CHO\end{matrix}$ (b) $(CH_2)_3\!\!<\!\!\begin{matrix}CH_2CHO\\CHO\end{matrix}$

(c) $(CH_2)_2\!\!<\!\!\begin{matrix}CH_2CHO\\CH_2CHO\end{matrix}$ (d) $(CH_2)_4\!\!<\!\!\begin{matrix}COOH\\COOH\end{matrix}$

304. Which of the following does not gives Schiff's reagent test at all :

(a)

(b) CH_3CHO

(c) CH_3COCH_3

(d)

305. The molecules that will have dipole moment are :
(a) 2, 2-dimethyl propane
(b) *trans* 2-pentene
(c) *cis* 3-hexene
(d) 2, 2, 3, 3-tetramethyl butane

306. The product formed in the reaction :

$ClCH_2 \cdot CHCl_2 \xrightarrow{OH^-}$ is :

(a) $CHCl = CHCl$ (b) $CH_2 = CCl_2$
(c) $CH_2OH—CHO$ (d) $CH_2Cl—CHO$

307. Correct increasing acidic nature of the given alcohols is :

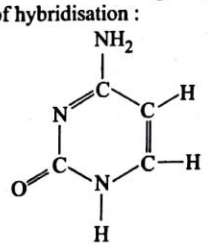
C_2H_5OH (I) CF_3CH_2OH (II) CCl_3CH_2OH (III)

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

308. Hydroxylation of ethylene can not be made by :
(a) cold alk. $KMnO_4$ (b) OsO_4 in pyridine
(c) Peroxy formic acid (d) $H_2O + O_2$

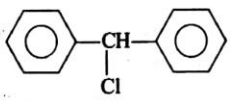
309. During free radical substitution of hydrocarbons, the abstraction of which hydrogen atom is easiest.
(a) Allylic (b) Vinylic
(c) CH_4 (d) 3°

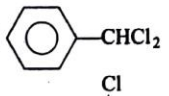
310. Which atom in the following compound shows more than one kind of hybridisation :

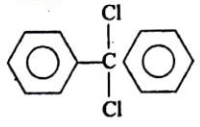


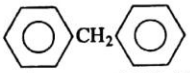
(a) C (b) N
(c) O (d) H

311. Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhy. $AlCl_3$?

(a) 

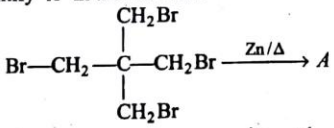
(b) 

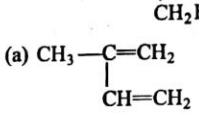
(c) 

(d) 

312. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory :
(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4
(c) by direct fluorination of benzene with F_2 gas
(d) by reacting bromobenzene with NaF solution

313. Identify '*A*' in the reaction :

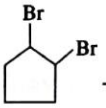


(a) 

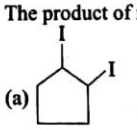
(b)

(c)

(d) $CH_3C \equiv C—CH=CH_2$

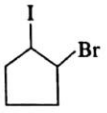
314.  $\xrightarrow{NaI/Acetone}$ Product.

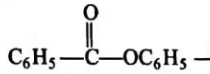
The product of reaction is :

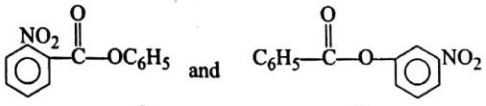
(a) 

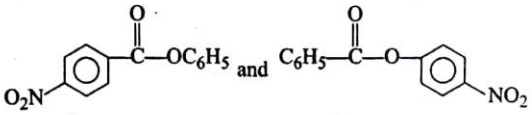
(b)

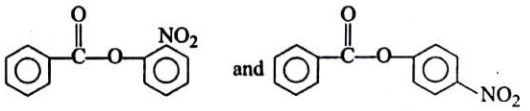
(c)

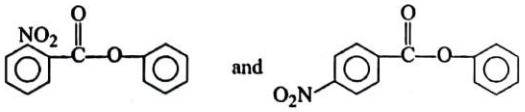
(d) 

315.  $\xrightarrow{\text{mononitration}}$ Products formed are :

(a) 

(b) 

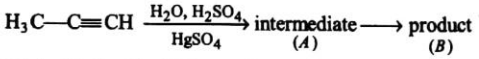
(c) 

(d) 

316. An example of a sigma bonded organometallic compound is :
(a) ruthenocene (b) Grignard's reagent
(c) ferrocene (d) cobaltocene

317. Mixture of chloroxylenol and terpineol acts as :
(a) analgesic (b) antiseptic
(c) antipyretic (d) antibiotic

318. Predict the correct intermediate and product in the following reaction :



(a) A : $H_3C-\underset{\underset{SO_4}{|}}{C}=CH_2$ B : $H_3C-\overset{\overset{O}{||}}{C}-CH_3$

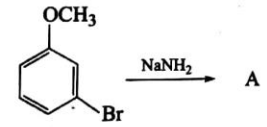
(b) A : $H_3C-\underset{\underset{OH}{|}}{C}=CH_2$ B : $CH_3-\underset{\underset{SO_4}{|}}{C}=CH_2$

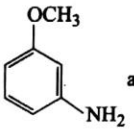
(c) A : $CH_3-\overset{\overset{O}{||}}{C}-CH_3$ B : $H_3C-C\equiv CH$

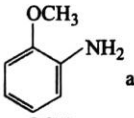
(d) A : $H_3C-\underset{\underset{OH}{|}}{C}=CH_2$ B : $H_3C-\overset{\overset{O}{||}}{C}-CH_3$

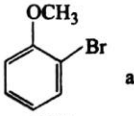
319. Which of the following reactions is appropriate for converting acetamide to methanamine?
(a) Carbylamine reaction
(b) Hofmann hypobromamide reaction
(c) Stephens reaction
(d) Gabriels phthalimide synthesis

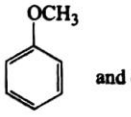
320. Identify A and predict the type of reaction :



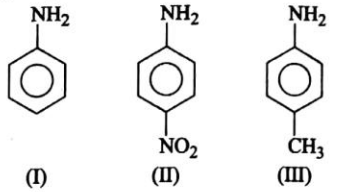
(a)  and substitution reaction

(b)  and elimination addition reaction

(c)  and cine substitution reaction

(d)  and cine substitution reaction

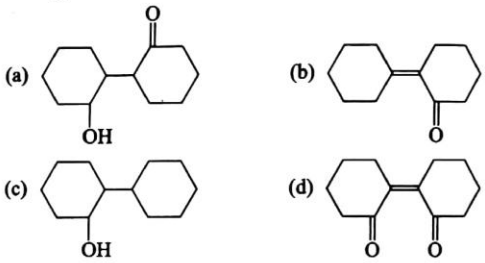
321. The correct increasing order of basic strength for the following compounds is :



(I) (II) (III)

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

322. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?

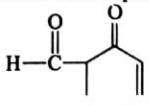


323. The correct statement regarding electrophile is :
(a) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile
(b) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile
(c) Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile
(d) Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile

324. The heating of phenyl-methyl ethers with HI produces :
(a) ethyl chlorides (b) iodobenzene
(c) phenol (d) benzene

325. Which of the following statement is not correct?
(a) Insulin maintains sugar level in the blood of a human body
(b) Ovalbumin is a simple food reserve in egg white
(c) Blood proteins thrombin and fibrinogen are involved in blood clotting
(d) Denaturation makes the proteins more active

326. The IUPAC name of the compound is :

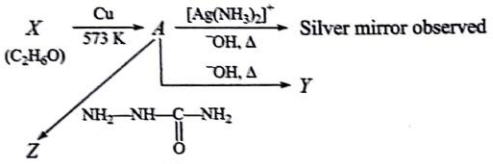


(a) 3-keto-2-methylhex-4-enal
(b) 5-formylhex-2-en-3-one

(c) 5-methyl-4-oxohex-2-en-5-al
(d) 3-keto-2-methylhex-5-enal

327. Which one is the correct order of acidity ?
(a) $CH_2{=}CH_2 > CH_3{-}CH{=}CH_2 > CH_3{-}C{\equiv}CH > CH{\equiv}CH$
(b) $CH{\equiv}CH > CH_3{-}C{\equiv}CH > CH_2{=}CH_2 > CH_3{-}CH_3$
(c) $CH{\equiv}CH > CH_2{=}CH_2 > CH_3{-}C{\equiv}CH > CH_3{-}CH_3$
(d) $CH_3{-}CH_3 > CH_2{=}CH_2 > CH_3{-}C{\equiv}CH > CH{\equiv}CH$

328. Consider the reaction :

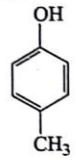


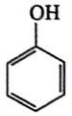
Identify *A*, *X*, *Y* and *Z*.
(a) *A*-methoxymethane, *X*-ethanoic acid, *Y*-acetate ion, *Z*-hydrazine
(b) *A*-methoxymethane, *X*-ethanol, *Y*-ethanoic acid, *Z*-semicarbazide
(c) *A*-ethanal, *X*-ethanol, *Y*-but-2-enal, *Z*-semicarbazone
(d) *A*-ethanol, *X*-acetaldehyde, *Y*-butanone, *Z*-hydrazone

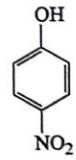
329. The most suitable method of separation of 1 : 1 mixture of ortho and para-nitrophenols is :
(a) sublimation (b) chromatography
(c) crystallisation (d) steam distillation

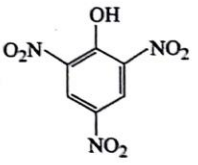
330. With respect to the conformers of ethane, which of the following statements is true?
(a) Bond angle remains same but bond length changes
(b) Bond angle changes but bond length remains same
(c) Both bond angle and bond length changes
(d) Both bond angles and bond length remains same

331. Which one is the most acidic compound ?

(a) 

(b) 

(c) 

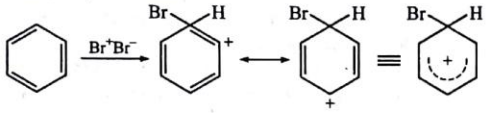
(d) 

SOLUTIONS (One Answer Correct)

1. (d) Ambiphiles are nucleophile as well as electrophile.

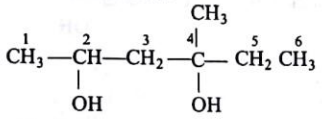
2. (a) I is neither having charge as well as each C and O-atom has complete octet.

3. (b)



4. (a) The ease of dehydration of alcohols giving conjugated diene in maximum.

5. (b)



6. (d)

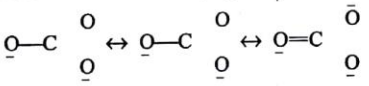
7. (b) $\dot{C}H_3 + e \longrightarrow :\bar{C}H_3$; *EA*

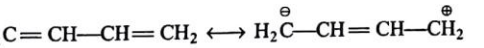
$\dot{C}H_3 \longrightarrow \overset{+}{C}H_3 + e$; *IE*

Gaining of electron leads to stable octet of carbanion ion whereas losing an electron leads to unstable carbocation with sextet of electron.

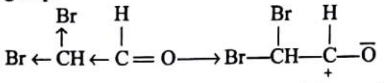
8. (b) The acidic character is *R*COOH > H_2O > *R*OH.

9. (d) Similar number of bonds in different canonical forms leads to isovalent resonance whereas different number of bonds in different canonical forms leads to heterovalent resonance, *e.g.*,





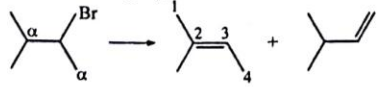
10. (a) Two Br-atoms are more closer to carbonyl group and thus produces more positive charge on C of carbonyl group.



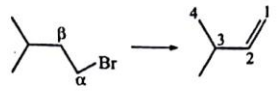
11. (c) 2,4-dimethyl pentan-2-one (a) and Benzophenone (b) will not show reaction due to steric effect of bulky di-isopropyl group and heavier phenyl groups on account of steric effect.

12. (b) 3° alkyl halides shows elimination as well as substitution reactions following S_N1 mechanism.

13. (b) I



II



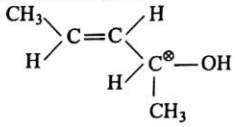
14. (a) Higher is the dielectric constant of medium, more is solvation of intermediate carbocation.

15. (c) Br-atom is replaced by CN^-; C—Cl bond energy > C—Br bond energy.

16. (c) 50% optical purity means, one enantiomer is 50% and in rest 50% the former one is 25% and the other enantiomer is 25%.

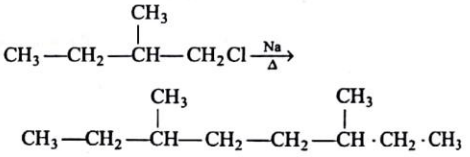
17. (a) (C_7H_{16}) 3-methyl hexane and 2,3-dimethyl pentane are chiral having molar mass 100 g mol^{-1}.

18. (d)

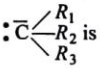


Doubly bonded carbon with $\underset{ab}{C}=\underset{ac}{C}$ and $C^{\otimes}$ chiral carbon. Also, it will show position, chain functional isomerism.

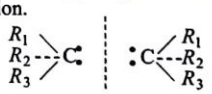
19. (c)



20. (c)

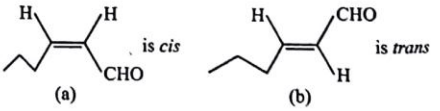


is chiral but the two isomers cannot be isolated due to umbrella type rapid inversion which leads for racemization.

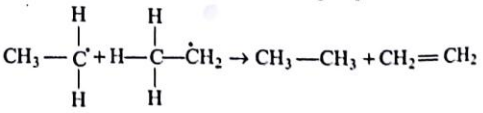


21. (b) It is chiral but do not possess chirality, *i.e.*, the property to rotate the plane of polarised light.

22. (b)

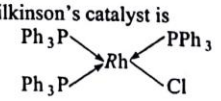


23. (d) Halogenation of alkanes involves free radical mechanism. The chain terminating step is



24. (a) The ease of dehydrohalogenation is 3° > 2° > 1°.

25. (d) Wilkinson's catalyst is

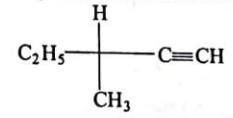


26. (d) All show addition according to peroxide effect.

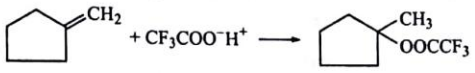
27. (d) All are used to produce diols from alkenes.

28. (d) All are facts.

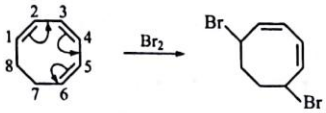
29. (a) The only chiral molecule having two enantiomer is



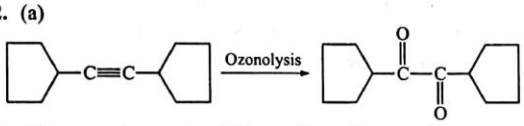
30. (b)



31. (a) Conjugated triene show 1,6-addition.



32. (a)



33. (d) Except hexene-1, all forms alkyne (propyne)

$$CH_3—C\equiv\overset{\ominus}{C}: \xrightarrow[b.H^+ \text{ from } CH_3OH]{a.H^+ \text{ from } H_2O} CH_3—C\equiv CH$$
$$c.H^+ \text{ from } NH_3$$

34. (b) Alkenes and alkynes from carbocation and HSO_4^- ions. In C_2H_2 the carbocation is $[CH_2=\overset{+}{C}]$ and in C_4H_6 it is $[CH_3\overset{+}{C}=CH—CH_3]$ more is the *s* character in the positively charged carbocation, lesser is its stability. However, in $CH_3\overset{+}{C}=CH—CH_3$, presence of electron releasing methyl group provide stability to this cation.

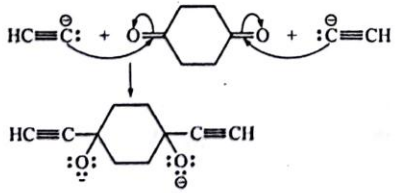
35. (c) $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot C\equiv CH$

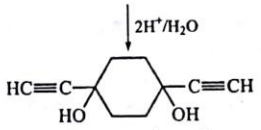
$(CH_3)_2CH\cdot CH_2\cdot C\equiv CH$

$(CH_3)_3CH_2\cdot C\equiv CH$

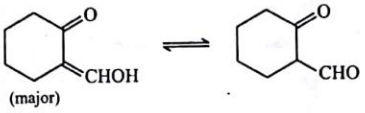
$CH_3\cdot CH_2\cdot \underset{\displaystyle CH_3}{\underset{|}{CH}}—C\equiv CH$

36. (a) $CH\equiv CH \longrightarrow CH\equiv\overset{\ominus}{C}: + H^+$

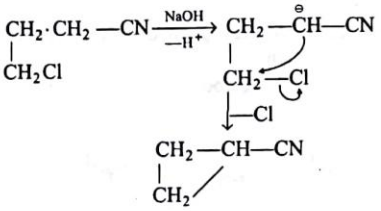




37. (a) This is Claisen condensation and the product is predominantly in enol form.



38. (b)



39. (c) The simplest cycloalkyne which is stable is cyclo octyne.

40. (d) Follow hydride shift.

41. (a) —OH group is not in the nucleus.

42. (b) Stronger bases are good nucleophile and poor leaving group.

43. (a) Rest all are facts.

44. (b) Rest all contains acidic H-atom and thus they would destroy Grignard reagent.

45. (c) The effect of increase in nucleophilicity due to increasing number of electron repelling group *R* is counteracted by the shielding of the reactive site by the *R* groups.

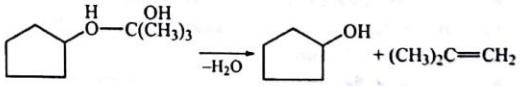
46. (b) Benzophenone does not have α-H-atom.

47. (d) $ZnCl_2 + HCl \longrightarrow H_2ZnCl_4$

$$H_2ZnCl_4 + ROH \longrightarrow RO\overset{\oplus}{H}_2 \xrightarrow[-H_2O]{} R^{\oplus} \xrightarrow[Cl^-]{} RCl$$

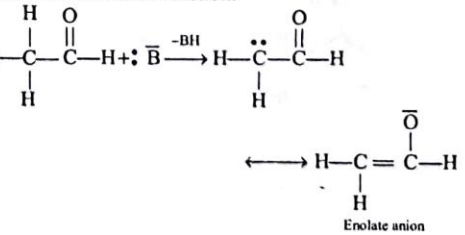
48. (b) $CH\cdot CH_2\cdot OH$ contains $\diagup$ CHOH group.
$\quad\quad|$
$\quad OC_2H_5$

49. (b)



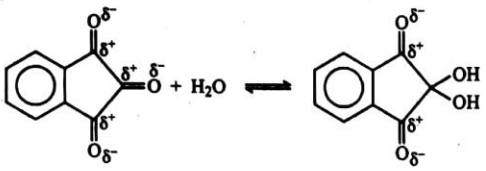
50. (c) This is Rosenmunds reaction.

51. (d)



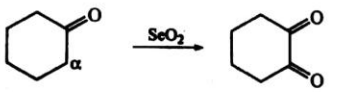
52. (d) These are facts about the respective reactions :
Clemmensen reduction : Zn—Hg + conc. HCl
Wolff Kishner reduction : alk. NH_2NH_2
Sterically hindered ketone are resistant to reduction

53. (b)

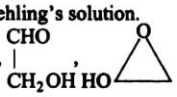


The adjacent δ^+ are separated by the hydration of middle carbonyl group.

54. (a) SeO_2 oxidises α-carbon to $-\overset{\overset{O}{\|}}{C}-$ group.



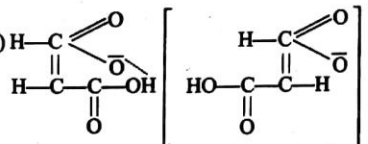
55. (c) It is a fact as it undergoes Cannizzaro reaction giving $C_6H_5CH_2OH$ and C_6H_5COOH. No doubt HCHO also undergoes Cannizzaro reaction but in it HCOOH is formed which give +ve test with Fehling's solution.

56. (d) $C_2H_4O_2$: CH_3COOH; $HOCH_2CHO$, 

Anhydrides have general formula $C_nH_{2n-2}O_{n-1}$.

57. (a) β-keto carboxylic acids on heating show decarboxylation.

58. (c)



maleate ion fumarate ion

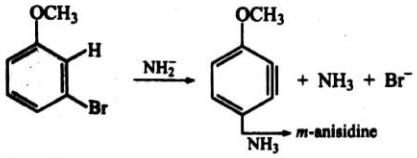
59. (b) Due to hyperconjugation

60. (c) *t*-nitro alkanes do not have α-H-atom.

61. (d) Alkylation of amine is made by 1° alkyl halides.

62. (d) It has α-H-atom.

63. (b) Due to the formation of benzyne intermediate.



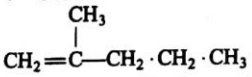
64. (d) Pent-1-ene, pent-2-ene, 2-methyl but-2-ene and two cyclic isomers: cyclobutane and methyl cyclopropane.

65. (b) Methylcyclobutane and cyclopentane; (1,1-dimethyl-cyclopropane; 1,2-dimethyl cyclopropane.)

66. (b) It has two CH_3 groups at one position.

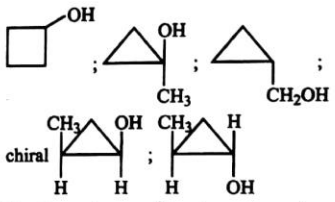
67. (a) Interconversion of *cis* to *trans* and *trans* to *cis* alkenes occurs on heating with I_2.

68. (c) $(CH_3)_2CH\cdot CH_2\cdot CH=CH_2$
$(CH_3)_2CH\cdot CH=CHCH_3$
$(CH_3)_2C=CH\cdot CH_2\cdot CH_3$



69. (a) The stability of alkanes increases with increasing branching.

70. (a)

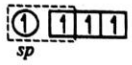


71. (d) Singlet carbene sp^2 has bent shape due to the presence of one lone pair.

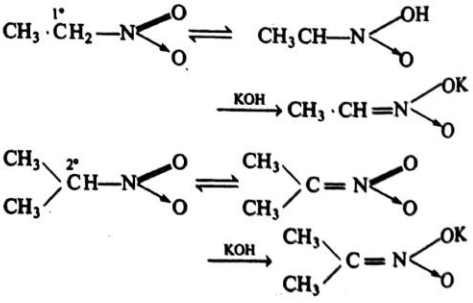
All the electrons are paired.

72. (d) Triplet methylene : CH_2, *i.e.*, H $\dot{\underset{\cdot}{C}}$ H

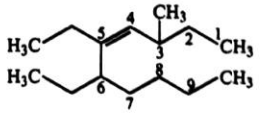
A diradical in which unshared electrons are not paired.



73. (c) *t*-nitro alkanes do not show tautomerism and not form aci-form.



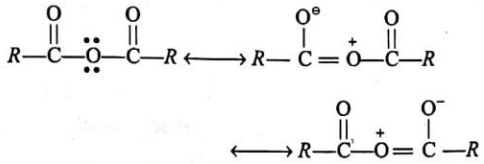
74. (a)



75. (a) Follow IUPAC rules.

76. (c) Ester hydrolysis by alkali is not reversible.

77. (a) A degree of cross conjugation exists in anhydride.



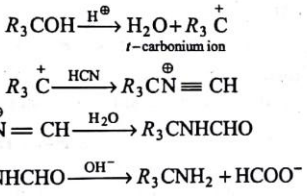
This decreases the delocalisation of electron to each carbonyl oxygen and provides less double bond character to C—O bond of $\rangle C=O$ group.

78. (c) Bivalent or polyvalent functional group compounds show only metamerism.

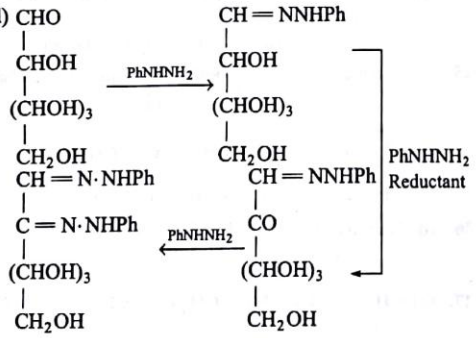
79. (d) *N* is attached to four carbon atoms.

80. (c) *t*-amines having the same molar mass possess lowest b.pt. as they do not show H-bonding.

81. (a) In Ritter method, tertiary alcohol reacts with HCN to give *p*-amine having tertiary alkyl group.



82. (d)



83. (b) Either of the three on treating with NaOH gives an equilibrium mixture of all the three sugars. This is known as Lobry-de Bruyn Van Ekenstein rearrangement.

$$\text{Glucose} \rightleftharpoons \text{Fructose} + \text{Mannose}$$

84. (c) It is $-I$ effect which play main role to deactivate ring. However, S_E reactions proceeds as $+T$ effect $\geq -I$ effect.

85. (a) $-NH_2$ dominates in directive influence.

86. (b) $C_6H_5NO_2 < C_6H_5Cl < C_6H_6 = C_6D_6$

87. (a) ΔH_{hy} of $3C=C = -29 \times 3 = -87$

$\therefore$ Resonance energy of $C_6H_6 = -87 - (-51)$

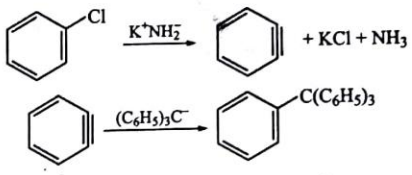
$= -36$ kcal mol^{-1}

88. (b) Due to steric hindrance of *t*-butyl group, *o*-derivative is not formed.

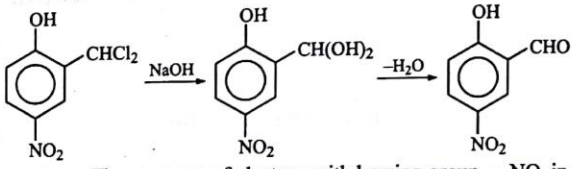
89. (b) $C_6H_5CHClCH_3$ gives white ppt. with $AgNO_3$.

90. (b) Follow mechanism.

91. (b)

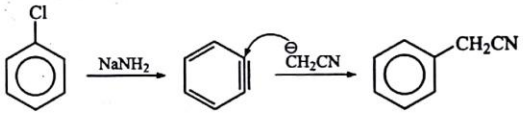


92. (d)



The presence of electron withdrawing group $-NO_2$ in *p*-position stabilizes the intermediate carbocation due to *IE* and *RE*.

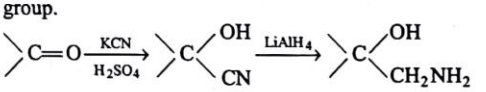
93. (a)



94. (a) Only *m*-cresol gives tri bromo derivative.

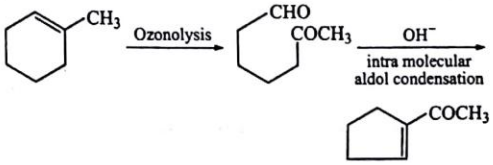
95. (a) *p*-amino benzoic acid is soluble in acid due to $-NH_2$ group.

96. (c)



97. (a) Any side chain in benzene ring is oxidises to —COOH group.

98. (a)



99. (a) CCl_3 is *m*-directing group.

100. (c) It is a fact.

101. (b) Carbenes do not form 1,4-addition with conjugated dienes. They show 1,2-addition.

102. (c) The ease of nucleophilic addition on $C=C$ is greatly enhanced in ease of $\alpha-\beta$ unsaturated carbonyl compounds.

103. (c) OsO_4 and $NaIO_4$ oxidises $C=C$ to —CHO groups.

104. (b) $CH_2=CH-\underset{n=2}{CH=CH_2} \xrightarrow{O_3}$

$HCHO + HCHO + \underset{\underset{CHO}{|}}{CHO}$

Products(n+1)

105. (b) —COOH is replaced by Br.

106. (d) $\underset{\underset{CH_2OH}{|}}{\overset{CH_2OH}{|}}{C=O} \xrightarrow{HIO_4} 2HCHO + CO_2$

(HIO_4 breaks C—C bond)

107. (d) Sucrose is non-reducing sugar.

108. (c) Follow IUPAC rules.

109. (d) $NH_2 \cdot \underset{Keto}{\overset{O}{\overset{||}{C}}}-NH_2 \rightleftharpoons HN=\underset{Enol}{\overset{OH}{\overset{|}{C}}}-NH_2$

110. (a) It is electrophilic substitution (I^+Cl^-).

111. (b) III gives aromatic ring, II gives conjugated system on dehydration.

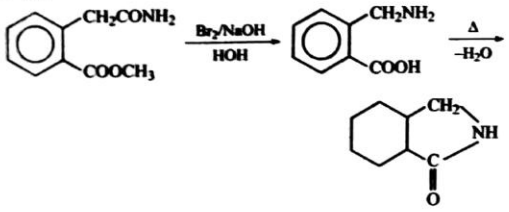
112. (d) $CH_3-\overset{+}{C}H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-CH_3 \longleftrightarrow CH_3 \cdot CH=\overset{+}{O}-CH_3$

Resonance most stable.

$CH_3 \cdot \overset{+}{C}H-COCH_3$ (CH_3COCH_3 is electron withdrawing and the charge on C^+ is intensified thus least stable)

113. (b) Position of Br is ortho to $-CH_3$ and *p-t* $-OCH_3$ para effect of $-OCH_3 > -CH_3$.

114. (c)



115. (d) $Br_2 + 2KOH \longrightarrow KBr + KBrO + H_2O$

$RCONH_2 + Br_2 \xrightarrow[KOH]{BrO^-} RCONHBr + KBr + H_2O$

$RCONHBr \xrightarrow{OH^-} RCONBr + H_2O$

$R-\overset{O}{\overset{||}{C}}-NBr \longrightarrow R-\overset{O}{\overset{||}{C}}-\overset{\cdot\cdot}{N}: + Br^-$

$R-\overset{O}{\overset{||}{C}}-\overset{\cdot\cdot}{N}: \longrightarrow R-N=C=O$

$R-N=C=O + 2KOH \longrightarrow RNH_2 + K_2CO_3$

116. (a) Follow priority rule of configuration.

117. (a) $CH_3-\underset{Keto\ form}{\overset{O}{\overset{||}{C}}}-CH_3 \rightleftharpoons CH_2=\overset{OH}{\overset{|}{C}}-CH_3 \xrightarrow{D_2O}$

$CH_2=\overset{OD}{\overset{|}{C}}-CH_3$

(H being acidic replaced by D.)

118. (d) $\overset{1}{CH_2}=\overset{2}{CH}-\underset{sp^2-sp^3}{\overset{3}{CH_2}}-\overset{4}{CH_2}-\overset{5}{C}\equiv\overset{6}{CH}$

119. (b) C: ① 1 1 1 — $\overset{1}{C}$— (sp^2)

120. (a) C: ① 1 1 1 — C — (sp)

121. (b) $-\overset{\cdot}{\underset{CH_3}{\overset{H}{\underset{|}{C}}}}-COOH$ is asymmetric.

122. (c) $CH_2=CH-CH_2-C\equiv N$: 9σ, 3π and 2 non-bonded electrons.

123. (d) Carbocations are stabilized by resonance

$\underset{\text{Allyl carbocation}}{CH_2=CH-\overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2-CH=CH_2}$

124. (b) More basic group has least leaving nature. Conjugate acid order

$HOSO_2CF_3 > HOSO_2Me > HOAc > HOMe$

125. (c) Resonance stabilizes both carbocation and carbanion

$CH_3-\overset{O}{\overset{||}{C}}-\overset{-}{C}H_2 \leftrightarrow CH_3-\overset{O^-}{\overset{|}{C}}=\overset{-}{C}H_2$

$CH_2=CH-\overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2-CH=CH_2$

126. (d) Due to aromaticity II and IV are least basic.

127. (a) $CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}ClCH_2CH_3$

$+ CH_3-\underset{(d\text{ and }l)}{\overset{CH_3}{\overset{|}{C}}H-\overset{\cdot}{C}HCl}\cdot CH_3 + CH_3-\overset{CH_3}{\overset{|}{C}}H\cdot CH_2\cdot CH_2Cl$

$+ CH_3-\underset{(d\text{ and }l)}{\overset{CH_2Cl}{\overset{|}{\overset{\cdot}{C}}}}HCH_2CH_3$

128. (d) All are correct.

129. (b) $CH_3CH=CH_2 \xrightarrow[\text{Peroxide}]{HCl} CH_3\overset{+}{C}H-CH_3$ (Addition is electrophilic); HCl addition is not influenced by peroxide.

130. (c) N is pentavalent which is not possible.

131. (a) The correct order in vapour phase is (a) whereas in liquid phase is (b).

132. (b) Follow IUPAC rules.

133. (a) Due to maximum strain according to Baeyer's strain theory.

134. (a) $(CH_3)_3CMgCl + DOD \longrightarrow (CH_3)_3CD + Mg\begin{matrix}Cl\\OD\end{matrix}$

135. (d) CH_3OH is stronger acid than C_2H_2.

136. (b) It is a fact.

137. (d) It does not have olefinic H-atom.

138. (a) Ethyl aceto acetate $CH_3COCH_2COOC_2H_5$ and diethyl malonate $\left(H_2C\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}\right)$ have acidic hydrogen.

Pentan-3-one does not contain CH_3—CO unit.

139. (b) On electrolysis Cl_2 is liberated which reacts with C_2H_5OH and NaOH (formed) to give chloroform.

140. (c) Chloroform gives carbylamine reaction.

141. (d) It is a fact.

142. (d) *p*-nitrophenol has strongest acidic nature.

143. (b) It is a fact.

144. (d) $CH_3CH_2COOH \xrightarrow[P]{Br_2} CH_3\underset{Br}{CH}COOH \xrightarrow{NH_3\ alc.}$

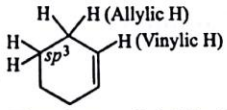
$CH_3\underset{NH_2}{CH}\cdot COOH$ Alanine

145. (a) β-keto acid on heating easily undergoes decarboxylation.

146. (a) A : $CH_2=CH_2$; B : CH_2BrCH_2Br; C : $\begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix}$;

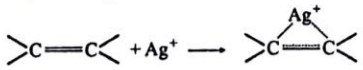
D : $\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}$

147. (c) $CH_3CHOH\cdot CH_2COOH \xrightarrow{-H_2O} CH_3\underset{\beta}{CH}=\underset{\alpha}{CH}COOH$

148. (c) 

(There is no *sp*-hybridized carbon)

149. (a) Ag^+ coordinates with alkene involving *d-p* π-bonding and producing ion.

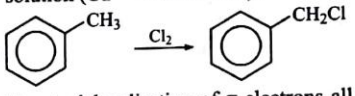


150. (c) Rate of nitration of benzene is same as that of hexadeuterobenzene.

151. (a) $CH_3CH_2CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2CH_2CHO$

$\xrightarrow{[O]} CH_3CH_2CH_2COOK + \underset{\text{Brown mass}}{MnO_2} + KOH$

152. (b) Aromatic aldehydes are not oxidised by Benedicts solution (Cu^{2+} + Citric acid).

153. (c) 

154. (c) Due to delocalisation of π electrons all carbon-carbon bonds become equal. So, the bond order lies between one and two.

155. (a) Single bond length is largest. The bond length is,

C—C > C=C > C≡C

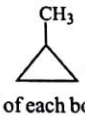
(1.5Å)(1.34 Å)(1.20Å)

156. (d) $CH_3\cdot\underset{\text{(acidic gp)}}{CH}(\underset{\text{(basic gp)}}{NH_2})\cdot COOH \xrightarrow[+H^+]{pH=2} CH_3\cdot\underset{|}{\overset{+}{N}H_3}\text{—}CH\text{—}COOH$

$\xrightarrow[-H^+]{pH=10} CH_3\text{—}\underset{|}{\overset{NH_2}{CH}}\text{—}COO^-$

157. (c) Methyl group is electron donating group, therefore it increases the electron density in benzene ring. Since SO_3 is electrophyle so, toluene is easily sulphonated.

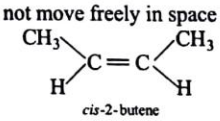
158. (c) $H_2C=CH-CH_2-CH_3$ (I) $CH_2=\underset{|}{\overset{CH_3}{C}}-CH_3$ (II)

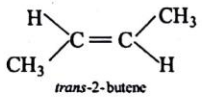
(III)  (IV)

159. (b) In CCl_4 the moment of each bond is cancelled out due to its regular tetrahedron structure.

160. (d) $\underset{sp^2}{H_2C}=\underset{sp}{C}=\underset{sp^2}{CH}-\underset{sp^3}{CH_3}$

161. (a) Geometrical isomerism arises due to the hindered rotation between $\rangle C=C\langle$ bond, *i.e.*, atoms or groups do not move freely in space :


cis-2-butene


trans-2-butene

162. (c) $\underset{4}{CH_3}-\underset{3}{\underset{|}{\overset{CH_3}{C}}}-\underset{2}{CH}=\underset{1}{CH_2}$

3, 3-dimethyl-1-butene

163. (a) $-CH_3$ gp. has + *I* and + *M* effect. It increases the electron density on benzene ring hence toluene is reactive towards electrophilic nitration.

164. (d) It is an experimental fact.

165. (c) $N\equiv\underset{1}{\overset{sp}{C}}-\underset{2}{\overset{sp^2}{CH}}=\overset{sp^2}{CH_2}$

166. (b) $CH_2{}^{1}=CH_2{}^{2}-CH^{3}(CH_3)(CH_3)^{4}$

3-methyl-1-butene

167. (a) Ethane (H_3C-CH_3) has least hindered rotation about C—C bond. Therefore, atoms or groups attached to it, move freely in space.

168. (b) The two compounds with different molar masses can have the same empirical formula but different molecular formulae.

169. (b) (i) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

(ii) $CH_3-CH(CH_3)-CH_2-CH_2-CH_3$

(iii) $CH_3-CH(CH_3)-CH(CH_3)-CH_3$

(iv) $CH_3-C(CH_3)_2-CH_2-CH_3$

(v) $CH_3-CH_2-CH(CH_3)-CH_2-CH_3$

170. (c) $Cl(H)C=C(H)Cl$ (*trans*)

Both the chlorine atoms are in opposite direction and cancel the moment of each other.

171. (d) Oxygen is highly electronegative than carbon, so it acquires partially negative charge and carbon atom acquires partially positive charge.

172. (a) Stronger is the acid or base, weaker is its conjugate acid or base.

Base strength :

$CH_3-\bar{C}H_2 > \bar{N}H_2 > HC\equiv C^- > OH^-$

Acid strength :

$H-OH > HC\equiv CH > NH_3 > CH_3-CH_3$

173. (a) The former compound has triangular planar structure while later one has tetrahedral structure.

174. (d) The difference of electronegativities between O and H is high, therefore undergo heterolytic cleavage.

175. (b) Tertiary butyl alcohol gives *t*-butyl carbonium ion which is more stable than primary and secondary carbonium ion.

176. (b) $H-C\equiv C-C\equiv C-H$ (with σ and π bonds marked)

σ – **bonds = 7**

π – **bonds = 3**

1-butene-3-yne

It contains 7 sigma and 3π bonds.

177. (d) $CH_3-CH_2-CH_2-CH(CH_3)-CH_3$

2-methyl pentane

178. (c) C—H bond length in saturated hydrocarbon is more in comparison to the C—H bond length of alkene and alkyne.

179. (a) In benzyl amine the lone pair of electron on 'N' atom does not come into resonance with ring.

180. (b) $HCN \rightleftharpoons H^+ + \underset{\text{Nucleophile}}{CN^-}$

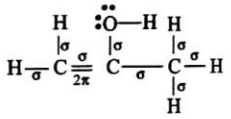
$R_2C^{+}-\ddot{O}-H + CN^- \longrightarrow R_2C(OH)CN$

Ketone → Cyanohydrin

It is an example of nucleophilic addition reaction.

181. (a) Enolic from of acetone contains 9 σ bonds, 1 π bond, 2 lone pair of electrons

$CH_2=C(OH)-CH_3$ (Enolic form) ⇌ $CH_3-C(=O)-CH_3$ (Keto form)



182. (c) $H-C\equiv C-C=C-C-H$ (sp, sp, sp^2, sp^2)

183. (a) Isomers obtained by the rotation of C—C single bond in space are called conformers.

184. (c) Rest all are correct. Point *b* and *d* suggest for more stable nature of benzoate ion.

185. (d) Rest all are oxidised. Benzaldehyde does not contain α-H atom.

186. (c) The electron donating groups facilitate the electrophilic substitution reactions.

187. (a) $CH_2COOH-CH_2COOH \xrightarrow[-H_2O]{\Delta} CH_2CO-CH_2CO-O$

$CH_2(COOH)_2 \xrightarrow[-CO_2]{\Delta} CH_3COOH$

⟶ Gives effervescence with $NaHCO_3$ solution

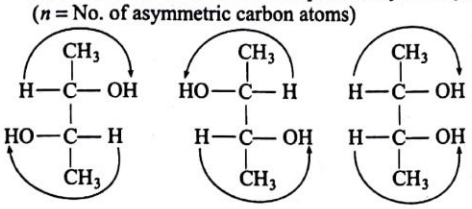
188. (b) In orthodichlorobenzene the resultant dipole moment is highest, because both the moments are in same direction.

189. (c) $HCOONH_4 \xrightarrow{\Delta} HCONH_2 + H_2O$

190. (a) CH_3COCl is most susceptible to nucleophilic attack because Cl atom is also electronegative atom which decreases the electron density on carbonyl carbon making it sensitive towards nucleophilic attack.

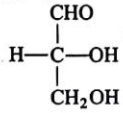
191. (b) $CH_3-\overset{\bullet}{C}H-\overset{\bullet}{C}H-CH_3$ (OH, OH)

It has two asymmetric C-atoms therefore optically active isomers $= 2^{n-1} = 2^{2-1} = 2$. It has an optically inactive meso form due to the molecular plane of symmetry. (n = No. of asymmetric carbon atoms)

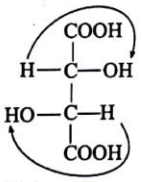


d-isomer (optically active) | *l*-isomer (optically active) | *meso*-isomer (optically inactive)

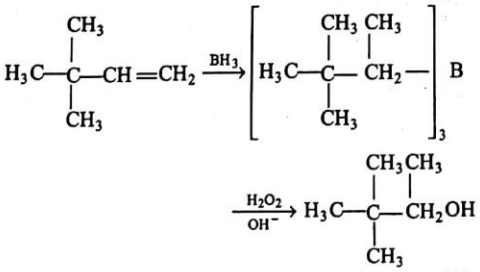
192. (c) D is used to represent the arrangement of —OH group in right side at second last carbon atom as in glyceraldehyde and (+) sign is used to represent the



optical rotation in clockwise direction. Hence (+) tartaric acid is :



193. (c) Hydroboration – oxidation follows anti Markownikoff addition



194. (b) Marsh gas mainly contains CH_4.

195. (b) The unsaturated compounds (alkenes and alkynes) decolourises alkaline $KMnO_4$ solution. (Test for unsaturation)

196. (a) The straight chain compounds have higher b.pt. than branched compounds. On branching, the tendency of close packing decreases.

197. (c) $CH_3-C\equiv CH \xrightarrow[HgSO_4]{H_2SO_4} CH_3-\underset{HSO_4}{\overset{HSO_4}{C}}-CH_3 \xrightarrow{H^+/H_2O}$

$CH_3-\underset{OH}{\overset{OH}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\underset{\text{Acetone}}{C}-CH_3$ (O)

198. (c) Hexane does not dissolve in conc. H_2SO_4.

199. (a) Cold dilute alkaline solution of potassium permanganate (1% cold alkaline $KMnO_4$) is known as Baeyer's reagent.

200. (a) Ethyne (terminal alkynes) has acidic H which can be easily replaced by metals.

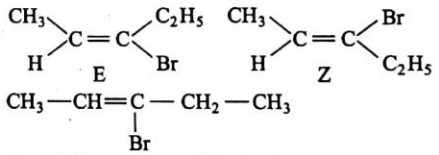
$HC\equiv CH + Na \xrightarrow[-(1/2)H_2]{180°C} HC\equiv CNa \xrightarrow[-(1/2)H_2]{200°C} \underset{\text{Disodium acetylide}}{NaC\equiv CNa}$

201. (c) But-2-ene is symmetrical alkene. So it does not show anti Markovnikoff addition.

202. (b) Follow answer 196.

203. (b) $CH_3-C\equiv C-CH_2-CH_3 + HBr \longrightarrow$

$CH_3-CH=\underset{Br}{C}-CH_2-CH_3$



E Z

$CH_3-CH=\underset{Br}{C}-CH_2-CH_3$

3-Bromo-pent-2-ene

$CH_3-\underset{Br}{C}=CH-CH_2-CH_3$

2-Bromo-pent-2-ene

204. (a) Alkens show electrophilic addition.

$CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2 \xrightarrow[H....Br, Slow]{\delta+\ \delta-} CH_3-\overset{+}{C}H-CH_3 \xrightarrow[Fast]{Br^-} CH_3-\underset{Br}{CH}-CH_3$

205. (b) This is a free radical reaction. A secondary free radical is more stable than primary free radical.

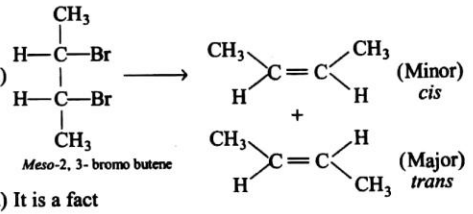
$CH_3CH_2CH_2CH_3 + Br_2 \xrightarrow{130°C}$

$\underset{\text{(Minor)}}{CH_3CH_2CH_2CH_2Br} + CH_3CH_2\underset{CH_3}{\underset{|}{CH}}-Br$ (Major)

206. (b) $(H_3C)_2CHCH_2MgBr + C_2H_5OH \xrightarrow{\text{dry ether}}$

$(H_3C)_2CH-CH_3 + MgBrOC_2H_5$

207. (d)

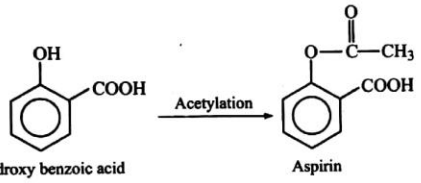


Meso-2, 3- bromo butene

(Minor) *cis* + (Major) *trans*

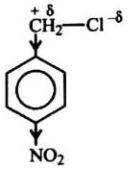
208. (d) It is a fact

209. (b)



o-hydroxy benzoic acid — Aspirin

210. (d) Electron withdrawing nature of $-NO_2$ gp increases polarity in CH_2Cl.

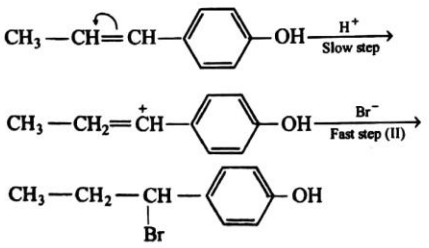


211. (b) Bakelite is condensation polymer of HCHO and phenol.

212. (b) $CH_3-CH=CH-C_6H_4-OH + HBr \longrightarrow$

$CH_3-CH_2-CH(Br)-C_6H_4-OH$

Mechanism



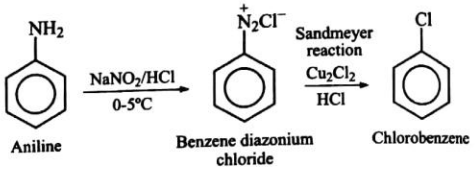
213. (a) $CH_3-CH_2-C\equiv CH \xrightarrow[Hg^{2+}/H_2SO_4]{H_2O}$

$CH_3-CH_2-C(OH)=CH_2 \underset{\text{Tautomerise}}{\rightleftharpoons} CH_3-CH_2-\underset{\text{Keto form}}{C(=O)}-CH_3$

The mechanism involves tautomerism.

214. (b) CCl_4 has a regular symmetrical structure therefore each bond moment is cancelled out from each other.

215. (d)

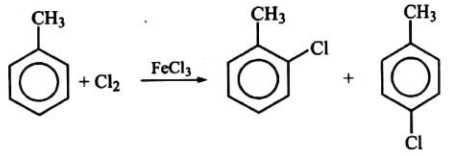


Aniline — Benzene diazonium chloride — Chlorobenzene

216. (a) Tert. carbonium ion is more stable than secondary or primary carbonium ion.

217. (a) $C_2H_6\,(\text{excess}) + Cl_2 \xrightarrow{\text{UV light}} C_2H_5Cl + HCl$

218. (d)



This is an electrophilic substitution reaction.

219. (b) Alc. KOH is a dehydrohalogenating agent.

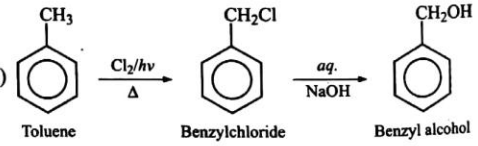
$CH_3-CH_2CH_2Br \xrightarrow{\text{ethanolic KOH}}$

n-propyl bromide

$CH_3-CH=CH_2 + KBr + H_2O$

propene

220. (d)



Toluene — Benzylchloride — Benzyl alcohol

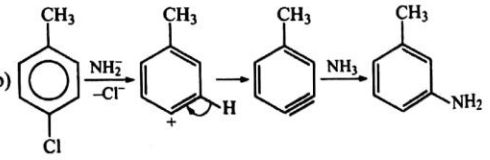
221. (a) $CH_3-CH_2-CH_2-CH_2-Cl + KOH\,(\text{alc.}) \longrightarrow$

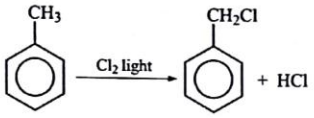
1-chlorobutane

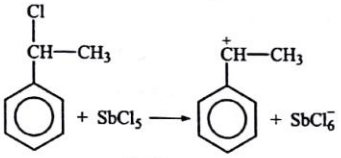
$CH_3-CH_2-CH=CH_2 + KCl + H_2O$

1-butene

222. (b)



223. (c) 

224. (d) 

225. (c) $C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4} H_2C{=}CH_2 + H_2O$

226. (a) $\underset{\text{C-Base}}{CH_3ONa} \xleftarrow{NaH} \underset{\text{Base}}{\overset{\text{Acid}}{CH_3OH}} \xrightarrow{H_2SO_4} \underset{\text{C-Acid}}{CH_3OH_2^+}$

227. (d) $C_2H_5{-}O{-}C_2H_5$, $CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_3$,
Both the compounds have different molecular formula.

228. (d) The test with Lucas reagent (conc. HCl + Anhyd. $ZnCl_2$) is based on the reactivity order of alcohols to replace —OH gp. by halogen atom, *i.e.*, *tert*-alcohol > sec-alcohol > *p*-alcohol.

$$R{-}OH \xrightarrow{HCl+ZnCl_2} R{-}Cl$$

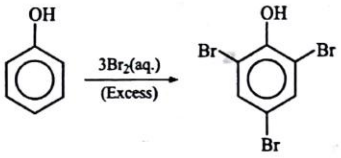
Primary alcohol $\xrightarrow[\text{room temp.}]{\text{Lucas reagent}}$ No cloudiness at room temp., it appears only on heating

Secondary alcohol $\xrightarrow[\text{room temp.}]{\text{Lucas reagent}}$ Cloudiness appears within 5 minutes

Tertiary alcohol $\xrightarrow[\text{room temp.}]{\text{Lucas reagent}}$ Cloudiness appears immediately

229. (c) $C_2H_5OC_2H_5 + 2HI \xrightarrow{\Delta} 2C_2H_5I + H_2O$

230. (a) $\underbrace{CO + H_2}_{\text{water gas}} + H_2 \xrightarrow[300°C]{Cr_2O_3-ZnO} \underset{\text{Methanol}}{CH_3OH}$

231. (d) 
2,4,6-Tribromophenol

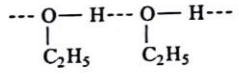
The —OH gp is an electron donating gp. and it activates the benzene ring for electrophilic substitution.

232. (c) Iodoform test is given by compounds having methyl ketones, sec. alcohol and ethyl alcohol (only *p*-alcohol).

233. (a) It is an experimental fact. Follow directive influence of gps.

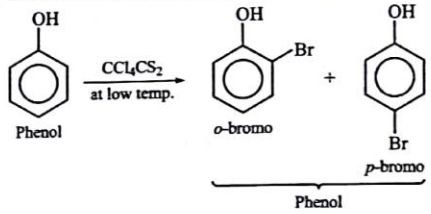
234. (c) Secondary alcohols are oxidised by $K_2Cr_2O_7 + H_2SO_4$ to produce ketone.

$$\underset{\text{2-Butanol}}{CH_3CHOHCH_2CH_3} \xrightarrow{(O)} \underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3}$$

235. (a) 

Hydrogen bonding is maximum in ethanol because it forms intermolecular H-bonding.

236. (b) This is controlled bromination reaction.



237. (b) $RSH + O_2 \longrightarrow CO_2(g) + H_2O(l) + SO_2(g)$.

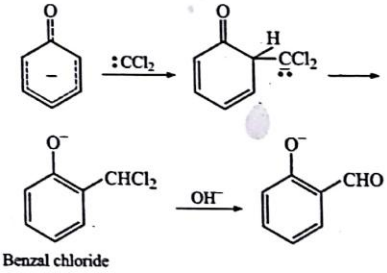
238. (a) In case of mixed ether the halogen atom gets attached to simple alkyl groups.

$$C_6H_5OCH_3 \xrightarrow{HI} C_6H_5OH + CH_3I$$

239. (d) This is a Reimer-Tiemann reaction, proceeds through an electron deficient intermediate dichlorocarbene.

$$HCCl_3 + OH^- \longrightarrow H_2O + :\ddot{\underset{\cdot\cdot}{C}}Cl_3$$

$$:\ddot{\underset{\cdot\cdot}{C}}Cl_3 \longrightarrow Cl^- + :CCl_2$$


Benzal chloride

240. (c) The order of reactivity depends upon the stability of the carbocations formed. Maximum is the stability of carbocation, maximum will be the reactivity of its conjugate counter part. Stability of carbocations is in the order.

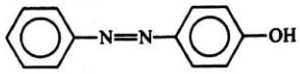
$FCH_2\overset{+}{C}HCH_3 < FCH_2CH_2\overset{+}{C}HCH_3 < CH_3\overset{+}{C}HCH_3 < Ph\overset{+}{C}H_2$

I(2°, F nearer) II(2° F away) III(2°) IV(Benzyl)

Hence the order of relative reactivity of the alcohols will follow the order : IV > III > II > I.

241. (b) It is a coupling reaction

$$C_6H_5N_2Cl + C_6H_5OH \xrightarrow[\text{Coupling reaction}]{OH^-}$$



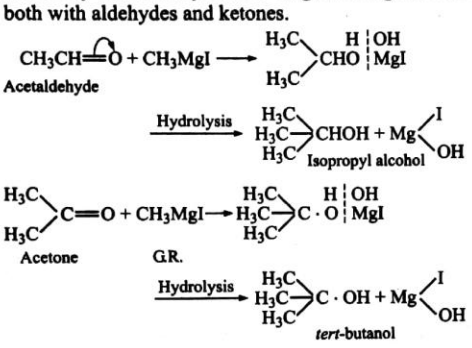
p-hydroxy-azobenzene
(Orange red dye)

242. (d) Order of acidic strength is :

$CH_3OH > HC \equiv CH > C_6H_6 > C_2H_6$

Although all are neutral towards the litmus paper.

243. (b) Fehling solution, Schiff's reagent and Tollen's reagent react only with aldehydes but Grignard reagents react both with aldehydes and ketones.



Acetaldehyde

Isopropyl alcohol

Acetone G.R.

tert-butanol

244. (b) Compounds having, $-\overset{\overset{O}{\|}}{C}-CH_3$ all sec. alcohol and C_2H_5OH (only in primary alcohol) give positive iodoform test

$$CH_3-CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

(pentanon-2) gives this test.

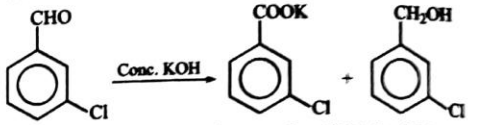
245. (c) The product is red ppt of cuprous oxide

$$\underset{\text{Fehling solution}}{CH_3CHO} + 2Cu^{2+} + OH^- \longrightarrow CH_3COOH + \underset{\text{red}}{Cu_2O}\downarrow$$

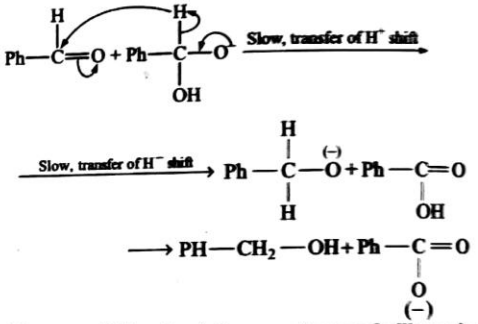
246. (b) Compounds not containing α-H undergo Cannizzaro reaction.

Acetaldehyde does not undergo Cannizzaro reaction since it has α-H atoms while formaldehyde, trimethylacetaldehyde and benzaldehyde undergo Cannizzaro reaction since they do not contain α-hydrogen atoms.

247. (d) *m*-chlorobenzaldehyde does not contains any α-H atom. So it undergo Cannizzaro reaction to form acid salt and alcohol.



248. (b) In Cannizzaro reaction the transfer of H^- (hydride ion) takes place in slow step

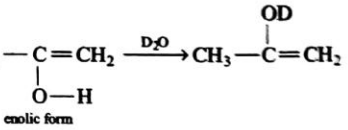


249. (d) Electron withdrawing (nitro group) group facilitates the release of hydride ion.

250. (b) CCl_3CHO reacts with water to give a stable chloral monohydrate.

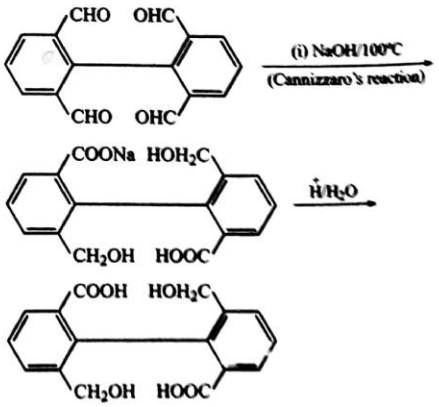
$$\underset{\text{Chloral}}{CCl_3CHO} \xrightarrow{H_2O} \underset{\text{Chloral monohydrate}}{CCl_3CH(OH)_2}$$

251. (a)



enolic form

252. (b) This is an intramolecular Cannizzaro reaction.



253. (c) It is an example of nucleophilic addition on carbonyl group which depends upon positive charge density and steric hindrance around carbonyl group.
Thus CH_3CHO is most reactive and $C_6H_5COC_6H_5$ is least.

254. (c) $H_3C-\underset{\text{2-Butanone}}{\overset{O}{\overset{\|}{C}}}-CH_2CH_3 \xrightarrow[\text{(haloform reaction)}]{I_2/OH}$

$$CHI_3\downarrow + CH_3CH_2COO^-Na^+ \xrightarrow{H^+} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

255. (c) This reaction is an example of Perkin reaction. This reaction proceeds through the carbanion mechanism. The compound X is $(CH_3CO)_2O$

$$C_6H_5CHO + H_2CHCO\cdot O\cdot COCH_3 \xrightarrow{HOH}$$
$$C_6H_5CH{=}\ CHCOOH\cdot COCH_3 + CH_3COOH$$

256. (c) In first step decarboxylation occurs and E is formed which is $PhCOCH_3$. The second step is iodoform reaction giving $PhCOO^-Na^+$ (F) and CHI_3 (G).

$$Ph-\overset{O}{\overset{\|}{C}}-\dot{C}H_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-CO_2]{\Delta} \underset{(E)}{Ph-\overset{O}{\overset{\|}{C}}-\dot{C}H_3}$$
$$\xrightarrow[NaOH]{I_2} \underset{(F)}{PhCOO^-Na^+} + \underset{(G)}{\dot{C}HI_3}$$

257. (b) This is Hofmann bromide reaction. In this reaction primary amine with one carbon less is formed.

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + H_2O$$

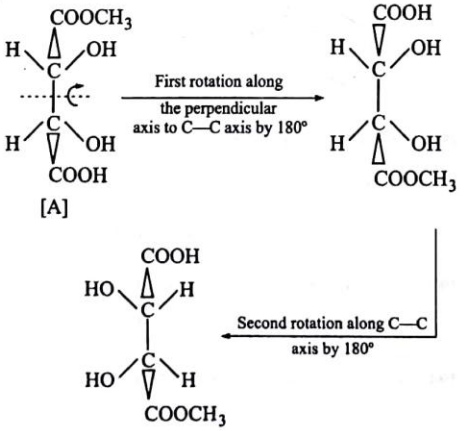
258. (b) In Rosenmund reaction partial hydrogenation occurs

$$\underset{\text{benzoyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow[\text{xylene}]{Pd/BaSO_4} \underset{\text{benzaldehyde}}{C_6H_5CHO} + HCl$$

259. (a) $\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$

260. (d) It is an experimental fact.

261. (d)



[A]

This is perfect mirror image of B and thus A and B are enantiomers.

262. (d) The carbon of CO_2 comes from bicarbonate

$$C_2H_5COOH + NaHCO_3 \rightarrow C_2H_5COONa + H_2O + CO_2$$

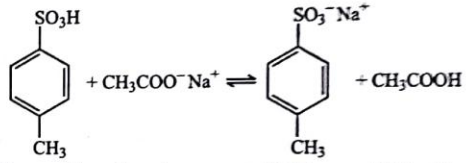
263. (a) The product is tertiary butyl alcohol

$$CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{CH_3MgBr} CH_3-\underset{CH_3}{\overset{OMgBr}{\overset{|}{\underset{|}{C}}}}-OC_2H_5$$

$$\xrightarrow{\left(Mg\begin{smallmatrix}Br\\OC_2H_5\end{smallmatrix}\right)} CO\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} \xrightarrow{CH_3MgBr}$$

$$(CH_3)_3\cdot C\cdot OMgBr \xrightarrow[-Mg\begin{smallmatrix}OH\\Br\end{smallmatrix}]{H_2O/H^+} (CH_3)_3C-OH$$

264. (a) This is an acid-base reaction



Strong acid Strong base Weak base Weak acid

265. (c) Secondary amines (aliphatic as well as aromatic) react with nitrous acid to form N-nitrosoamines.

$$(C_2H_5)_2NH + HONO \longrightarrow \underset{N\text{-nitrosodiethylamine}}{(C_2H_5)_2-N=O} + H_2O$$

266. (b) Carbylamine test is given by only aliphatic and aromatic primary amines. It react, with alkaline $CHCl_3$ to form bad smelling isocyanides.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

267. (d) Propyl chloride reacts with alcoholic KCN to from butane nitrile.

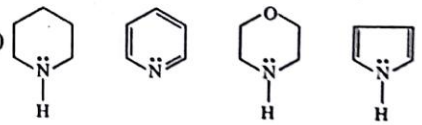
$$CH_3CH_2CH_2Cl + KCN \longrightarrow \underset{\text{Butane nitrile}}{CH_3CH_2CH_2CN} + KCl$$

268. (c) Second canonical structure can not be acceptable because N-atom has ten valence electron which is not possible.

269. (a) According to Bronsted Lowry theory, H_2SO_4 is a proton donor species and a stronger acid than HNO_3. Therefore, H_2SO_4 acts as an acid and HNO_3 as base.

$$HNO_3 + H_2SO_4 \longrightarrow H_2^+NO_3 + HSO_4^-$$
$$H_2^+NO_3 \longrightarrow H_2O + NO_2^+$$

270. (d)



I II III IV

In structure I and III the lone pair of N-atom present in sp^3 hybridization structure, I is more basic than III

because in structure III the lone pair of electrons shifts towards oxygen atom to a lesser extent. In structure II and IV the N-atom is sp^2 hybridized. In structure IV the lone pair of electrons involves in aromatic sextet but not in structure II.

271. (c) The rate of nitration of benzene C_6H_6 takes place at the same rate because the rate determining step is the formation of carbocation which is same for both the compounds.

272. (a) β-keto carboxylic acid undergoes decarboxylation on heating.

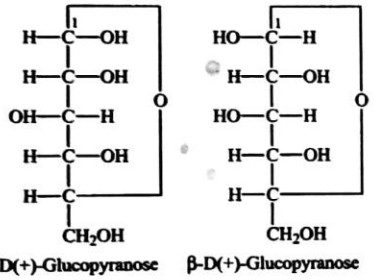
273. (c) 'N' can not accommodate 10 electrons because of non availability of *d*-orbitals.

274. (d) Glucose reduces Tollen's reagent into silver mirror.

$$CH_2OH(CHOH)_4CHO + Ag_2O \rightarrow \underset{\text{Gluconic acid}}{CH_2OH(CHOH)_4COOH} + \underset{\text{Silver mirror}}{2Ag}$$

Fructose being a ketohexose reduces Tollen's reagent (ammonical solution of silver nitrate) into silver mirror because the alkaline reagents rearrange fructose to give D-glucose and D-mannose which are strong reducing agents.

275. (b)



α-D(+)-Glucopyranose β-D(+)-Glucopyranose

Two forms of D-glucopyranose are α-D(+)-Glucopyranose and β-D(+)-Glucopyranose. These are anomers (a pair of stereoisomers which differ in configuration only around C_1 are called anomers).

276. (b) Due to H-bonding, stronger in carboxylic acid.

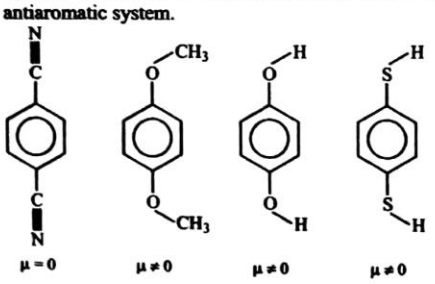
277. (c) Addition of water acc. to Markownikoff rule.

278. (b) Conc. H_3PO_4 acts as dehydrating agent.

279. (a) $C_6H_5COOH + NaH\overset{14}{C}O_3 \rightarrow C_6H_5COONa + \overset{14}{C}O_2 + H_2O$

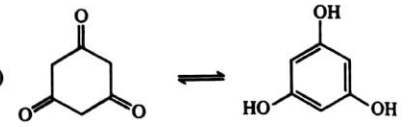
280. (b) I represents conjugated diene *i.e.*, most stable ; IV is an isolated diene; III is cumulated diene where II is antiaromatic system.

281. (a)



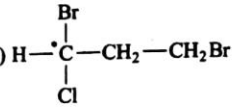
μ = 0 μ ≠ 0 μ ≠ 0 μ ≠ 0

282. (c)



(due to 3α-H-atoms)

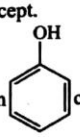
283. (b)



284. (d) Compounds containing polyvalent functional gps shows only metamerism. Never report chain or position isomerism if functional gp is polyvalent.

285. (d) follow concept.

286. (d) Enolic form



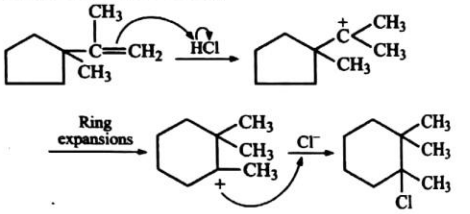
can be confirmed by $FeCl_3$ solution.

287. (b) $CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$

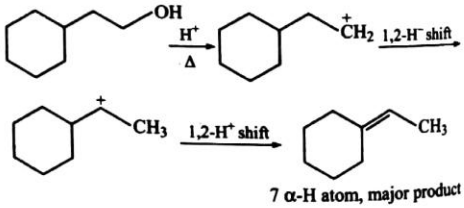
288. (d) It is wurtz reaction.

289. (d) Rest all will give phenol after elimination of HBr.

290. (c) Due to expansion of ring

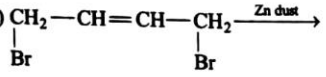


291. (b)



7 α-H atom, major product

292. (d)

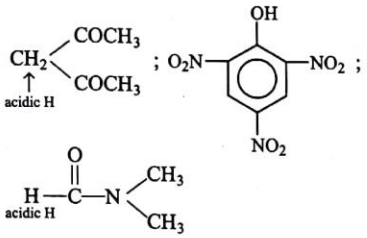


$$CH_2{=}CH{-}CH{=}CH_2 + ZnBr_2$$

Conjugated diene

293. (a) Clemensen reduction converts $\rangle CO$ gp to $\rangle CH_2$. Here 1,2-methyl shift also occurs during the course of reaction.

294. (c) $CO + NaOH(s) \xrightarrow{\Delta} HCOONa \xrightarrow{HOH}$ HCOOH (reducing agent)

295. (d) 

296. (a) $CH_3-CH=CH-Cl \xrightarrow{-HCl} CH_2=C=CH_2$

297. (a) Pyruvic acid is $CH_3 \cdot CO \cdot COOH$ *i.e.*, CH_3CO is attached to C.

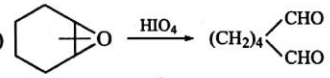
298. (c) Br attached on nucleus is weaker leaving gp due to partial bond character.

299. (d) $RS^- > CN^- > I^- > RO^- > OH^- > Br^- > C_6H_5O^- > Cl^- > Me_3N$ (Nucleophilicity order)

300. (d) $LiAlH_4$ in ether does not reduces $>C=C<$ to $>CH-C<$

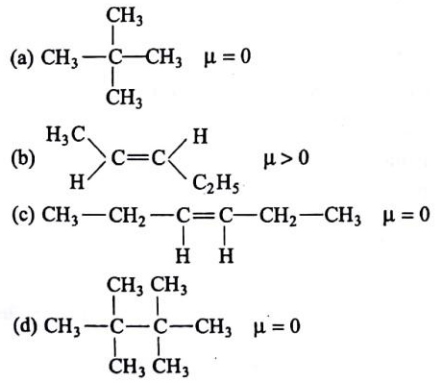
301. (b) Oxidation of unsymmetrical ketone gives two acids. According to Popff's rule the carbonyl gp goes with smaller alkyl gp.

302. (b) *t*-alkyl halides undergoes elimination reaction with sodium alkoxide to give alkene.

303. (a) 

304. (d) All aldehydes restores pink colour to Schiff's reagent readily. Acetone restores colour but slowly. *o*-hydroxy benzaldehyde does not restore pink colour due to intramolecular H-bonding.

305. (b) The symmetrical molecule has lesser or zero dipole moment.



306. (b) $ClCH_2=CHCl_2 \xrightarrow[-HCl]{OH^-} CH_2=CCl_2$

307. (a) Due to –ve IE effect of F atom.

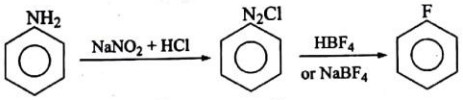
308. (d) Rest all shows hydroxylation of ethylene.

309. (a) The order of ease of abstraction of H-atom is : Allylic > 3° > 2° > 1° > CH_4 > vinyle

310. (b) N is sp^2 and sp^3 hybridised.

311. (d) A modified or extended Friedel-Craft's reaction

$$C_6H_6 + CH_2Cl_2 \xrightarrow{AlCl_3} C_6H_5CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5$$

312. (b) 

313. (b) Product will be spiro compound.

314. (b) 1,2-bromocyclopentane on heating with I^- in presence of acetone gives cyclopentene.

315. (c) $-NO_2$ group attacks on benzene ring attached to $-O-\overset{\overset{O}{\|}}{C}-$ group.

316. (b) $RMgX$ is an organometallic compound having only sigma bonds.

317. (b) It is fact.

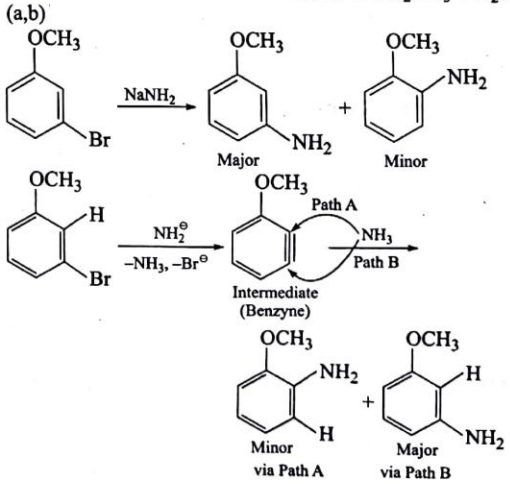
318. (d) $H_3C-C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} H_3C-\underset{\underset{\text{Intermediate (enol form) less stable (A)}}{OH}}{\overset{}{C}}=CH_2$

$\xrightleftharpoons{\text{tautomerism}}$ $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$ Ketoform more stable (B)

319. (b) Hofmann hypobromamide reaction is used to convert $-CONH_2$ gp to $-NH_2$ gp

$$\underset{\text{Acetamide}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2} + Br_2 + NaOH \longrightarrow \underset{\text{Methanamine}}{CH_3NH_2} + NaBr + Na_2CO_3 + H_2O$$

320. (a,b)



Product A is the major product of the reaction formed via path A. This is cine substitution following mechanism of elimination addition reaction.

321. (d) Electron withdrawing groups ($-I$ and $-M$ effect) decreases basic strength of aniline while electron donating groups ($+I$ and $+M$ effect) increases basic strength of aniline at para positions.

(I) (II)

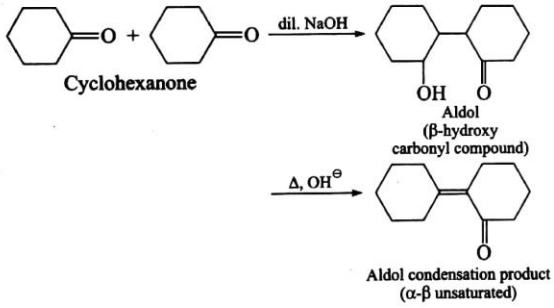
($-M$ effect of $-NO_2$ group)

(III)

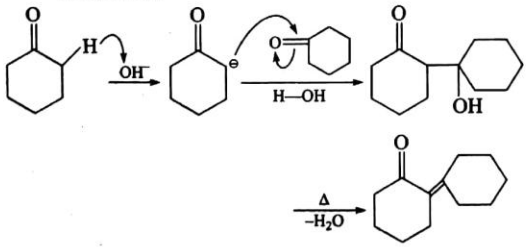
(Hyper conjugation effect of $-CH_3$ group)

So, the correct order of basic strength of following compounds is : II < I < III.

322. (b) It is Aldol condensation reaction.

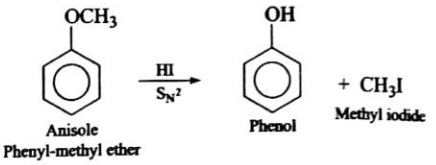


Mechanism

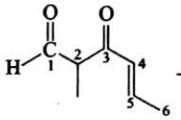


323. (d) It is definition of electrophile. NO_2^+ (nitronium ion) is positively charged electrophile, SO_3 is neutral electrophile.

324. (c) In case of mixed ether, halogen atom is attached to simpler alkyl gp.



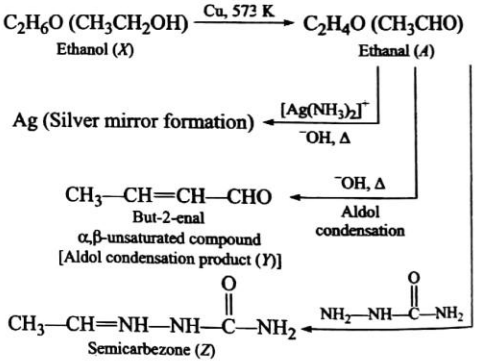
325. (d) Denaturation of protein makes the protein inactive as all the properties of protein are lost.

326. (a)  → 3-keto-2-methylhex-4-enal

327. (b) Alkynes are more acidic than alkenes which are further more acidic than alkanes due to the different electronegativity of sp, sp^2 and sp^3 hybridised carbon (order of electro- negativity = $sp > sp^2 > sp^3$) + I effect decreases the acidic strength of alkynes so the overall order of acidic strength will be :

$CH{\equiv}CH > CH_3{-}C{\equiv}CH > CH_2{=}CH_2 > CH_3{-}CH_3$

328. (c)



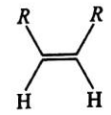
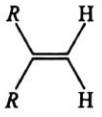
329. (d) Ortho nitrophenol show intramolecular H-bond while paranitrophenol show intermolecular H-bond. Thus b.pt. of *p*-nitrophenol > b.pt. of *o*-nitrophenol. So the mixture of both can be separated by steam distillation which is the technique to separate the components of a mixture on the basis of boiling point.

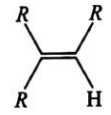
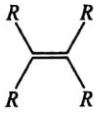
330. (d) Among the three conformers of ethane (Eclipsed, staggered, gauche) bond angle and bond length remains the same while their energy, stability and dihedral angle are different.

331. (d) Presence of three strong electron withdrawing NO_2 groups ($-M$ effect) at ortho and para positions enables picric acid (2,4,6-trinitro phenol) to show more acidic nature.

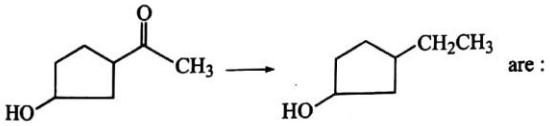
PREVIOUS YEAR OBJECTIVE PROBLEMS (One Answer Correct)

1. Which one of the following alkenes will react fastest with H_2 under catalytic condition ? **(IIT 2000)**

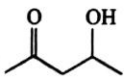
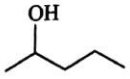
(a)  (b) 

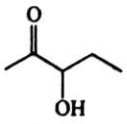
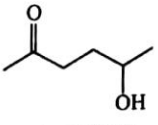
(c)  (d) 

2. Which of the following compounds will exhibit geometrical isomerism? **(IIT 2000)**
   (a) 1-phenyl-2-butene (b) 3-phenyl-1-butene
   (c) 2-phenyl-1-butene (d) 1,1-diphenyl-1-propene
3. Which of the following has the highest nucleophilicity? **(IIT 2000)**
   (a) F^- (b) OH^-
   (c) $\overline{CH_3}$ (d) $\overline{NH_2}$
4. Propyne and propene can be distinguished by : **(IIT 2000)**
   (a) conc. H_2SO_4 (b) Br_2 in CCl_4
   (c) dil. $KMnO_4$ (d) Amm. $AgNO_3$
5. The order of reactivities of the following alkyl halides for a S_N2 reaction is : **(IIT 2000)**
   (a) $RF > RCl > RBr > RI$ (b) $RF > RBr > RCl > RI$
   (c) $RCl > RBr > RF > RI$ (d) $RI > RBr > RCl > RF$
6. The appropriate reagents for the following transformation.

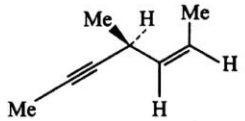
 are :

(IIT 2000)
   (a) Zn(Hg), HCl (b) NH_2, NH_2, OH^-
   (c) H_2/Ni (d) $NaBH_4$
7. Which one of the following will most readily be dehydrated in acidic condition : **(IIT 2000)**

(a)  (b) 

(c)  (d) 

8. Benzoyl chloride is prepared from benzoic acid by : **(IIT 2000)**
   (a) $Cl_2, h\nu$ (b) SO_2Cl_2
   (c) $SOCl_2$ (d) Cl_2, H_2O
9. Which of the following has the most acidic hydrogen? **(IIT 2000)**
   (a) 3-hexanone (b) 2,4-hexanedione
   (c) 2,5-hexanedione (d) 2,3-hexanedione
10. Among the following, the strongest base is : **(IIT 2000)**
    (a) $C_6H_5NH_2$ (b) p-NO_2—$C_6H_4NH_2$
    (c) m-NO_2—$C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$
11. A S_N2 reaction at an asymmetric carbon of a compound always gives : **(IIT 2001)**
    (a) an enantiomer of the substrate
    (b) a product with opposite optical rotation
    (c) a mixture of diastereoisomer
    (d) a single stereoisomer
12. The number of isomers for the compound with molecular formula $C_2BrClFI$ is : **(IIT 2001)**
    (a) 3 (b) 4
    (c) 5 (d) 6
13. In the presence of a peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff addition to alkenes because : **(IIT 2001)**
    (a) both are highly ionic
    (b) one is oxidising and the other is reducing
    (c) one of the steps is endothermic in both the cases
    (d) all the steps are exothermic in both the cases
14. Hydrogenation of the given compound in the presence of poisoned palladium catalyst gives : **(IIT 2001)**

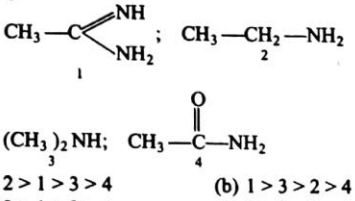


    (a) an optically active compound
    (b) an optically inactive compound
    (c) a racemic mixture
    (d) a diastereomeric mixture
15. The reaction of propene with HOCl proceeds *via* the addition of : **(IIT 2001)**
    (a) H^+ in the first step
    (b) Cl^+ in the first step
    (c) OH^- in the first step
    (d) Cl^+ and OH^- in a single step
16. 1-propanol and 2-propanol can be best distinguished by : **(IIT 2001)**
    (a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
    (b) oxidation with acidic dichromate followed by reaction with Fehling solution
    (c) oxidation by heating with copper followed by reaction with Fehling solution
    (d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

17. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives : **(IIT 2001)**
(a) Benzyl alcohol and sodium formate
(b) Sodium benzoate and methyl alcohol
(c) Sodium benzoate and sodium formate
(d) Benzyl alcohol and methyl alcohol

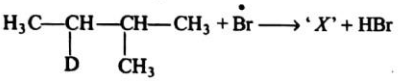
18. The compound that will react most readily with NaOH to form methanol is : **(IIT 2001)**
(a) $(CH_3)_4N^+I^-$ (b) CH_3OCH_3
(c) $(CH_3)_3S^+I^-$ (d) $(CH_3)_3CCl$

19. The correct order of basic nature of the following compounds is : **(IIT 2001)**

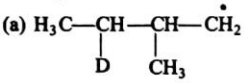


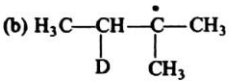
(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4
(c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

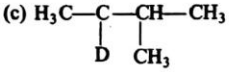
20. Consider the following reaction :

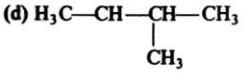


Identify the structure of the major product '*X*' : **(IIT 2002)**

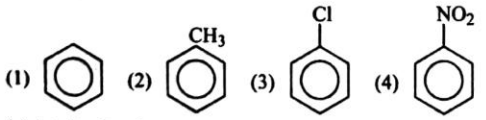
(a) 

(b) 

(c) 

(d) 

21. Identify the correct order of reactivity in S_E reactions of the following compounds : **(IIT 2002)**

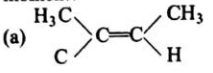


(a) 1 > 2 > 3 > 4 (b) 4 > 3 > 2 > 1
(c) 2 > 1 > 3 > 4 (d) 2 > 3 > 1 > 4

22. Which of the following compounds exhibits stereoisomerism ? **(IIT 2002)**
(a) 2-methylbutene-1 (b) 3-methylbutene-1
(c) 3-methylbutanoic acid (d) 2-methylbutanoic acid

23. The nodel plane in the π-bond of ethene is located in : **(IIT 2002)**
(a) the molecular plane
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon-carbon σ-bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon-carbon σ-bond

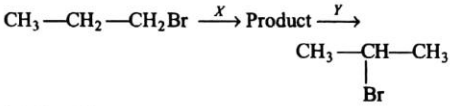
24. Which of the following hydrocarbons has the lowest dipole moment? **(IIT 2002)**

(a)  (b) $CH_3C{\equiv}CCH_3$

(c) $CH_3CH_2C{\equiv}CH$ (d) $CH_2{=}CH{-}C{\equiv}CH$

25. Identify the reagents from the following list which can easily distinguish between 1-butyne and 2-butyne: **(IIT 2002)**
(a) Bromine, CCl_4
(b) H_2, Lindlar's catalyst
(c) Dil. H_2SO_4, $HgSO_4$
(d) Ammoniacal Cu_2Cl_2 solution

26. Identify the set of reagent/reaction conditions '*X*' and '*Y*' in the following set of transformations : **(IIT 2002)**



(a) *X* = dilute aqueous NaOH, 20°C ; *Y* = HBr/acetic acid, 20°C
(b) *X* = concentrated alcoholic NaOH, 80°C; *Y* = HBr/acetic acid, 20°C
(c) *X* = dilute aqueous NaOH, 20°C; *Y* = $Br_2/CHCl_3$, 0°C
(d) *X* = concentrated alcoholic NaOH, 80°C; *Y* = $Br_2/CHCl_3$, 0°C

27. Identify the correct order of boiling points of the following compounds : **(IIT 2002)**
1. $CH_3CH_2CH_2CH_2OH$ 2. $CH_3CH_2CH_2CHO$
3. $CH_3CH_2CH_2COOH$
(a) 1 > 2 > 3 (b) 3 > 1 > 2
(c) 1 > 3 > 2 (d) 3 > 2 > 1

28. Which of the following acids has the smallest dissociation constant? **(IIT 2002)**
(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH
(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

29. Compound '*A*' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product '*B*' (molecular formula C_3H_6O). '*B*' forms a shining silver mirror on warming with ammoniacal silver nitrate. '*B*' when treated with an aqueous solution of $H_2NCONHNH_2 \cdot HCl$ and sodium acetate gives a product '*C*'. Identify the structure of '*C*' : **(IIT 2002)**
(a) $CH_3CH_2CH{=}NNCONH_2$

(b) $CH_3-C(CH_3)=NNHCONH_2$

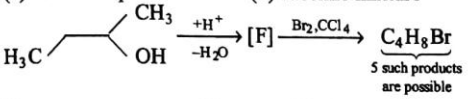
(c) $CH_3-C(CH_3)=NCONHNH_2$

(d) $CH_3CH_2CH=NCONHNH_2$

30. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one Chiral carbon. The ester formed will be : **(IIT 2003)**

(a) optically active mixture (b) pure enantiomer

(c) *meso* compound (d) racemic mixture

31. 

How many structures of F are possible ? **(IIT 2003)**

(a) 2 (b) 5

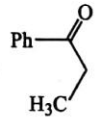
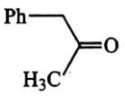
(c) 6 (d) 3

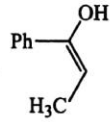
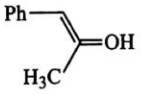
32. Which of the following represents the given mode of hybridization $sp^2-sp^2-sp-sp$ from left to right ? **(IIT 2003)**

(a) $H_2C=CH-C\equiv CH$ (b) $HC\equiv C-C\equiv CH$

(c) $H_2C=C=C=CH_2$ (d)

33. $Ph-C\equiv C-CH_3 \xrightarrow{Hg^{2+}/H^+} A$, A is : **(IIT 2003)**

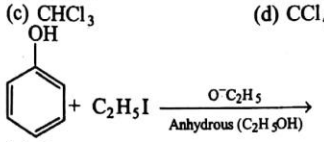
(a)  (b) 

(c)  (d) 

34. Among the following, the molecule with the highest dipole moment is : **(IIT 2003)**

(a) CH_3Cl (b) CH_2Cl_2

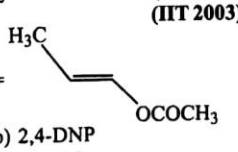
(c) $CHCl_3$ (d) CCl_4

35.  **(IIT 2003)**

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$

(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

36. The product of acid hydrolysis of P and Q can be distinguished by : **(IIT 2003)**

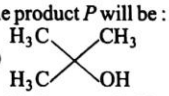
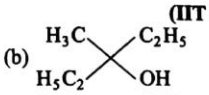
$P = H_2C=C(OCOCH_3)(CH_3)$ $Q =$ 

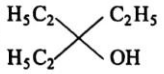
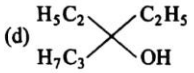
(a) Lucas reagent (b) 2,4-DNP

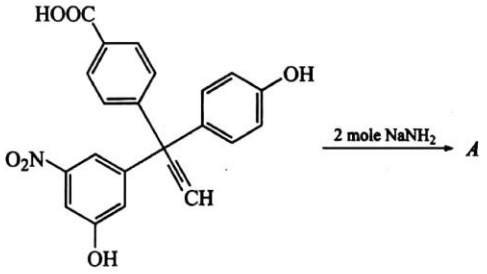
(c) Fehling's solution (d) $NaHSO_3$

37. Ethyl ester $\xrightarrow[\text{Excess}]{CH_3MgBr} P$

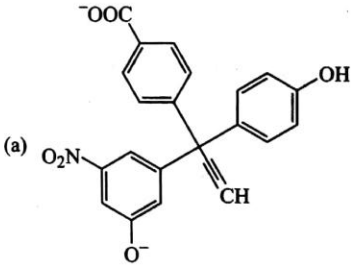
The product P will be : **(IIT 2003)**

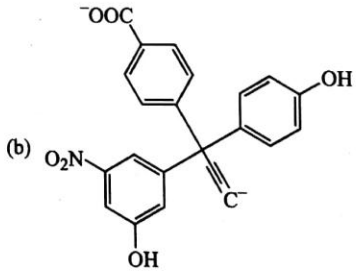
(a)  (b) 

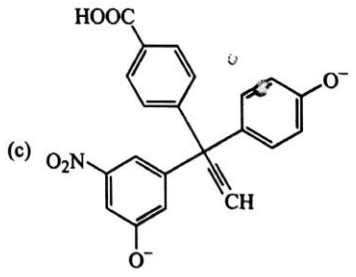
(c)  (d) 

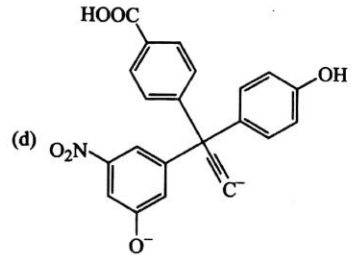
38. 

The product A will be : **(IIT 2003)**

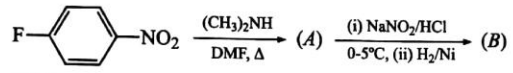
(a) 

(b) 

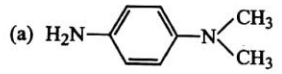
(c) 

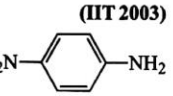
(d) 

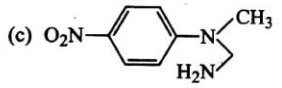
39.

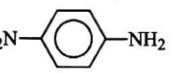


B is : **(IIT 2003)**

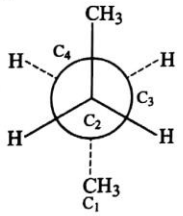
(a) 

(b) 

(c) 

(d) 

40. In the given conformation C_2 is rotated about C_2—C_3 bond and clockwise by an angle of 120°. Then the formation obtained is : **(IIT 2004)**



(a) Fully eclipsed conformation
(b) Partially eclipsed conformation
(c) Gauche conformation
(d) Staggered conformation

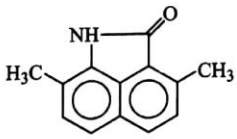
41. On monochlorination of 2-methyl butane, the total number of chiral compound is : **(IIT 2004)**
(a) 2 (b) 4
(c) 6 (d) 8

42. The product of acid catalysed hydration of 2-phenyl propene is : **(IIT 2004)**
(a) 3-phenyl-2-propanol (b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol (d) 2-phenyl-1-propanol

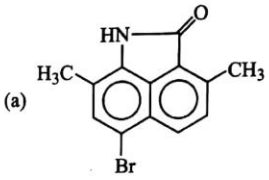
43. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexene ? **(IIT 2004)**
(a) H_2 / Pd / $BaSO_4$ (b) H_2 / PtO_2
(c) $NaBH_4$ (d) Li—NH_3 / C_2H_5OH

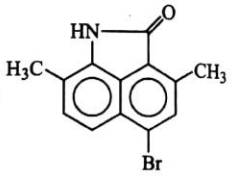
44. Benzamide on reaction with $POCl_3$ gives : **(IIT 2004)**
(a) Aniline (b) Chlorobenzene
(c) Benzylamine (d) Benzonitrile

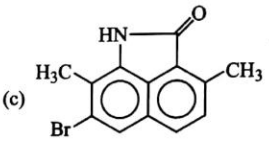
45. The major product obtained when Br_2 / Fe is treated with : **(IIT 2004)**

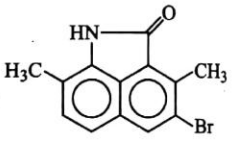


is :

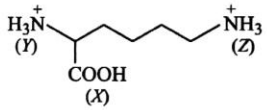
(a) 

(b) 

(c) 

(d) 

46. In the compound given below :

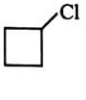


The correct order of acidic nature is : **(IIT 2004)**
(a) $Z > X > Y$ (b) $X > Y > Z$
(c) $X > Z > Y$ (d) $Y > X > Z$

47. Which of the following resonating structures of 1-methoxy-1, 3-butadiene is least stable : **(IIT 2005)**
(a) $\bar{C}H_2—CH=CH—CH=\overset{+}{O}—CH_3$
(b) $CH_2=CH—\bar{C}H—CH=\overset{+}{O}—CH_3$
(c) $\bar{C}H_2—\overset{+}{C}H—CH=CH—O—CH_3$
(d) $CH_2=CH—\bar{C}H—\overset{+}{C}H—O—CH_3$

48. What would be the product formed when 1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether ? **(IIT 2005)**

(a)

(b) 

(c)

(d)

49. When phenyl magnesium bromide reacts with *t*-butanol, the product would be : **(IIT 2005)**
(a) C_6H_6 (b) C_6H_5OH
(c) *t*-butyl benzene (d) *t*-butyl phenyl ether

50. When benzene sulphonic acid and *p*-nitrophenol are treated with $NaHCO_3$ the gases released respectively are : **(IIT 2006)**
(a) SO_2, NO_2 (b) SO_2, NO
(c) SO_2, CO_2 (d) CO_2, CO_2

51. The correct increasing order of b.pt. of the following is : **(IIT 2006)**

(I) 1, 2-dihydroxy benzene (II) 1,3-dihydroxy benzene
(III) 1,4-dihydroxy benzene (IV) Hydroxy benzene
(a) I < II < III < IV (b) I < II < IV < III
(c) IV < I < II < III (d) IV < II < I < III

52. The product formed in the reaction,
$CH_3—CH=CH_2 + NOCl \longrightarrow$ is : **(IIT 2006)**

(a) $CH_3CHCl \cdot CH_2NO$ (b) $CH_3\underset{\displaystyle NO}{\underset{|}{C}}H \cdot CH_2Cl$

(c) $CH_3 \cdot \underset{\displaystyle Cl}{\underset{|}{CH}} \cdot CH_2 \cdot \underset{\displaystyle NO}{\underset{|}{}}$ (d) $\underset{\displaystyle NO}{\underset{|}{CH_2}} \cdot CH_2 \cdot CH_2Cl$

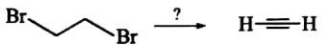
53. In $CH_3NH_2 + CHCl_3 + KOH \longrightarrow A + KCl + H_2O$, A is : **(IIT 2006)**

(a) CH_3CN (b) CH_3NHCH_3
(c) $CH_3\overset{-}{\underset{+}{N}}C$ (d) $CH_3\overset{+}{N}\rightleftarrows\overset{-}{C}$

54. The IUPAC name of C_6H_5COCl is : **(IIT 2006)**

(a) Benzoyl chloride
(b) Benzene chloroketone
(c) Benzene carbonyl chloride
(d) Chlorophenyl ketone

55. The reagent (s) used for the following conversion are : **(IIT 2007)**



(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) Zn/CH_3OH
(d) aqueous KOH followed by $NaNH_2$

56. The number of structural isomers for C_6H_{14} is : **(IIT 2007)**

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

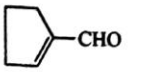
57. The number of stereoisomers obtained by bromination of *trans*-2-butene is : **(IIT 2007)**

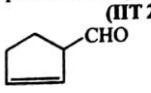
(a) 1 (b) 2
(c) 3 (d) 4

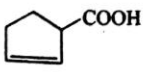
58. Sodium extract of aniline on treatment with $FeSO_4$ and H_2SO_4 in presence of air gives a prussian blue precipitate. The blue colour is due to : **(IIT 2007)**

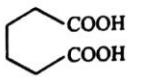
(a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

59. Cyclohexane on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with KOH($aq.$) yields compound F. Compound F is : **(IIT 2007)**

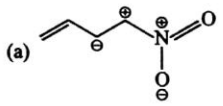
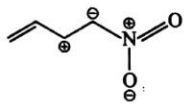
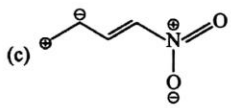
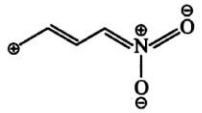
(a) 

(b) 

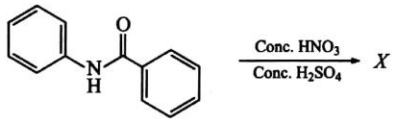
(c) 

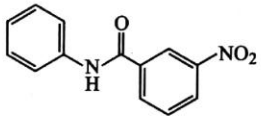
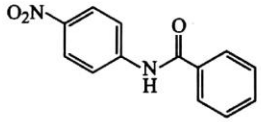
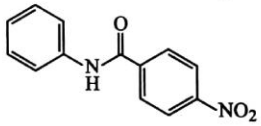
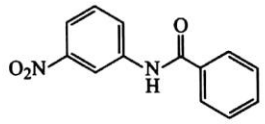
(d) 

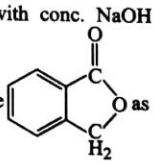
60. Among the following, the least stable resonance structure is: **(IIT 2007)**

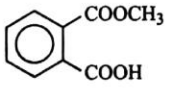
(a) 
(b) 
(c) 
(d) 

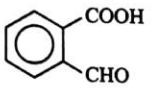
61. In the following reactions, the structure of major product X is : **(IIT 2007)**

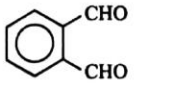


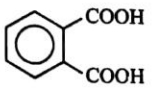
(a) 
(b) 
(c) 
(d) 

62. Which of the following on reaction with conc. NaOH followed by acidification gives the lactone  as the only product : **(IIT 2006)**

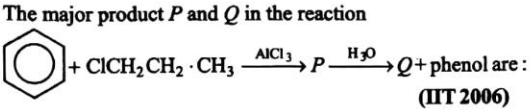
(a) 

(b) 

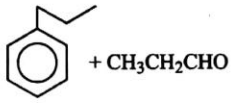
(c) 

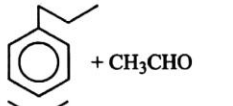
(d) 

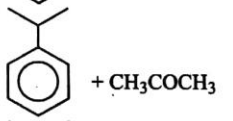
63. The major product P and Q in the reaction

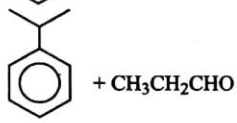


(IIT 2006)

(a) 

(b) 

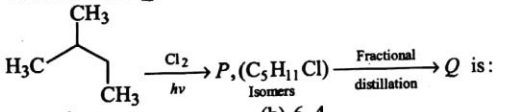
(c) 

(d) 

64. The smallest ketone and its next homologous are reacted with NH_2OH to form oximes as : **(IIT 2006)**

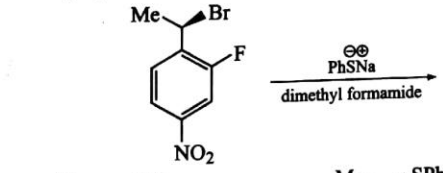
(a) two different oximes
(b) three different oximes
(c) two oximes are optically active
(d) three oximes are optically active

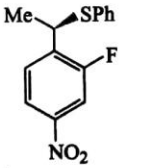
65. What are P and Q in the reaction : **(IIT 2006)**

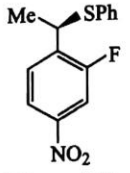


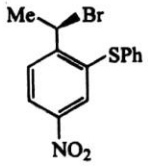
(a) 6, 6 (b) 6, 4
(c) 4, 4 (d) 3, 3

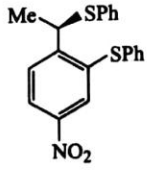
66. The major product of the following reaction is : **(IIT 2008)**



(a) 

(b) 

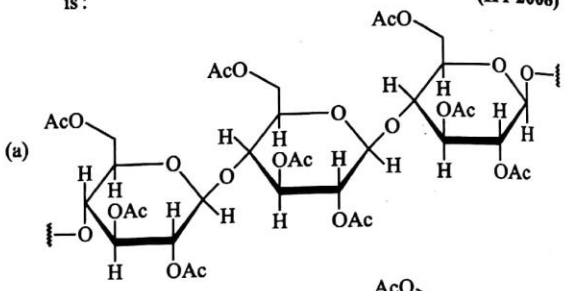
(c) 

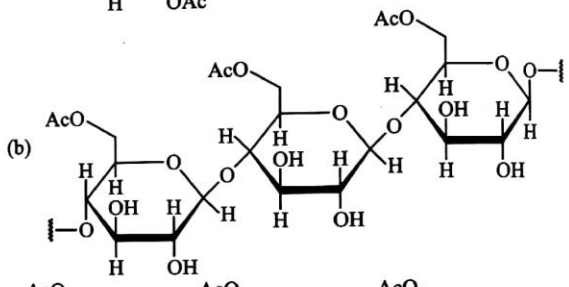
(d) 

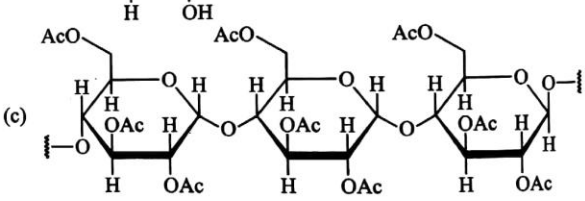
67. Hyperconjugation involves overlap of the following orbitals: **(IIT 2008)**

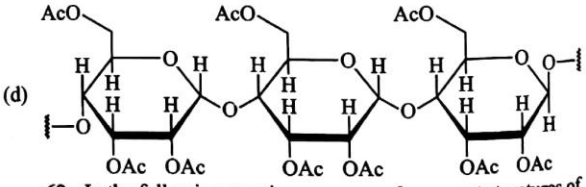
(a) $\sigma - \sigma$ (b) $\sigma - p$
(c) $p - p$ (d) $\pi - \pi$

68. Cellulose upon acetylation with excess acetic anhydride/ H_2SO_4 (catalytic) gives cellulose triacetate whose structure is : **(IIT 2008)**

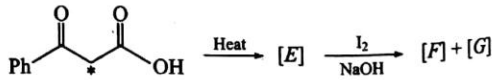
(a) 

(b) 

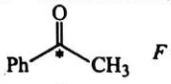
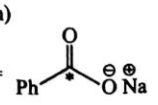
(c) 

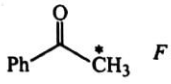
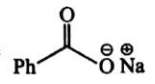
(d) 

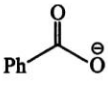
69. In the following reaction sequence, the correct structures of E, F and G are :

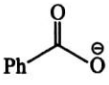


(*implies ^{13}C labelled carbon) **(IIT 2008)**

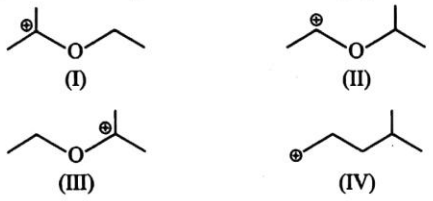
(a) $E =$  $F =$  $G = CHI_3$

(b) $E =$  $F =$  $G = CHI_3$

(c) $E =$ $F =$  $G = \overset{*}{C}HI_3$

(d) $E =$ $F =$  $G = \overset{*}{C}H_3I$

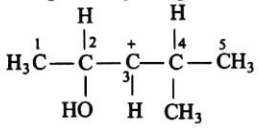
70. The correct stability order for the following species is :



(I) (II) (III) (IV)

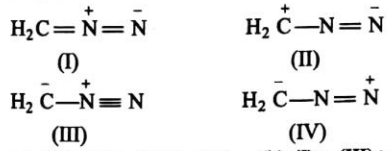
(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)
(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

71. In the following carbocation, H/CH_3 that is most likely to migrate to the positively charged carbon is : **(IIT 2009)**



(a) CH_3 at C-4 (b) H at C-4
(c) CH_3 at C-2 (d) H at C-2

72. The correct stability order of the following resonance structures is : **(IIT 2009)**



(I) (II) (III) (IV)

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

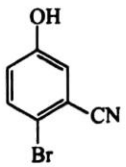
73. The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10} is : **(IIT 2009)**

(a) 2 (b) 4
(c) 7 (d) 6

74. Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is : **(IIT 2009)**

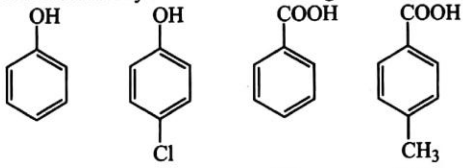
(a) Nylon (b) Poly (vinyl chloride)
(c) Cellulose (d) Natural Rubber

75. The IUPAC name of the following compound is : **(IIT 2009)**



(a) 4-Bromo-3-cyanophenol
(b) 2-Bromo-5-hydroxybenzonitrile
(c) 2-Cyano-4-hydroxybromobenzene
(d) 6-Bromo-3-hydroxybenzonitrile

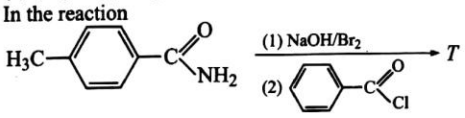
76. The correct acidity order of the following is : **(IIT 2009)**



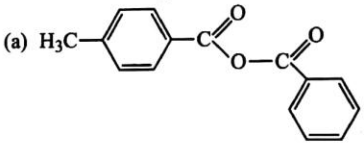
(I) (II) (III) (IV)

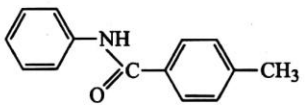
(a) (III) > (IV) > (II) > (I) (b) (IV) > (III) > (I) > (II)
(c) (III) > (II) > (I) > (IV) (d) (II) > (III) > (IV) > (I)

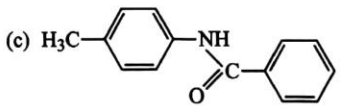
77. In the reaction

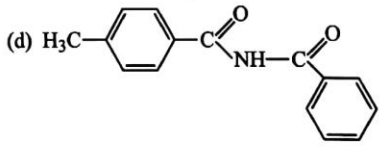


the structure of the product *T* is : **(IIT 2010)**

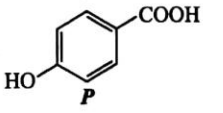
(a) 

(b) 

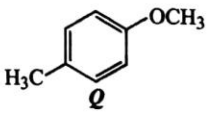
(c) 

(d) 

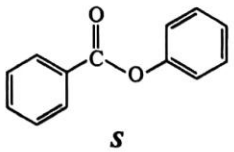
78. The compounds *P*, *Q* and *S*



P

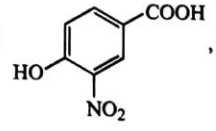
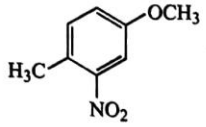
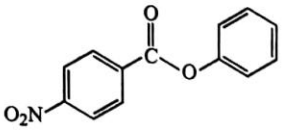


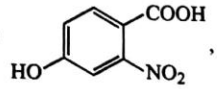
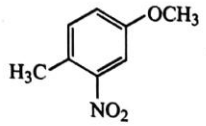
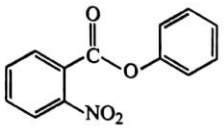
Q

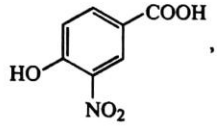
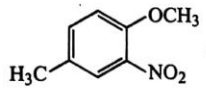
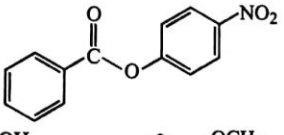


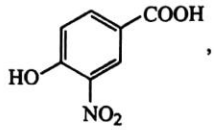
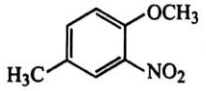
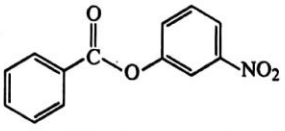
S

were separately subjected to nitration using HNO_3/H_2SO_4 mixture. The major product formed in each case respectively, is : **(IIT 2010)**

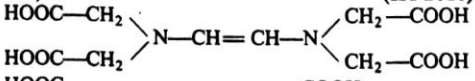
(a)  ,  , 

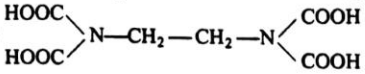
(b)  ,  , 

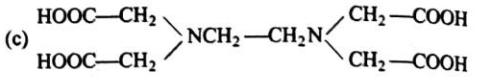
(c)  ,  , 

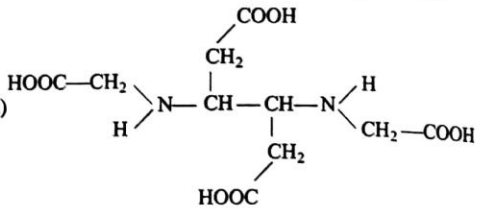
(d)  ,  , 

79. Correct structure of ethylenediaminatetraacetic acid (EDTA) is : **(IIT 2010)**

(a) 

(b) 

(c) 

(d) 

80. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and alkyne. The bromoalkane and alkyne respectively are : **(IIT 2010)**

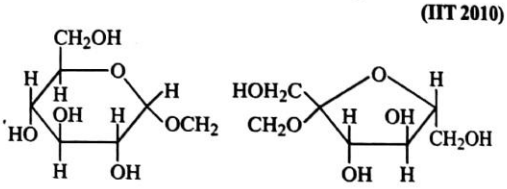
(a) $BrCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ and $CH_3CH_2C{=}CH$

(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$

(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C{\equiv}CH$

(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$

81. The correct statement about the following disaccharide is : **(IIT 2010)**



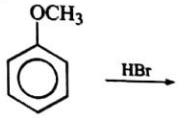
(a) Ring (a) is pyranose with α-glucosidic link

(b) Ring (a) is furanose with α-glucosidic link

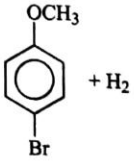
(c) Ring (b) is furanose with α-glucosidic link

(d) Ring (b) is pyranose with β-glucosidic link

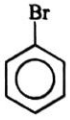
82. In the reaction:



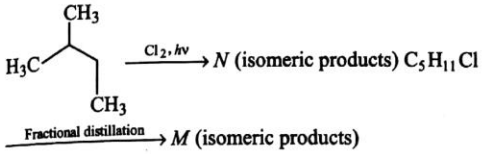
The products are : **(IIT 2010)**

(a)  + H_2

(b) + CH_3Br

(c)  + CH_3OH

(d) + CH_3Br

83. 

What are N and M ?

(a) 6, 6 (b) 6, 4

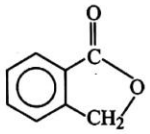
(c) 4, 4 (d) 3, 3 **(IIT 2006)**

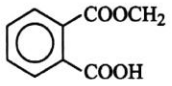
84. Which of the following compounds form two isomeric oximes on reacting with NH_2OH?

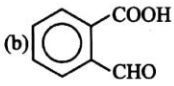
(a) R—CHO (b) R—COR

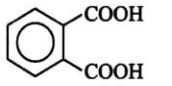
(c) R—COR' (d) HCHO **(IIT 2006)**

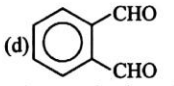
85. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product? **(IIT 2006)**



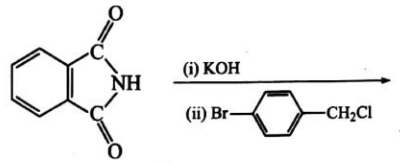
(a) 

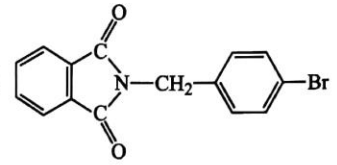
(b) 

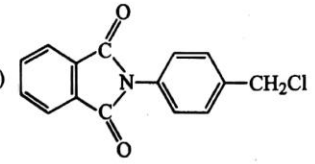
(c) 

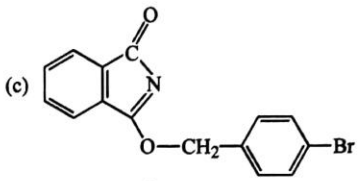
(d) 

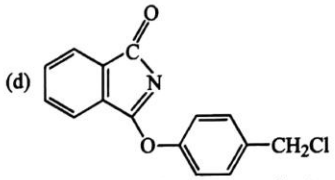
86. The major product of the following reaction is : **(IIT 2011)**



(a) 

(b) 

(c) 

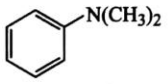
(d) 

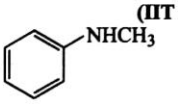
87. Among the following compounds, the most acidic is : **(IIT 2011)**

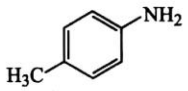
(a) p-nitrophenol (b) p-hydroxybenzoic acid

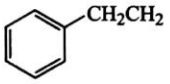
(c) o-hydroxybenzoic acid (d) p-toluic acid

88. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is : **(IIT 2011)**

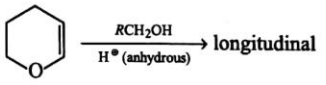
(a) 

(b) 

(c) 

(d) 

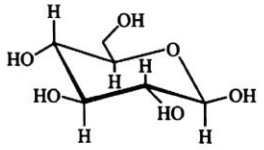
89. The major product of the following reaction is : **(IIT 2011)**



(a) a hemiacetal (b) an acetal

(c) an ether (d) an ester

90. The following carbohydrate is : **(IIT 2011)**



(a) a ketohexose (b) an aldohexose

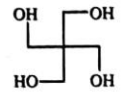
(c) an α-furanose (d) an α-pyranose

91. The carboxyl functional group (— COOH) is present in: **(IIT 2012)**

(a) picric acid (b) barbituric acid

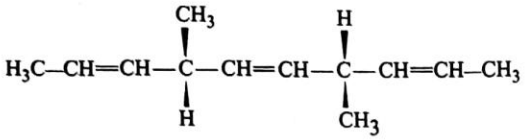
(c) ascorbic acid (d) aspirin

92. The number of aldol reaction(s) that occurs in the given transformation is : **(IIT 2012)**

$CH_3CHO + 4HCHO \xrightarrow{\text{conc. aq. NaOH}}$ 

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

93. The number of optically active products obtained from the complete ozonolysis of the given compound is: **(IIT 2012)**



(a) 0 (b) 1
(c) 2 (d) 4

94. The major product *H* of the given reaction sequence is:

$CH_3-CH_2-CO-CH_3 \xrightarrow{\ominus CN} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$

(IIT 2012)

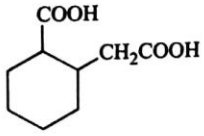
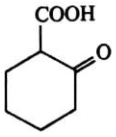
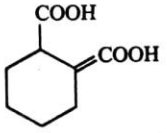
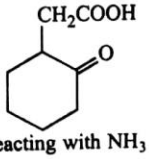
(a) $CH_3-CH=C(CH_3)-COOH$

(b) $CH_3-CH=C(CH_3)-CN$

(c) $CH_3-CH_2-C(OH)(CH_3)-COOH$

(d) $CH_3-CH=C(CH_3)-CO-NH_2$

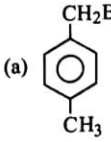
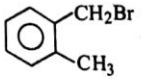
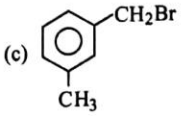
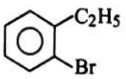
95. The compound that undergoes decarboxylation most readily under mild condition is: **(IIT 2012)**

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

96. An organic compound *A* upon reacting with NH_3 gives *B*. On heating, *B* gives *C*. *C* in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. *A* is: **[JEE (Main) 2013]**

(a) $CH_3-CH(CH_3)-COOH$ (b) CH_3CH_2COOH
(c) CH_3COOH (d) $CH_3CH_2CH_2COOH$

97. Compound (*A*), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (*A*) gives an acid (*B*), $C_8H_6O_4$. (*B*) easily forms anhydride on heating. Identify the compound (*A*). **[JEE (Main) 2013]**

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

98. A compound with molar mass 180 is acylated with CH_3COCl to get a compound with molar mass 390. The number of amino groups present per molecule of the former compound is: **[JEE (Main) 2013]**

(a) 4 (b) 6
(c) 2 (d) 5

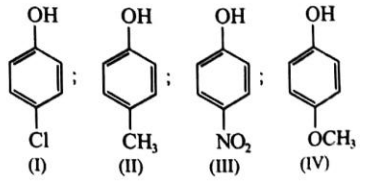
99. A solution of (–) –1 – chloro – 1 – phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of: **[JEE (Main) 2013]**

(a) carbocation (b) free radical
(c) carbanion (d) carbene

100. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts the fastest and by what mechanism? **[JEE (Main) 2013]**

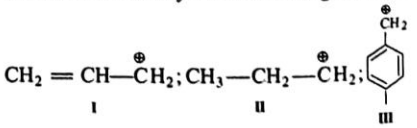
(a) secondary alcohol by S_N2
(b) tertiary alcohol by S_N2
(c) secondary alcohol by S_N1
(d) tertiary alcohol by S_N1

101. Arrange the following compounds in order of decreasing acidity: **[JEE (Main) 2013]**


(I) (II) (III) (IV)

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

102. The order of stability of the following carbocations


(I) (II) (III)

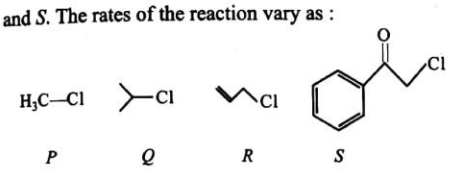
is:

[JEE (Main) 2013]

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

103. Synthesis of each molecule of glucose in photosynthesis involves : **[JEE (Main) 2013]**
(a) 8 molecules of ATP (b) 6 molecules of ATP
(c) 18 molecules of ATP (d) 10 molecules of ATP

104. KI in acetone, undergoes S_N2 reaction with each of *P*, *Q*, *R* and *S*. The rates of the reaction vary as :



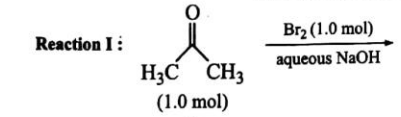
P *Q* *R* *S*

[JEE (Advanced) I 2013]
(a) $P > Q > R > S$ (b) $S > P > R > Q$
(c) $P > R > Q > S$ (d) $R > P > S > Q$

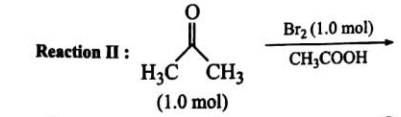
105. The compound that does **NOT** liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is : **[JEE (Advanced) I 2013]**
(a) Benzoic acid (b) Bezenesulphonic acid
(c) Salicylic acid (d) Carbolic acid (Phenol)

106. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to : **[JEE (Advanced) I 2013]**
(a) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations
(b) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations
(c) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations
(d) p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations

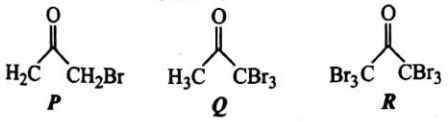
107. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is (are) : **[JEE (Advanced) II 2013]**



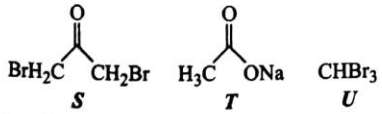
(1.0 mol)



(1.0 mol)



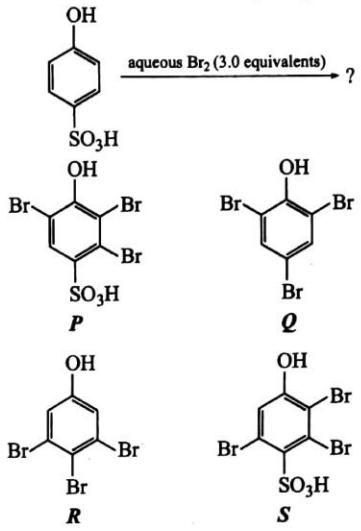
P *Q* *R*



S *T* *U*

(a) Reaction I : *P* and Reaction II : *P*
(b) Reaction I : *U*, acetone and Reaction II : *Q*, acetone
(c) Reaction I : *T*, *U*, acetone and Reaction II : *P*
(d) Reaction I : *R*, acetone and Reaction II : *S*, acetone

108. The major product(s) of the following reaction is (are) : **[JEE (Advanced) I 2013]**



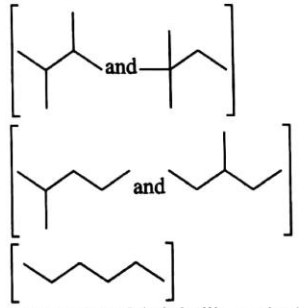
P *Q* *R* *S*

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

109. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was : **[JEE (Main) 2013]**
(a) Ammonia (b) Phosgene
(c) Methylisocyanate (d) Methylamine

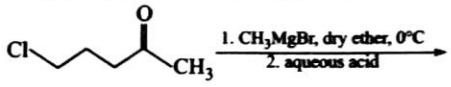
110. For the identification of β-naphthol using dye test, it is necessary to use : **[JEE (Advanced II) 2014]**
(a) dichloromethane solution of β-naphthol
(b) acidic solution of β-naphthol
(c) neutral solution of β-naphthol
(d) alkaline solution of β-naphthol

111. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.

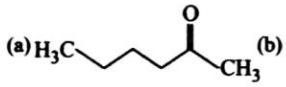


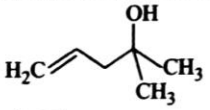
The correct order of their boiling point is : **[JEE (Advanced II) 2014]**
(a) I > II > III (b) III > II > I
(c) II > III > I (d) III > I > II

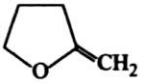
112. The major product in the following reaction is :

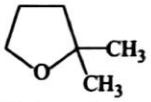


[JEE (Advanced II) 2014]

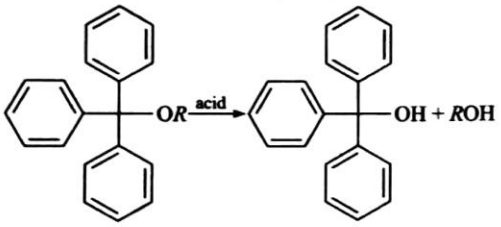
(a) 

(b) 

(c) 

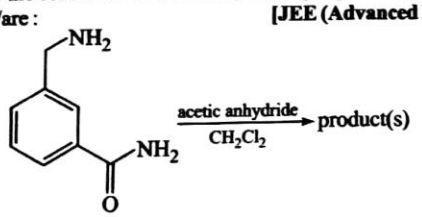
(d) 

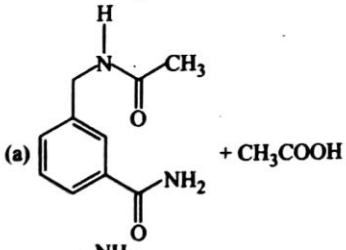
113. The acidic hydrolysis of ether (X) shown below is fastest when : **[JEE (Advanced II) 2014]**

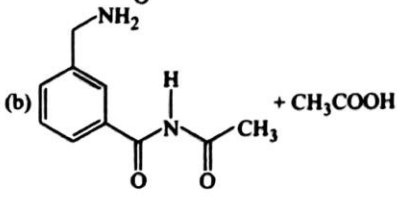


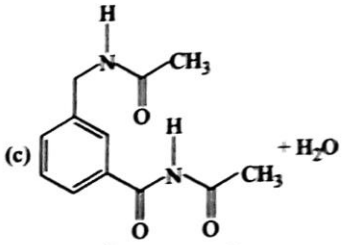
(a) one phenyl group is replaced by a methyl group
(b) one phenyl group is replaced by a para- methoxyphenyl group
(c) two phenyl groups are replaced by two para-methoxyphenyl groups
(d) no structural change is made to X

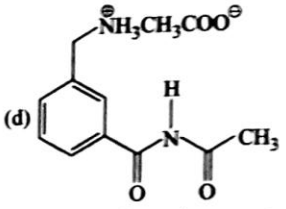
114. In the reaction shown below, the major product(s) formed is/are : **[JEE (Advanced I) 2014]**



(a) 

(b) 

(c) 

(d) 

115. In S_N2 reactions, the correct order of reactivity for the following compounds : CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is : **[JEE (Main) 2014]**

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$
(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

116. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is : **[JEE (Main) 2014]**

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

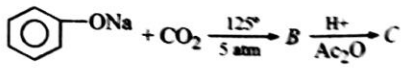
117. The most suitable reagent for the conversion of $R—CH_2—OH \longrightarrow R—CHO$ is : **[JEE (Main) 2014]**

(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) CrO_3
(d) PCC (Pyridinium Chlorochromate)

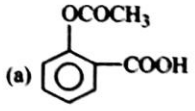
118. The major organic compound formed by the reaction of 1, 1, 1- trichloroethane with silver powder is : **[JEE (Main) 2014]**

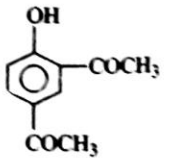
(a) Acetylene (b) Ethene
(c) 2-Butyne (d) 2-Butene

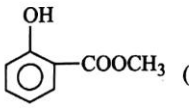
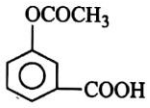
119. Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C.



The major product C would be : **[JEE (Main) 2014]**

(a) 

(b) 

(c)  (d) 

120. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value?
[JEE (Main) 2014]
(a) $(CH_3)_2NH$ (b) CH_3NH_2
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

121. For which of the following molecule significant $\mu \neq 0$?
[JEE (Main) 2014]
(a) Only (i) (b) (i) and (ii)
(c) Only (iii) (d) (iii) and (iv)

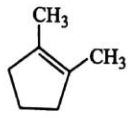
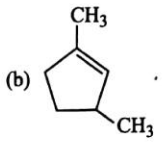
122. In the reaction,
$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{\text{Alc. KOH}} C$, the product C is:
[JEE (Main) 2014]
(a) Acetaldehyde (b) Acetylene
(c) Ethylene (d) Acetyl chloride

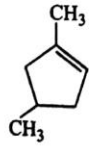
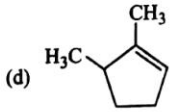
123. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralization. The precentage of nitrogen in the compound is:
[JEE (Main) 2014]
(a) 6% (b) 10%
(c) 3% (d) 5%

124. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is:
(at. mass Ag = 108; Br = 80)
[JEE (Main) 2015]
(a) 24 (b) 36
(c) 48 (d) 60

125. Which of the following compounds will exhibit geometrical isomerism?
[JEE (Main) 2015]
(a) 1-Phenyl-2-butene
(b) 3-Phenyl-1-butene
(c) 2-Phenyl-1-butene
(d) 1, 1-Diphenyl-1-propane

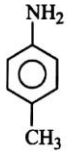
126. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis?
[JEE (Main) 2015]

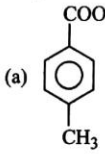
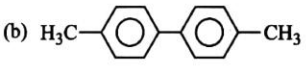
(a)  (b) 

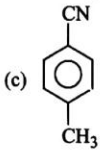
(c)  (d) 

127. The synthesis of alkyl fluorides is best accomplished by:
[JEE (Main) 2015]
(a) Free radical fluorination
(b) Sandmeyer's reaction
(c) Finkelstein reaction
(d) Swart's reaction

128. In the following sequence of reactions:
$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$,
the product C is:
[JEE (Main) 2015]
(a) C_6H_5COOH (b) $C_6H_5CH_3$
(c) $C_6H_5CH_2OH$ (d) C_6H_5CHO

129. In the reaction  $\xrightarrow[0-5°C]{NaNO_2/HCl} D \xrightarrow[\Delta]{CuCN/KCN} E + N_2$,
the product E is:
[JEE (Main) 2015]

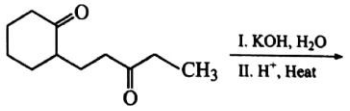
(a)  (b) 

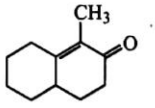
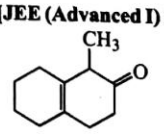
(c)  (d)

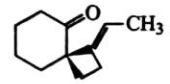
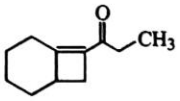
130. Which polymer is used in the manufacture of paints and lacquers?
[JEE (Main) 2015]
(a) Bakelite (b) Glyptal
(c) Polypropene (d) Poly vinyl chloride

131. Which of the vitamins given below is water soluble?
[JEE (Main) 2015]
(a) Vitamin C (b) Vitamin D
(c) Vitamin E (d) Vitamin K

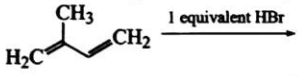
132. Which of the following compounds is not an antacid?
[JEE (Main) 2015]
(a) Aluminium hydroxide (b) Cimetidine
(c) Phenelzine (d) Ranitidine

133. The major product of the following reaction is:

[JEE (Advanced I) 2015]

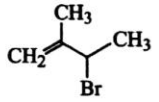
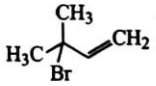
(a)  (b) 

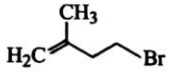
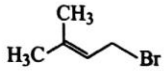
(c)  (d) 

134. In the following reaction, the major product is :

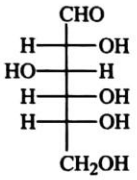


[JEE (Advanced I) 2015]

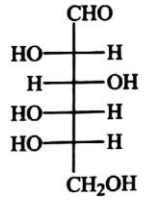
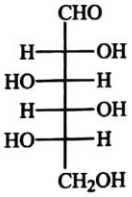
(a)  (b) 

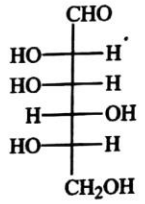
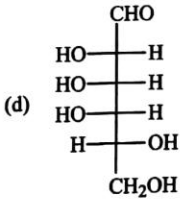
(c)  (d) 

135. The structure of *D*-(+)-glucose is :

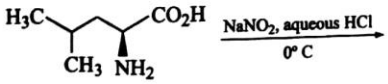


The structure of *L*(–)-glucose is :

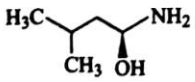
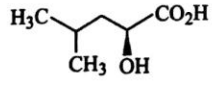
(a)  (b) 

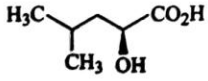
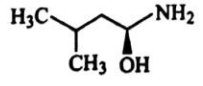
(c)  (d) 

136. The major product of the reaction is :

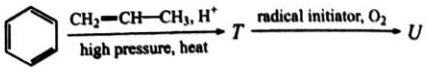


[JEE (Advanced I) 2015]

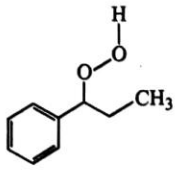
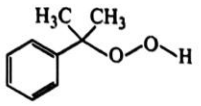
(a)  (b) 

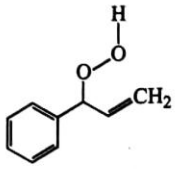
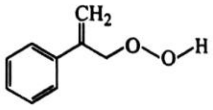
(c)  (d) 

137. The major product *U* in the following reactions is :

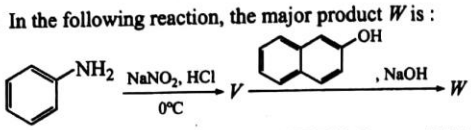


[JEE (Advanced II) 2015]

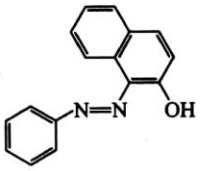
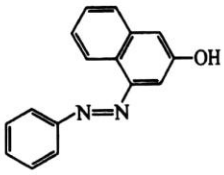
(a)  (b) 

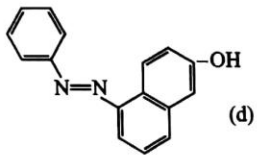
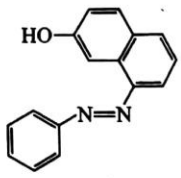
(c)  (d) 

138. In the following reaction, the major product *W* is :

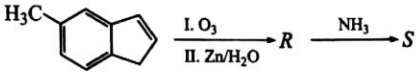


[JEE (Advanced II) 2015]

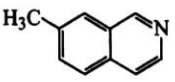
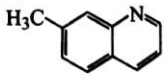
(a)  (b) 

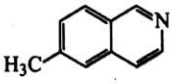
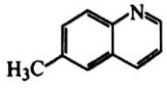
(c)  (d) 

139. In the following reactions, the product *S* is :



[JEE (Advanced II) 2015]

(a)  (b) 

(c)  (d) 

140. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields : **[JEE (Main) 2016]**

(1) $C_2H_5CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OCH_3$

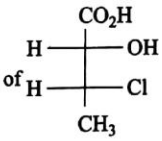
(2) $C_2H_5CH_2\underset{\displaystyle CH_3}{\overset{}{\underset{|}{C}}}=CH_2$

(3) $C_2H_5CH=\underset{\displaystyle CH_3}{\overset{}{\underset{|}{C}}}-CH_3$

(a) (1) and (3) (b) (3) only
(c) (1) and (2) (d) All of these

141. Which of the following statements about low density polythene is **FALSE**? **[JEE (Main) 2016]**
(a) It is a poor conductor of electricity
(b) Its synthesis requires dioxygen or a peroxide initiator as a catalyst
(c) It is used in the manufacture of buckets, dust-bins etc.
(d) Its synthesis requires high pressure

142. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is : **[JEE (Main) 2016]**
(a) fractional distillation
(b) steam distillation
(c) distillation under reduced pressure
(d) simple distillation

143. The absolute configuration of  is: **[JEE (Main) 2016]**

(a) (2*S*, 3*R*) (b) (2*S*, 3*S*)
(c) (2*R*, 3*R*) (d) (2*R*, 3*S*)

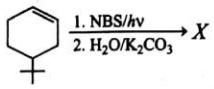
144. The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of : **[JEE (Main) 2016]**
(a) Lead (b) Nitrate
(c) Iron (d) Fluoride

145. Thiol group is present in : **[JEE (Main) 2016]**
(a) Cystine (b) Cysteine
(c) Methionine (d) Cytosine

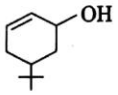
146. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are : **[JEE (Main) 2016]**
(a) four moles of NaOH and two moles of Br_2
(b) two moles of NaOH and two moles of Br_2
(c) four moles of NaOH and one mole of Br_2
(d) one mole of NaOH and one mole of Br_2

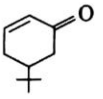
147. The reaction of propene with HOCl $(Cl_2 + H_2O)$ proceeds through the intermediate : **[JEE (Main) 2016]**
(a) $CH_3-CH^+-CH_2-Cl$
(b) $CH_3-CH(OH)-CH_2^+$
(c) $CH_3-CHCl-CH_2^+$
(d) $CH_3-CH^+-CH_2-OH$

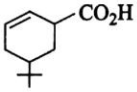
148. The product of the reaction given below is :



[JEE (Main) 2016]

(a) 

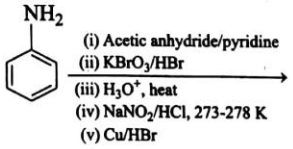
(b) 

(c) 

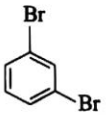
(d)

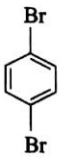
149. On complete hydrogenation, natural rubber produces: **[JEE (Advanced) I 2016]**
(a) ethylene-propylene copolymer
(b) vulcanised rubber
(c) polypropylene
(d) polybutylene

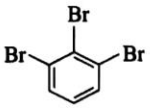
150. The product(s) of the following reaction sequence is(are):

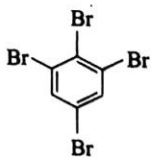


[JEE (Advanced) I 2016]

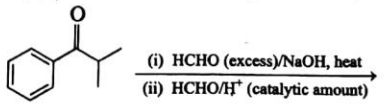
(a) 

(b) 

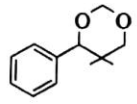
(c) 

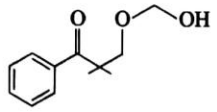
(d) 

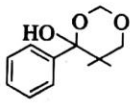
151. The major product of the following reaction sequence is :

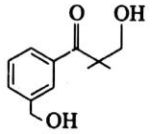


[JEE (Advanced) II 2016]

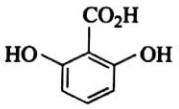
(a) 

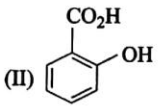
(b) 

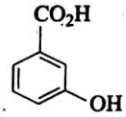
(c) 

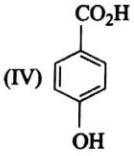
(d) 

152. The correct order of acidity for the following compounds is :

(I) 

(II) 

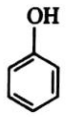
(III) 

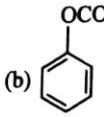
(IV) 

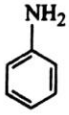
[JEE (Advanced) II 2016]

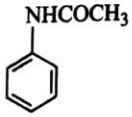
(a) I > II > III > IV (b) III > I > II > IV
(c) III > IV > II > I (d) I > III > IV > II

153. Which of the following compounds will form significant amount of *meta* product during mono-nitration reaction?
[JEE (Main) 2017]

(a) 

(b) 

(c) 

(d) 

154. The increasing order of the reactivity of the following halides for the $S_{N}1$ reaction is : **[JEE (Main) 2017]**

(i) $CH_3CH(Cl)CH_2CH_3$

(ii) $CH_3CH_2CH_2Cl$

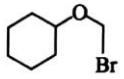
(iii) p—H_3CO—C_6H_4—CH_2Cl

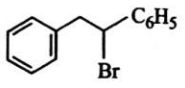
(a) (iii) < (ii) < (i) (b) (ii) < (i) < (iii)
(c) (i) < (iii) < (ii) (d) (ii) < (iii) < (i)

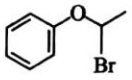
155. The formation of which of the following polymers involves hydrolysis reaction? **[JEE (Main) 2017]**

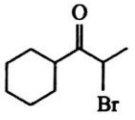
(a) Nylon 6 (b) Bakelite
(c) Nylon 6, 6 (d) Terylene

156. Which of the following, upon treatment with *tert.*-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine? **[JEE (Main) 2017]**

(a) 

(b) 

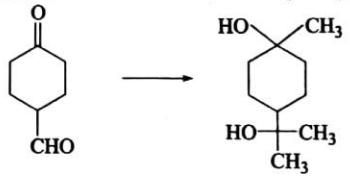
(c) 

(d) 

157. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is : **[JEE (Main) 2017]**

(a) six (b) zero
(c) two (d) four

158. The correct sequence of reagents for the following conversion will be : **[JEE (Main) 2017]**



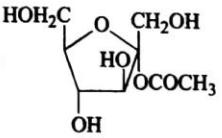
(a) $[Ag(NH_3)_2]^+OH^-$, H^+/CH_3OH, CH_3MgBr

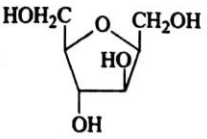
(b) CH_3MgBr, H^+/CH_3OH, $[Ag(NH_3)_2]^+OH^-$

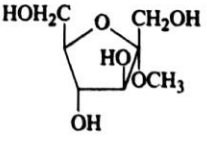
(c) CH_3MgBr, $[Ag(NH_3)_2]^+OH^-$, H^+/CH_3OH

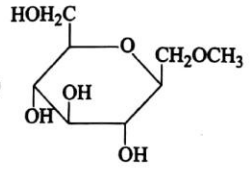
(d) $[Ag(NH_3)_2]^+OH^-$, CH_3MgBr, H^+/CH_3OH

159. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution? **[JEE (Main) 2017]**

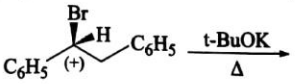
(a) 

(b) 

(c) 

(d) 

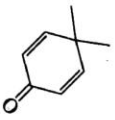
160. The major product obtained in the following reaction is :



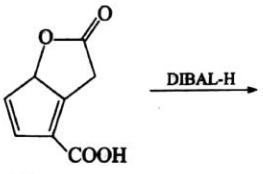
[JEE (Main) 2017]

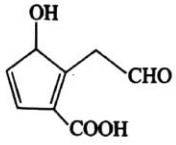
(a) $(\pm)C_6H_5CH(OtBu)CH_2C_6H_5$
(b) $C_6H_5CH{=}CHC_6H_5$
(c) $(+)C_6H_5CH(OtBu)CH_2C_6H_5$
(d) $(-)C_6H_5CH(OtBu)CH_2C_6H_5$

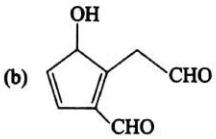
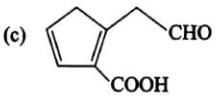
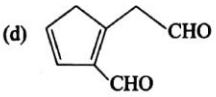
161. Which of the following molecules is least resonance stabilized? **[JEE (Main) 2017]**

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

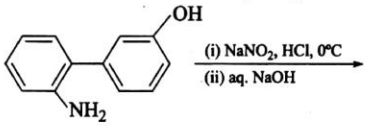
162. The major product obtained in the following reaction is: **[JEE (Main) 2017]**

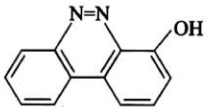
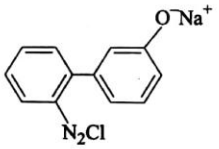
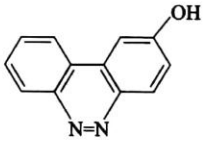
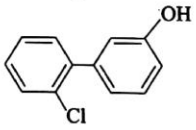


(a) 

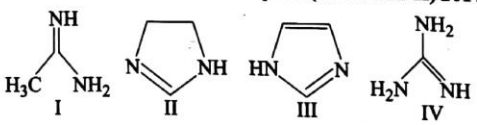
(b) 
(c) 
(d) 

163. The major product of the following reaction is : **[JEE (Advanced-II) 2017]**



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

164. The order of basicity among the following compounds is: **[JEE (Advanced-II) 2017]**

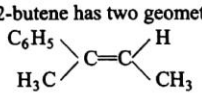


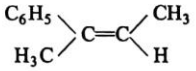
(a) II > I > IV > III
(b) IV > II > III > I
(c) I > IV > III > II
(d) IV > I > II > III

PREVIOUS YEAR OBJECTIVE PROBLEMS SOLUTION

1. (a) More is the heat of hydrogenation of alkene, easier is its hydrogenation or more is its reactivity.

2. (a) 1-phenyl-2-butene has two geometrical isomers as :

cis  and

trans 

3. (c) Stronger is the acid, weaker is its conjugate base or weaker is nucleophile. The order of acidic nature $HF > H_2O > NH_3 > CH_4$.

4. (d) Propyne has one acidic hydrogen and thus, forms propylides with $AgNO_3$ in ammonia.

$$CH_3C{\equiv}CH + Ag_2O \longrightarrow \underset{\text{Silver propylide}}{CH_3C{\equiv}C{\cdot}Ag}$$

5. (d) The rate of reaction follows $RI > RBr > RCl > RF$ whether it obeys S_N1 or S_N2 mechanism.

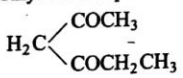
6. (b) Both Zn-Hg/HCl and $NH_2 \cdot NH_2/OH^-$ reduce $\rangle C{=}O$ gp. to $\rangle CH_2$ but reduction with Zn-Hg/HCl is not useful for acid sensitive substances.

7. (a) It undergoes dehydration easily as the product obtained is conjugated which is more stable.

8. (c) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl + SO_2$

—OH group of —COOH is replaced by PCl_3 or $SOCl_2$.

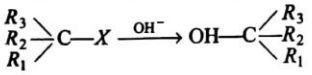
9. (b) Two electron withdrawing groups attached on H_2C < group makes the H-atom of H_2C < (or methylene group) acidic in nature and the compounds are called reactive methylene compounds.

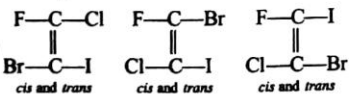


*R*CO is electron withdrawing group.

10. (d) Aliphatic amines are more basic.

11. (d) S_N2 reaction at an asymmetric carbon always leads to 100% inversion in molecule, *i.e.*, a stereoisomer.



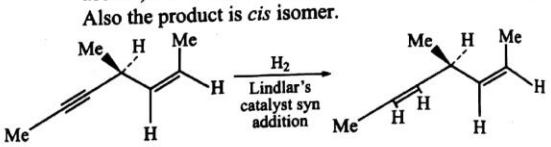
12. (d) 

cis and *trans* *cis* and *trans* *cis* and *trans*

Each has different dipole moment.

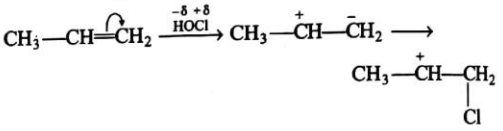
13. (c) In addition of HCl on alkene in presence of peroxide, the second step of chain propagation is endothermic whereas in HI, first step of chain propagation is endothermic.

14. (b) Lindlar's catalyst (Pd on $CaCO_3$ deactivated by lead acetate) is used to convert a triple bond to double bond. Also the product is *cis* isomer.



The product has a plane of symmetry and thus, is optically inactive.

15. (b) Addition is electrophilic in alkene and thus, Cl^+ being an electrophile attacks negative centre.



16. (c) $CH_3CH_2CH_2OH \xrightarrow{Cu,\,\Delta} CH_3CH_2CHO \xrightarrow{\text{Fehling sol.}}$ Red ppt.

$$CH_3CHOHCH_3 \xrightarrow{Cu,\,\Delta} CH_3COCH_3$$

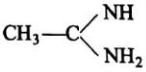
17. (a) This is crossed Cannizzaro's reaction :

$$HCHO + C_6H_5CHO \xrightarrow{NaOH} HCOONa + C_6H_5CH_2OH$$

18. (a) $(CH_3)_4N^+I^- \xrightarrow[\Delta,\,P]{NaOH} (CH_3)_4N^+OH + NaI$

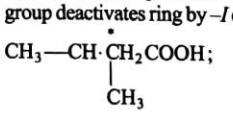
$\hookrightarrow (CH_3)_3N + CH_3OH$

The reaction will be more spontaneous when it has the best leaving group, *i.e.*, I^-. Also methyl group with +ve *N* is more active due to +ve *IE* of CH_3 group.

19. (b) 2° amines are more basic than 1° amines due to +ve *IE* of $-CH_3$ group. In amide the resonance gives rise to less availability to electron pair for coordination and thus, it is less basic. The negative charge developed on N in  due to resonance makes it more basic.

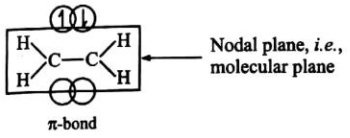
20. (b) Br is less reactive and more selective and thus, formation of 3° free radical will be the major product.

21. (c) C_6H_6 ring is activated for S_E reaction by the + *I* effect as well as hyperconjugation of CH_3 gp. —Cl deactivates ring as –*I* effect predominates over + *M* effect. $-NO_2$ group deactivates ring by –*I* effect as well as by –*M* effect.

22. (d) 

C is asymmetric or Chiral carbon.

23. (a) A π-bond has a nodal plane passing through the two bonded nuclei, *i.e.*, molecular plane.



24. (b) $CH_3C{\equiv}CCH_3$ is linear at C≡C and symmetrical and thus, dipole moment is zero.

25. (d) Ammoniacal Cu_2Cl_2 gives red precipitate with terminal alkynes (1-butyne) only.

26. (b) $CH_3CH_2CH_2Br \xrightarrow[\text{Dehydrobromination}\ (-HBr)]{NaOH\ (alc.)} CH_3CH{=}CH_2$

$$\xrightarrow[20°C\ \text{Acc. to Markownikoff's rule}]{HBr/\text{acetic acid}} CH_3CHBr\cdot CH_3$$

27. (b) More is the tendency for hydrogen bonding, higher will be the boiling point. In carboxylic acids H-bonding is more than alcohols.

28. (c) $BrCH_2CH_2COOH$ is the weakest acid and has lowest dissociation constant. $-I$ effect of Br is lesser than F and is far away from —COOH group.

29. (a) $CH_3CH_2\cdot CH_2OH \xrightarrow{[O]} CH_3CH_2CHO \xrightarrow{H_2NCONHNH_2}$

$$CH_3CH_2CH{=}N\cdot NHCONH_2$$

30. (a) The product will be optically active because the chiral carbon atoms of both the acid and alcohol retain their configuration.

31. (d) $CH_3CH_2\underset{OH}{\underset{|}{CH}}\cdot CH_3 \xrightarrow{H^+}$

$$CH_3CH_2CH{=}CH_2 + \underset{H}{\overset{CH_3}{>}}C{=}C\underset{H}{\overset{CH_3}{<}}$$

Butene-1 — Br_2 → $CH_3CH_2CHBr\cdot CH_2Br$ (*d* and *l* forms)

cis-2-butene — Br_2 → $CH_3CHBr\cdot CHBrCH_3$ Racemic (*d* and *l*) of 2,3-dibromobutane

+ *trans*-2-butene — Br_2 → $CH_3CHBrCHBrCH_3$ *Meso*-2,3 dibromobutane

F has only three structures. F $\xrightarrow{Br_2}$ in all 5 compounds.

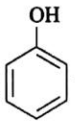
32. (a) $\underset{sp^2}{CH_2}{=}\underset{sp^2}{CH}-\underset{sp}{C}{\equiv}\underset{sp}{CH}$

33. (a) $C_6H_5C{\equiv}CCH_3 \xrightarrow[Hg^{2+},\ H_2SO_4]{H_2O} C_6H_5\overset{+}{C}{=}\overset{-}{C}CH_3$

$$\xrightarrow{HOH} C_6H_5\cdot\underset{OH}{\underset{|}{C}}{=}CHCH_3 \rightleftharpoons C_6H_5COCH_2CH_3$$

34. (a) $\mu_{CCl_4} = 0, \mu_{CHCl_3} = 1.0\ D, \mu_{CH_2Cl_2} = 1.6\ D,$

$\mu_{CH_3Cl} = 1.86\ D$

35. (b)  $+ C_2H_5I \xrightarrow{\bar{O}C_2H_5} C_2H_5OC_2H_5$

$C_2H_5O^-$ will abstract proton from phenol producing phenoxide ion. Now $C_6H_5O^-$ and $C_2H_5O^-$ (in excess) will try to attack methylene carbon of ethyl iodide. Since, $C_2H_5O^-$ is a better nucleophile and thus, it will succeed to give ether.

$C_6H_5OH + O^-C_2H_5 \longrightarrow C_6H_5O^- + C_2H_5OH$

36. (c) $H_2C{=}\underset{CH_3}{\overset{OCOCH_3}{<}} \xrightarrow{HOH/H^+} H_2C\underset{CH_3}{\overset{OH}{<}}$

$$\rightleftharpoons CH_3CO\cdot CH_3$$

$$H_3C\diagup\!=\!\diagdown OCOCH_3 \xrightarrow{HOH/H^+} H_3C-CH{=}CHOH \rightleftharpoons CH_3CH_2CHO$$

Aldehyde formed will reduce Fehling solution.

37. (a) $R\text{COOC}_2H_5 \xrightarrow{CH_3MgBr} R-\underset{CH_3}{\underset{|}{C}}{=}O \xrightarrow{CH_3MgBr}$

$$R-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$$

The product should contain at least two methyl groups and one OH group.

38. (a) Two mole of $NaNH_2$ (—NH_2 base) will abstract two mole of most acidic H-atoms out of four acidic H-atoms. The acidic character is —COOH > —OH (phenolic deactivated by NO_2 > OH > alkyne H).

39. (a) $F-\!\!\diagup\!\!\diagdown\!\!-NO_2 \xrightarrow[\text{Nucleophilic aromatic substitution}]{(CH_3)_2NH}$

$$H_3C\diagup N-\!\!\diagup\!\!\diagdown\!\!-NO_2 \xrightarrow[0\text{-}5°C]{(i)\ NaNO_2/HCl} \text{No reaction}$$

$$\xrightarrow{(i)\ H_2Ni} H_3C\diagup N-\!\!\diagup\!\!\diagdown\!\!-NH_2$$

40. (d) The given molecule is the staggered form of compound. A rotation of 60° converts staggered conformation into an eclipsed conformation and *vice-versa*. Rotation between 0° to 60° and more than 60° but less than 120°

produces many conformations between staggered and eclipsed forms. These are called gauche forms.

41. (b) $CH_3—\underset{\displaystyle CH_3}{\overset{|}{CH}}—CH_2—CH_3 \longrightarrow (CH_3)_2CClCH_2CH_3$; $(CH_3)_2\dot{C}HCHClCH_3$; $(CH_3)_2CHCH_2CH_2Cl$; $CH_3—\underset{\displaystyle CH_2Cl}{\overset{|}{\dot{C}H}}\cdot CH_2\cdot CH_3$

Thus, out of four isomers only two have chiral carbon atoms. Each has two isomer.

42. (c) The reaction proceeds *via* carbocation formation.

$$C_6H_5C(CH_3)=CH_2 \xrightarrow{+H^+} C_6H_5—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^+}}}} \xrightarrow{H_2O}$$

$$C_6H_5—C(CH_3)_2—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH \xleftarrow{-H^+}$$

43. (d) Reduction of alkyne to alkene by Li—NH_3/C_2H_5OH is known as Birch reaction. The product formed is *trans*-hex-2-ene.

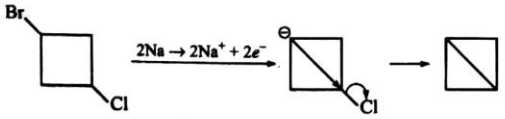
44. (d) $C_6H_5CONH_2 \xrightarrow[-H_2O]{POCl_3} C_6H_5CN$

45. (a) Electrophilic substitution involves the attack of electrophile on *o*- and *p*-position. The ring attached with NH has rich electron density. As ortho position is occupied, *p*-position is attached by Br^+.

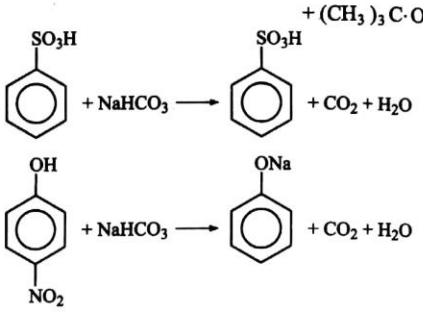
46. (b) The ease with which any compound or group can lose H^+ is called acidic nature. Position of *X* is most acidic due to resonance stabilization of —COOH. (*Y*) is more acidic than (*Z*) due to *–I* effect of —COOH group.

47. (c) The octet of all atoms are complete in structure of options (a) and (b). In structure of option (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 of option (c).

48. (d) This is a internal Wurtz's type reaction and the only obvious choice is :



49. (a) $(CH_3)_3C\cdot OH + C_6H_5MgBr \longrightarrow C_6H_6 + (CH_3)_3C\cdot OMgBr$

50. (d) 

51. (c) Due to chelation in I and dipole moment.

52. (a) Follow Markownikoff addition (NO^+Cl^-).

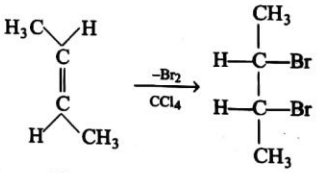
53. (d) Isocyanide test of carbylamine reaction.

54. (c) Follow IUPAC rule.

55. (b) Elimination of HBr by KOH gives less reactive vinyl bromide. To eliminate HBr from vinyl bromide strong base $NaNH_2$ is used.

56. (c) *n*-hexane, 2-methyl pentane, 3-methyl pentane, 2,3-dimethyl butane, 2,2-dimethyl butane.

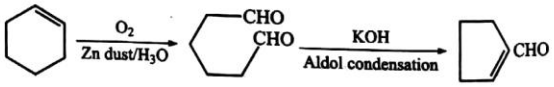
57. (a) Anti addition of Br_2 on *trans* alkene products *meso* compound.



58. (a) $Na + C + N \longrightarrow NaCN$

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

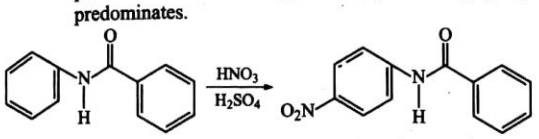
$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$

59. (a) 

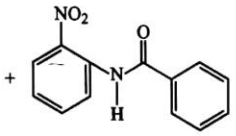
60. (a) Similar charge on nearest atoms give rise to lesser stability.

61. (b) —$\ddot{N}H$ group is *o*-, *p*- directing as well as an activating group whereas $>C=O$ group is *m*-directing and deactivating. When two different nature groups are

present in benzene ring, the *o*-, *p*-directing group predominates.

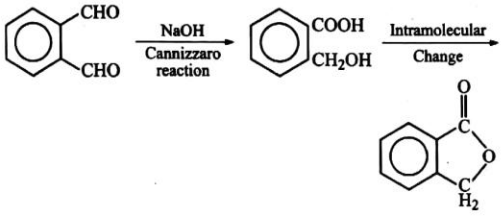


p-isomer major



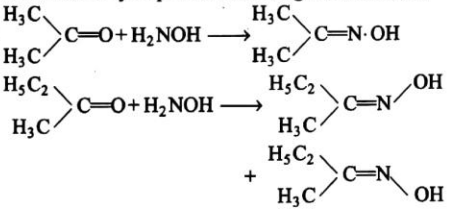
o-isomer minor

62. (c)

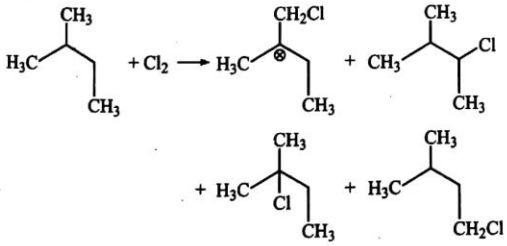


63. (c) It is cumene hydroperoxide rearrangement reaction.

64. (b)



65. (b)



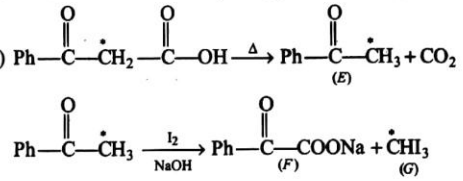
66. (a)

It is easier to do nucleophilic substitution on side chain halides than on aryl halides.

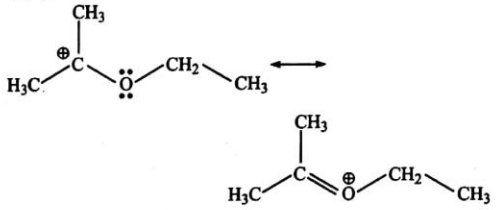
67. (b) Hyperconjugation involves $\sigma - p$ orbitals.

68. (a) Like celluose which has β 1-4 glycosidic linkage.

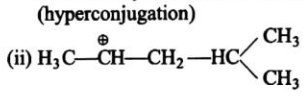
69. (c)



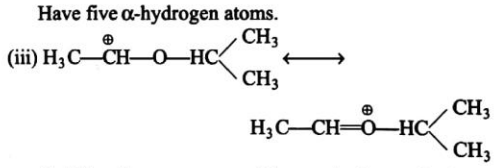
70. (d) (i)



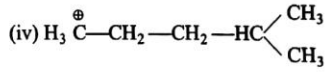
Stabilizes by resonance and have six α-hydrogen atoms (hyperconjugation)

(ii) 

Have five α-hydrogen atoms.

(iii) 

Stabilizes by resonance and have only three α-hydrogen atoms.

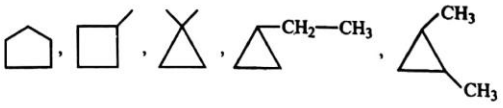
(iv) 

Have only two α-hydrogen atoms.

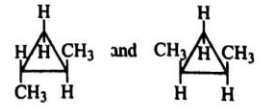
71. (d) Due to H^- shift from C_2 to C_3. Driving force is conjugation from oxygen. Also bulky gp. hinders in hydride shift.

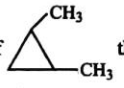
72. (b) Stability of cononical form $\propto$ negative formal charge on more electronegative atom α minimum distance between unlike charges.

73. (d)



are five structural isomers



are geometrical isomers of  thus, is all six.

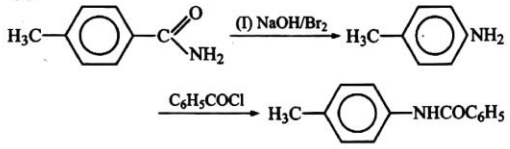
74. (d) Natural rubber involves weak van der Waals' forces.

75. (b) Priority order is CN > ON > Br.

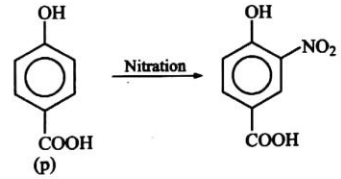
76. (a) Electron repelling gp. decreases the strength of aromatic carboxylic acid and phenol.

Benzoic acid	*p*-methyl benzoic acid
C_6H_5COOH	1.26×10^{-5}
K_a: 6.76×10^{-5}	
Phenol	*p*-chlorophenol
1.05×10^{-10}	4.16×10^{-10}

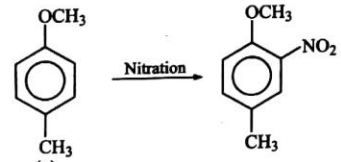
77. (c)



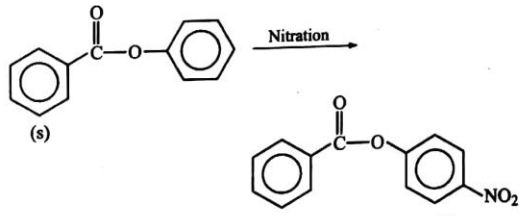
78. (c)



(p)



(q)



(s)

[NO_2^+ attacks at *o*-, *p*- with respect to —$OCOC_6H_5$]

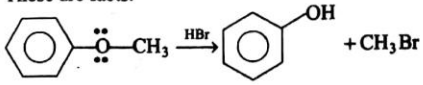
79. (c) It is the formula of EDTA.

80. (d) $CH_3\cdot CH_2\cdot C{\equiv}CH + NaNH_2 \rightarrow CH_3CH_2\cdot C{\equiv}C^-Na^+$

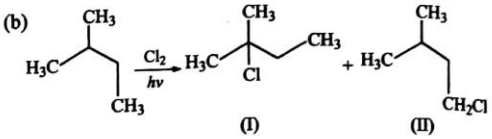
$CH_3CH_2CH_2CH_2Br$

$CH_3CH_2\cdot C{\equiv}C{-}CH_2\cdot CH_2\cdot CH_2\cdot CH_3$ ← Octyne-3

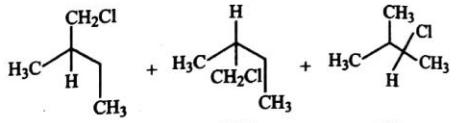
81. (a) These are facts.

82. (d)  + CH_3Br

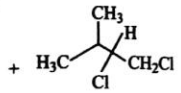
83. (b)



(I) (II)



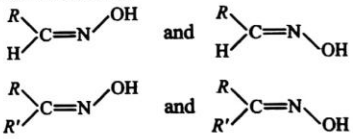
(III) (IV) (V)



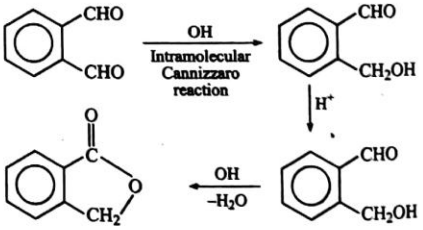
(VI)

In these (iii) + (iv) and (v) + (vi) are enantiomers to each other. Thus total six isomers will be possible for *N*. In these only four isomers will be obtained on fractional distillation without resolution because enantiomers cannot be separated by fractional distillation, Hence $N = 6, M = 4$

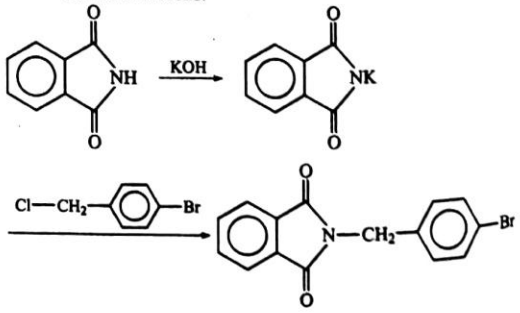
84. (c) An aldehyde and a unsymmetrical ketone form two isomeric oxime



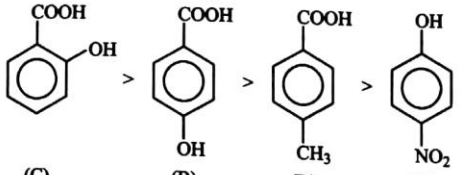
85. (d)



86. (a) The replacement of Cl is due to the formation of stable benzyl carbocation. Alternatively Cl is present in side chain and thus replaced whereas Br is attached in benzene nucleus.



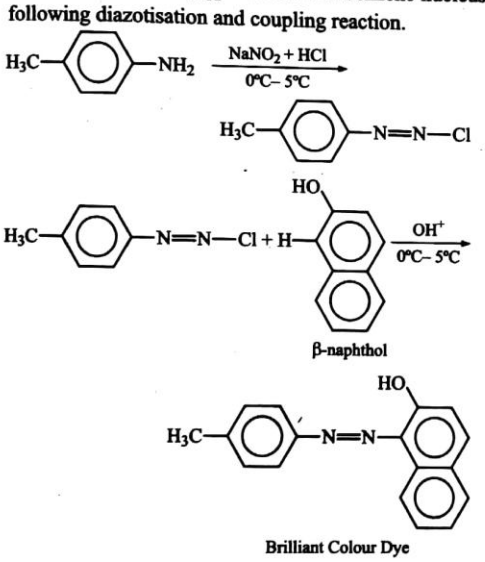
87. (c) Due to orthoeffect; Ortho benzoic acid is most acidic because its anion is highly stabilized due to strong intramolecular H-bonding.



(C) (B) (D) (A)

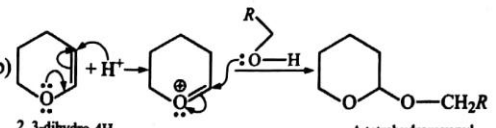
K_a: 1.0×10^{-3} 2.9×10^{-5} 1.26×10^{-5} 6.9×10^{-8}

88. (c) It is a test for $-NH_2$ gp. attached on benzene nucleus following diazotisation and coupling reaction.



Brilliant Colour Dye

89. (b)

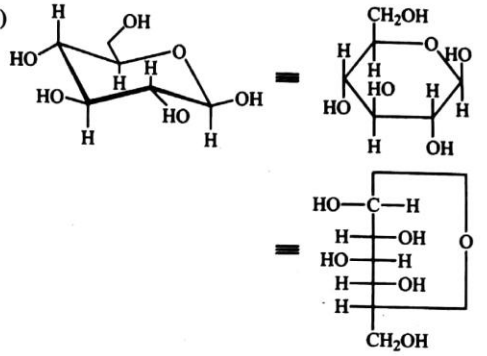


2, 3-dihydro-4H pyran (DHP)

A tetrahydropyranyl ether (ATHP ether) Better to call Acetal

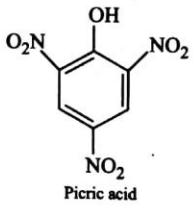
Note : Because of its special structure, there are two ether oxygen attached to same carbon, making it acetal.

90. (b)

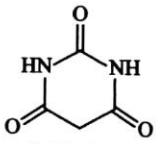


In β-D glucopyranose all the OH groups and CH_2OH group occupy equatorial position in the most stable conformer.

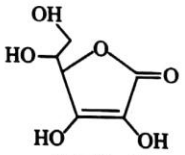
91. (d) Aspirin is acetyl salicylic acid.



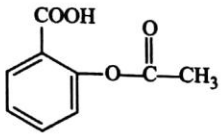
Picric acid



Barbituric acid



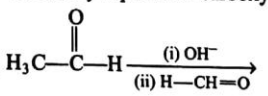
Ascorbic acid

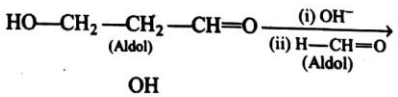


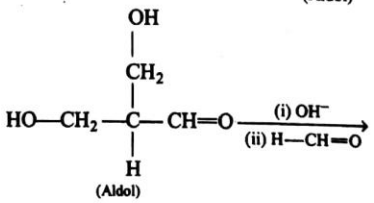
Aspirin

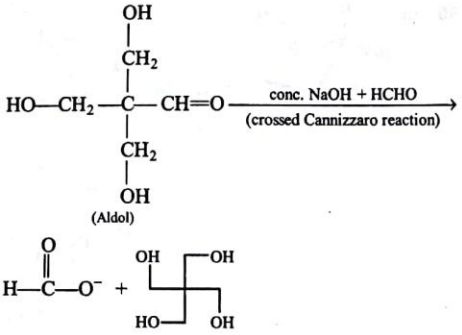
Thus, only aspirin has carboxylic group.

92. (c)

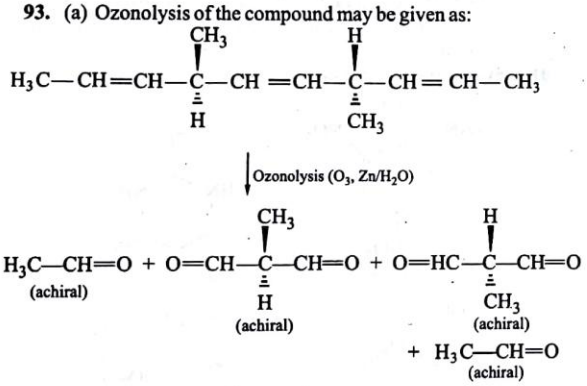




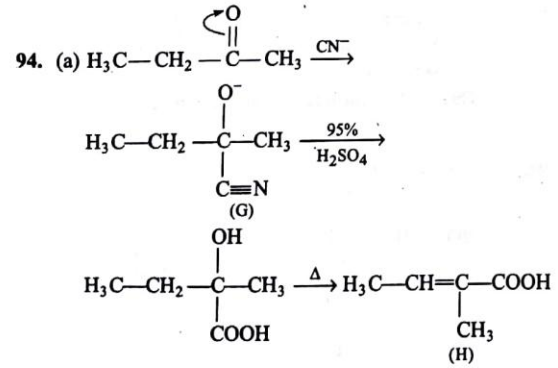




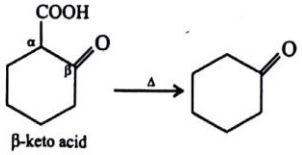
93. (a) Ozonolysis of the compound may be given as:



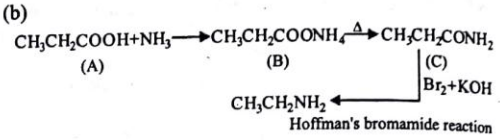
94. (a)



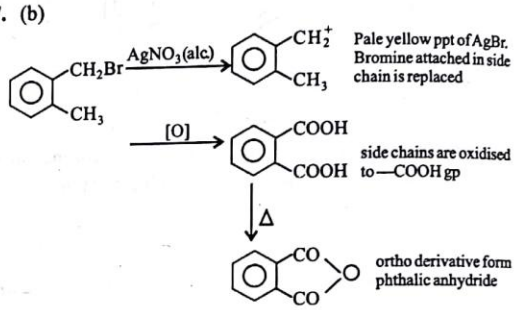
95. (b) β-keto acids undergo decarboxylation most easily on heating.



96. (b)



97. (b)



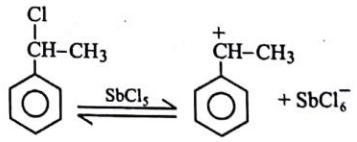
98. (d) $-NH_2 \xrightarrow[-HCl]{CH_3COCl} -NHCOCH_3$

Presence of one $-NH_2$ shows an increase of molar mass by 42 units (one CH_3CO-1H)

Total increase 210 unit

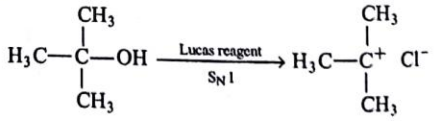
$\therefore$ No. of $-NH_2$ gps in molecules $= \frac{210}{42} = 5$

99. (a)



(The attack on this carbocation takes place from either side and thus recemisation occures)

100. (d)



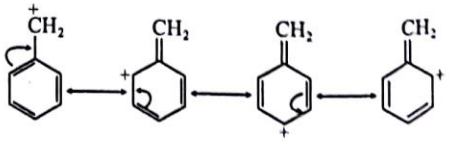
(most stable 3° carbocation)

101. (a) p-nitrophenol is strongest acid among all

102. (b) More is the no. of canonical forms, more is stability

$CH_2 = CH - CH_2^+ \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2$

$CH_3 \cdot CH_2 \cdot CH_2^+$ has no resonance



103. (c)

$$12NADP + 18ADP + 12H_2O \xrightarrow{h\nu} 18ATP + 12NADPH + 6O_2$$

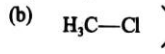
$$6CO_2 + 12NADPH + 18ATP \xrightarrow{dark} C_6H_{12}O_6$$

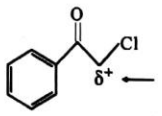
$$+12NADP + 18ADP + 6H_2O$$

Net reaction $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$

One carbon atom of glucose requires 3ATP for its synthesis in photosynthesis.

104. (b)





more charge as a result of – I.E. of Cl due to electron withdrawing nature of Cl as well as >C= 0 group stabilises its transition state.

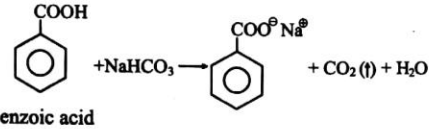
$$\text{Rate of } S_N2 \propto = \frac{1}{\text{steric hendrance}}$$

$\propto \delta^+$ charge on carbon

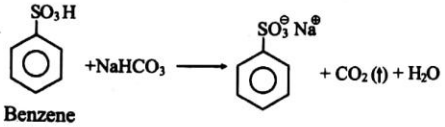
$\propto$ Stability of transition state

So, $S > P > R > Q$

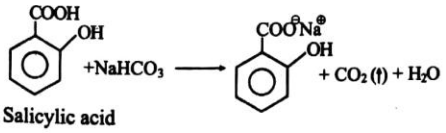
105. (d) Organic molecules having — COOH group liberate CO_2 with $NaHCO_3$ solution



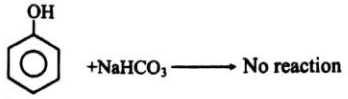
Benzoic acid



Benzene Sulphonic acid



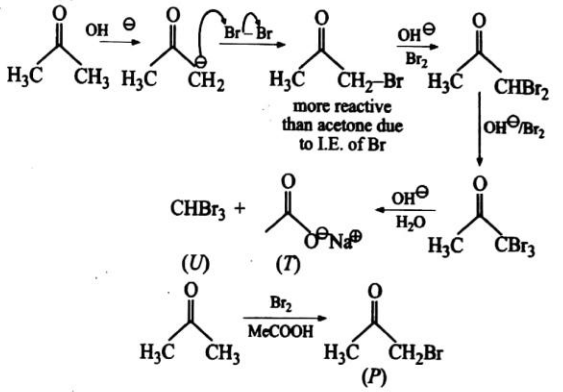
Salicylic acid



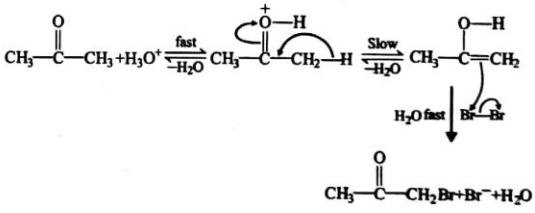
Phenol

106. (a) $(CH_3)_3C^+$; Carbon showing sp^2 hybridisation has one p orbital vacant. Thus $\sigma - p$ empty orbital hyperconjugation. $CH_3—CH=CH—CH_3$; The hyperconjugation involves σ of CH_3 gp and π bond of its nearest C *i.e.* $\sigma - \pi^*$ electron delocalization.

107. (c)

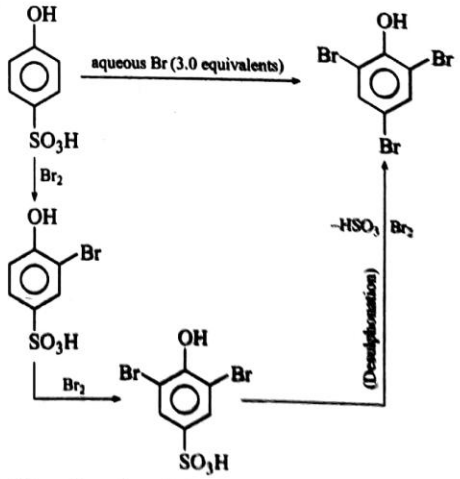


In acidic medium reaction takes place via enol form



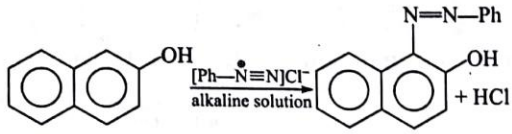
The enol form of $CH_3—\overset{O}{\overset{\|}{C}}—CH_2Br$ *i.e.*, $CH_3—\overset{OH}{\overset{|}{C}}=CHBr$ is less reactive than enol form of CH_3COCH_3 *i.e.*, $CH_3—\overset{OH}{\overset{|}{C}}=CH_2$ and thus only monosubstitution takes place at α – C.

108. (b)



109. (c) $CH_3—N=C=O$ (methyl isocyanate) was leaked.

110. (d)

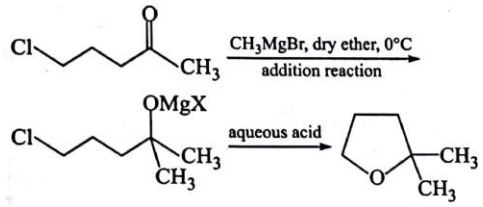


Dye formation is favoured in alkaline medium

111. (b) III > II > I

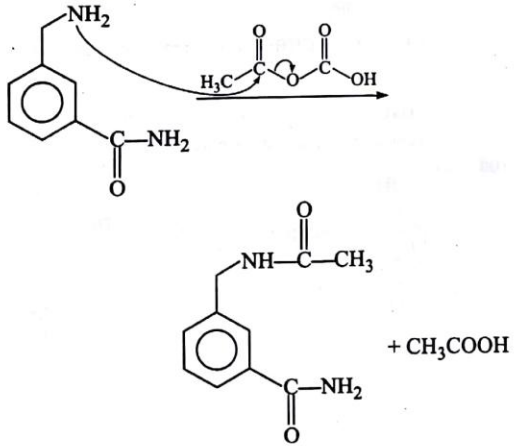
More the branching in an alkane, lesser will be the surface area, as the shape approaches to spherical, leading to decrease in van der Waals' forces. Therefore lesser will be the boiling point.

112. (d)



113. (c) When two phenyl groups are replaced by two para-methoxy group, carbocation formed will be more stable.

114. (a) Amino gp. ($-NH_2$) undergo acetylation and amide gp. ($-CONH_2$) does not undergo acylation therefore acetic anhydride shows acetylation with amino gp.



115. (b) Due to more $-I.E.$ of attached groups in $(CH_3)_3CCl$ or due to max crowding round central carbon atom favours S_N1 mechanism.

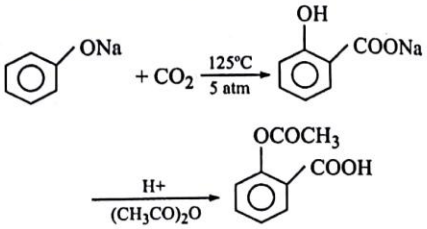
116. (d) This is carbylamine reaction

$$RNH_2 + CHCl_3 + 3KOH(alc.) \longrightarrow \underset{\text{unpleasant smell}}{RNC} + 3KCl + 2H_2O$$

117. (d) PCC is milder oxidant and oxidises alcohol to aldehyde only.

118. (c) $CH_3 \cdot CCl_3 + Cl_3C \cdot CH_3 \xrightarrow{\text{Ag powder}} CH_3C \equiv CCH_3$

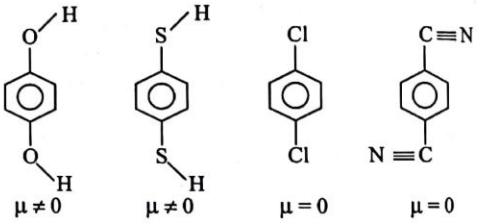
119. (a)



120. (a) Order of basic nature in a aqueous solution on the basis of K_b.

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$

121. (d)



122. (c) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow{KOH\ (Alc)} CH_2 = CH_2$

123. (b) Meq. of acid (H_2SO_4) taken $= \frac{1}{10} \times 2 \times 60 = 12$

Meq. of acid used by NaOH = Meq. of NaOH $- \frac{1}{10} \times 20 = 2$

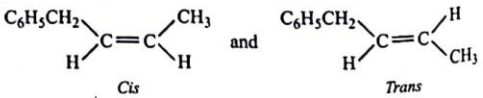
$\therefore$ Meq. of acid used by $NH_3 = 12 - 2 = 10 =$ Meq. of NH_3

$$\% \text{ of } N = \frac{\text{Meq. of } NH_3 \times 1.4}{\text{Mass. of organic compound}} = \frac{10 \times 1.4}{1.4} = 10$$

124. (a) $\%Br = \dfrac{\text{At. mass of Br}}{\text{Molar mass of AgBr}} \times \dfrac{\text{mass of AgBr}}{\text{mass of organic compound}} \times 100$

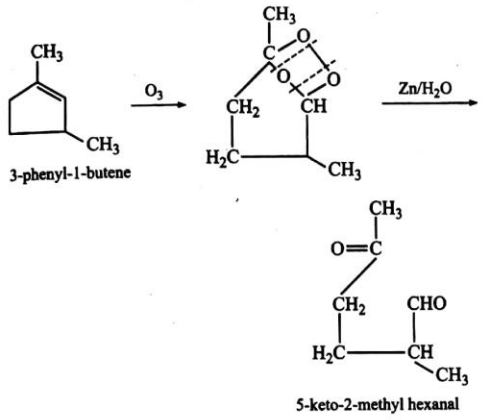
$$= \frac{80}{188} \times \frac{141}{250} \times 100 = 24\%$$

125. (a) $\begin{matrix} C_{ab} \\ \| \\ C_{ab} \end{matrix}$ type molecules show geometrical isomerism.



Cis *Trans*

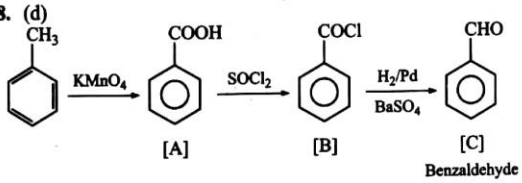
126. (b)



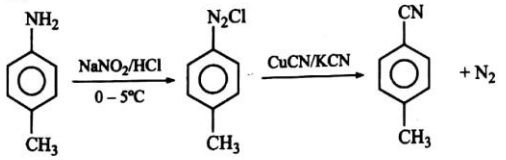
127. (d) $R-I+AgF \longrightarrow R-F+AgI$

This is Swart's reaction to prepare alkyl fluorides more conveniently by heating chloro or bromo alkane with inorganic fluorides.

128. (d)



129. (c)

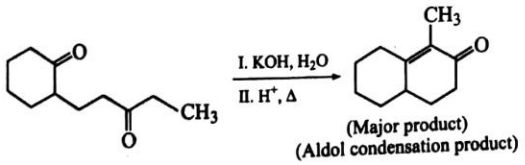


130. (b) Glyptal is used in the manufacture of paints and lacquers.

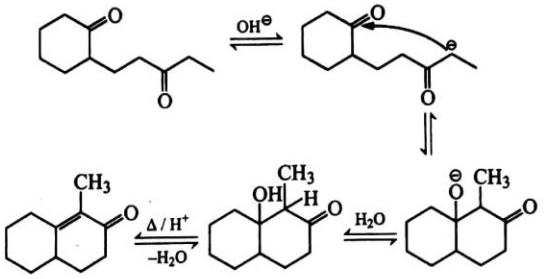
131. (a) Vitamins 'B' and 'C' are water soluble. Vitamins A, D, E, K are water insoluble.

132. (c) Phenelzine is antidepressent (a tranquilizer) and not antacid. Rest all are antacids.

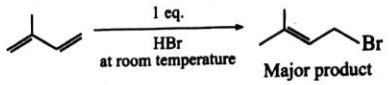
133. (a)



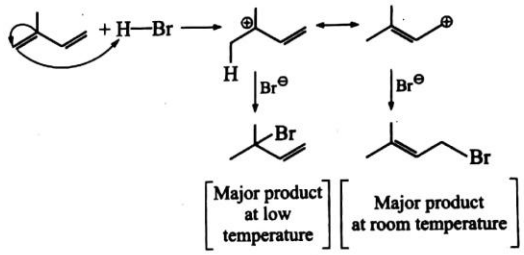
Mechanism :



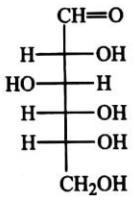
134. (d)



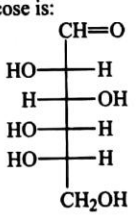
Mechanism :



135. (a) The structure of $D(+)$-glucose is:



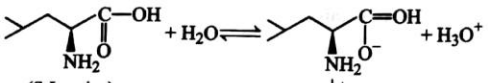
The structure of $L(-)$ glucose which is enantiomer of $D(+)$-glucose is:



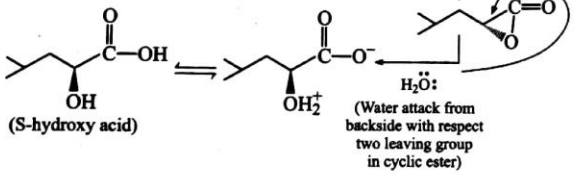
136. (c) $NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

$HNO_2 + HCl \rightleftharpoons \overset{\oplus}{H_2}ONO + Cl^-$

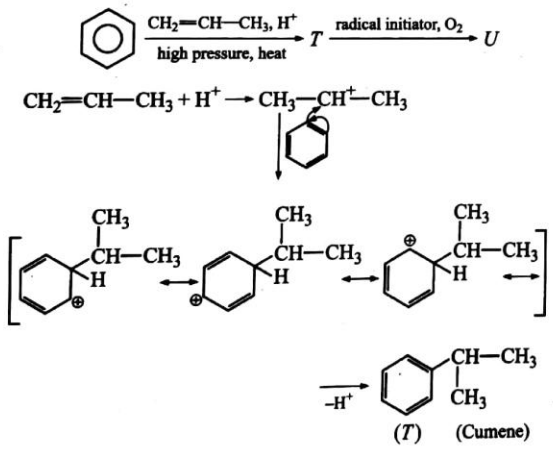
$\overset{\oplus}{H_2}ONO \longrightarrow H_2O + NO^+$

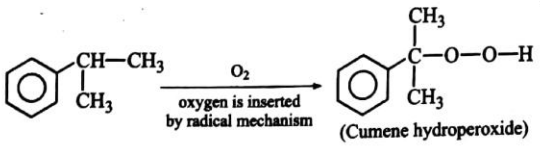


Two times backside attack leads to retention of configuration



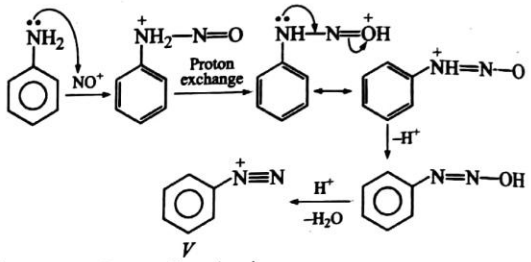
137. (b)





138. (a) $NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

$HNO_2 + HCl \rightleftharpoons H_2NO_2^+ + Cl^-$

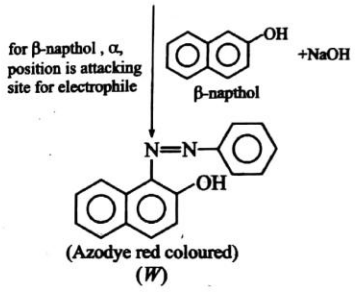


V

Benzenediazonium ion

$H_2NO_2^+ \longrightarrow H_2O + NO^+$

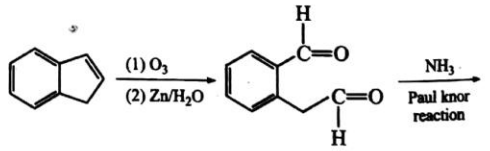
(*V*)

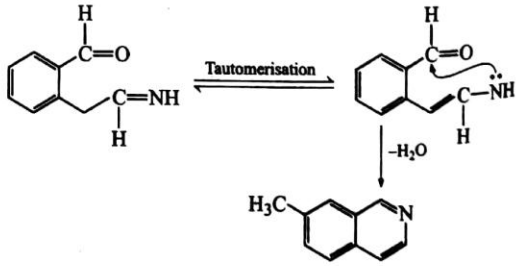


The formation of *V* is example of diazotisation reaction.

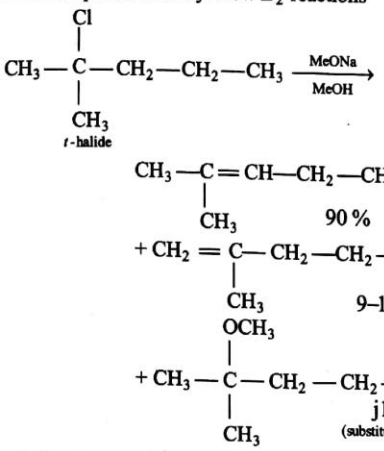
The formation of *W* from *V* is example of diazocoupling reaction.

139. (a)





140. (d) t-halides predominantly show E_2 reactions



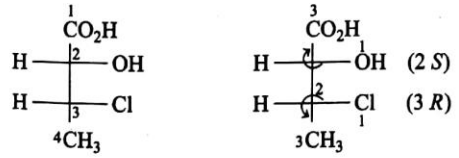
Elimination reactions predominate over substitution and thus all the products are possible.

141. (c) Buckets, dustbins are manufactured by high density polythene.

142. (c) Glycerol being high boiling point liquid (290°C) is made to boil at lower temperature by lowering pressure on its surface, *i.e.*, at reduced pressure. Glycerol is therefore separated from spent-lye by distillation under reduced pressure without decomposition. Note that glycerol decomposes at its boiling point.

143. (a) Carbon number 2 and 3 are chiral. On 2nd carbon two vertical positions are attached with carbon ($CHClCH_3$ and COOH) and horizontal position with OH and H. O has high priority than H.

On 3rd carbon two vertical position are attached with carbon [CHOH(COOH) and CH_3] and horizontal positions with H and Cl. Cl has high priority than H.



(2nd carbon seems to be *R* but H on horizontal position and thus *S*)

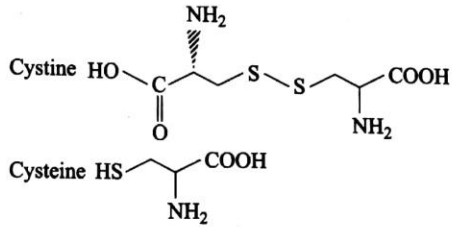
(3rd carbon seems to be *S* but H on horizontal position and thus *R*)

144. (b) Highest concentration of nitrate (100 ppm) is reported.

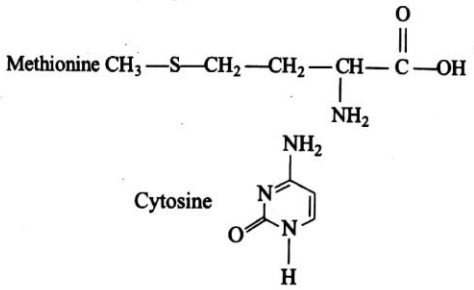
	International standard Beuro	NCERT
Lead	15 ppb	50 ppb
Nitrate	50 ppm	50 ppm

Note : Again there may be two answers according to ISB of environmental pollution.

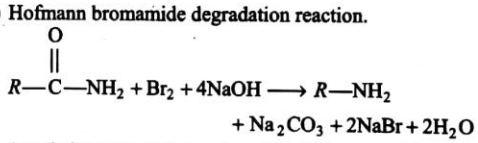
145. (b)



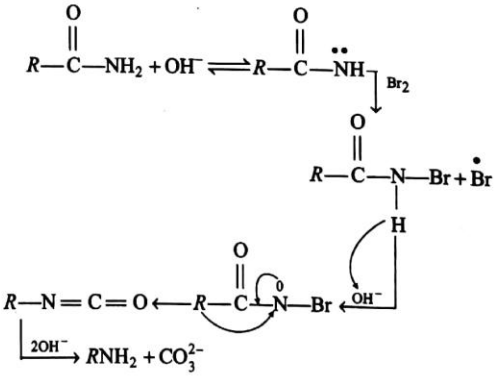
(— SH is thiol group)



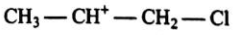
146. (c) Hofmann bromamide degradation reaction.



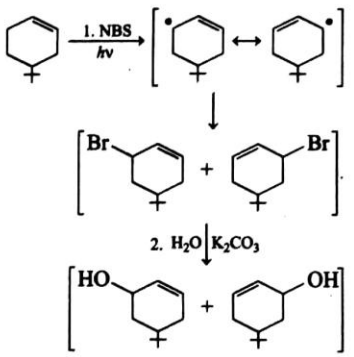
1 mole bromine and 4 moles of NaOH are used for one mole of amine produced.



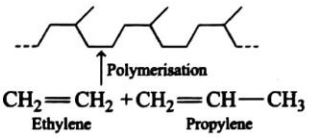
147. (a) The reaction proceeds through formation of carbonium ion



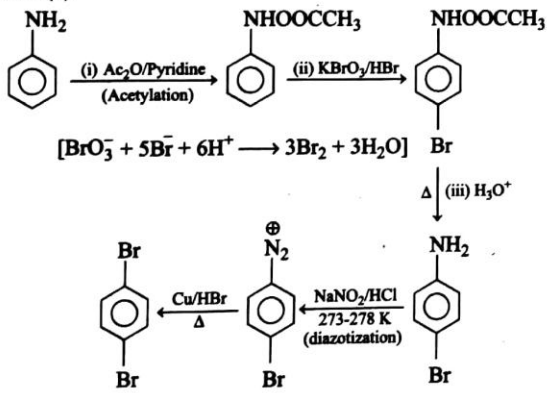
148. (a)



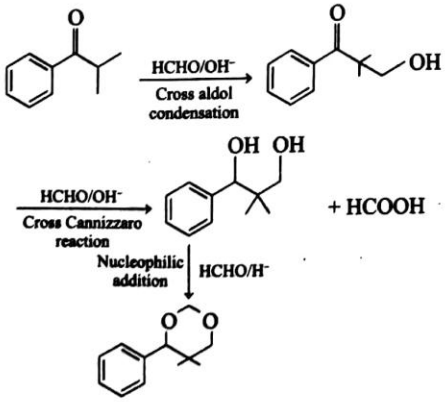
149. (a) Natural rubber $\xrightarrow{H_2/Ni}$



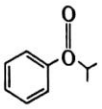
150. (b)



151. (a)



or choices (b) and (c) represents hemiacetals (O—C—OH) and are unstable. Choice (d) can be formed from only when it undergoes Gatterman-Koch reaction if aromatic ring is electron rich.

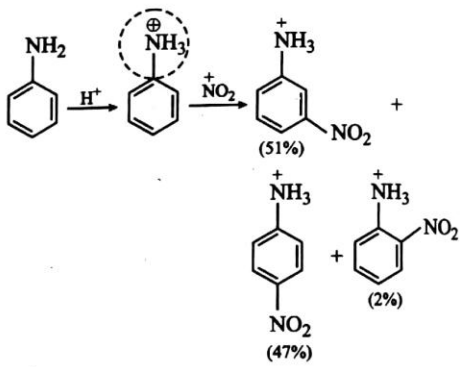


152. (a) *Ortho* substituted benzoic acid is more acidic than *meta* and *para* isomers due to *ortho* effect.

or

Conjugate base of *ortho* hydroxybenzoic acid is more acidic than its *meta* and *para* isomers due to strong H-bonding.

153. (c)



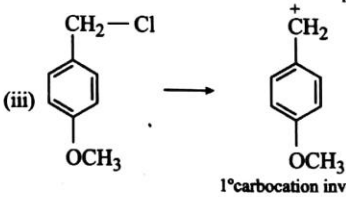
NH_3^+ is *meta* directing gp. and deactivating gp.

154. (b) Rate of S_{N1} reaction ∝ stability of carbocation

(i) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3 \longrightarrow CH_3-\overset{+}{C}H-CH_2-CH_3$ (2° carbocation)

(ii) $CH_3-CH_2-CH_2-Cl \longrightarrow CH_3-CH_2-\overset{+}{C}H_2$ (1° carbocation)

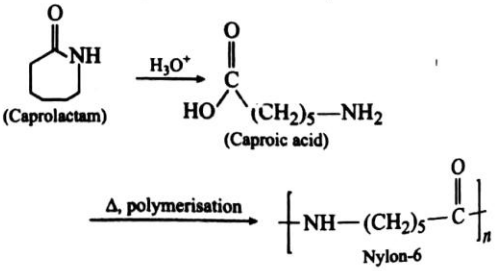
(iii)



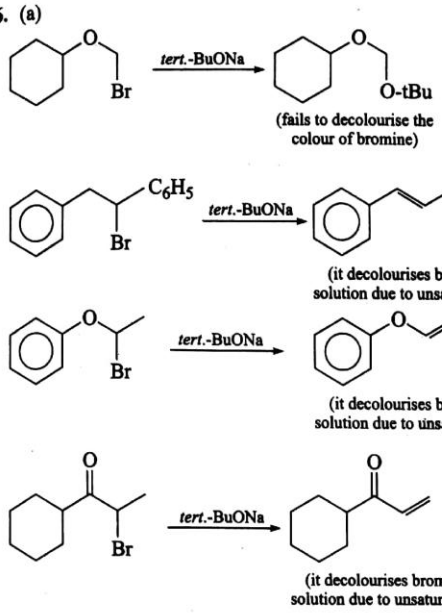
1°carbocation involving ring

Increase stability of carbocation is II < I< III.

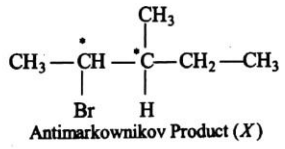
155. (a) Caprolactam is hydrolysed to produce caproic acid which undergoes condensation to produce Nylon-6.



156. (a)



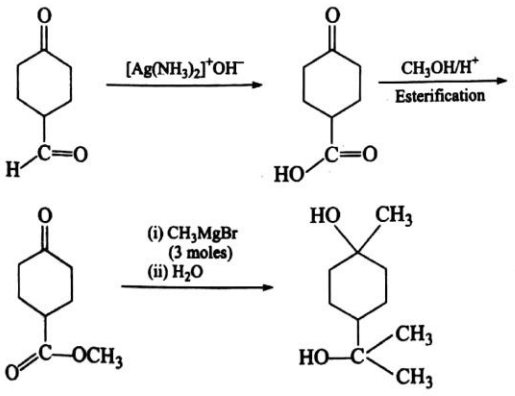
157. (d) $CH_3-CH=\underset{\text{3-Methylpent-2-ene}}{C}-CH_2-CH_3 \xrightarrow[R_2O_2]{HBr}$



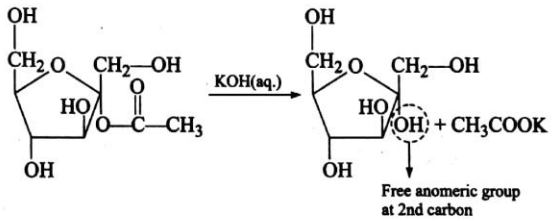
Antimarkownikov Product (X)

Product (X) contains two chiral centres* and unsymmetrical. Thus, total stereoisomers = $2^2 = 4$.

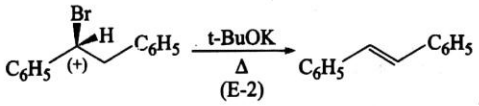
158. (a)



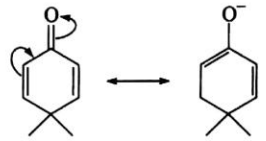
159. (a) Sugars having free anomeric — OH group are reducing sugars.



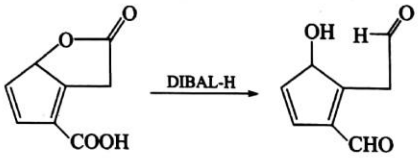
160. (b)



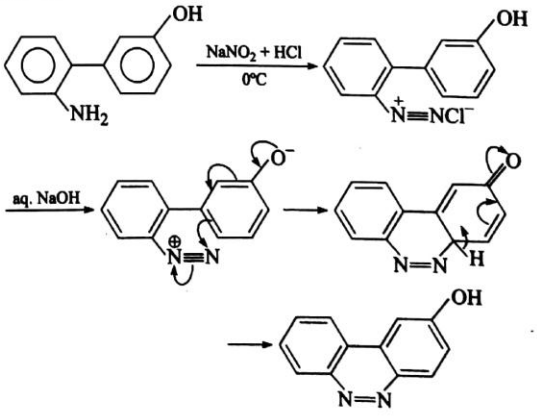
161. (d) All are stabilized by resonance. First three being aromatic are more stabilized. The fourth one being non-aromatic is least stabilized.



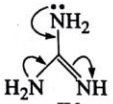
162. (b) DIBAL—H is a reducing agent and reduces cyanide, esters, amides, lactones, esters and carboxylic acids into corresponding aldehydes.



163. (c)

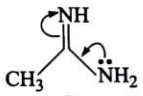


164. (d)



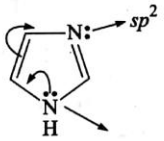
IV

Resonance with two $\ddot{N}H_2$ groups increases electron density on '*N*' of =NH



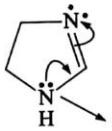
I

Lesser increase of electron density on =NH due to only one resonance with one $-NH_2$



III

The lone pair of electron of NH is used in aromatic sextet and thus least basic.



II

The lone pair of electron of NH is not involve in aromaticity. So more available also, 'N' is bonded to sp^3 C on one side.

$\therefore$ IV > I > II > III

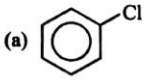
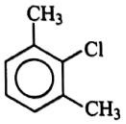
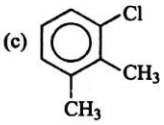
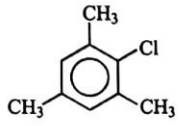
OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Select the correct statements :
   (a) A compound having enantiomers must be chiral
   (b) A compound having enantiomers must have chiral centres
   (c) Mirror image molecules are always enantiomers
   (d) 2,3-pentadiene has two enantiomers
2. Select the correct statements :
   (a) All asymmetric carbons are stereocentres
   (b) A compound with open chain structure is chiral if it has no plane of symmetry
   (c) A molecule containing chiral centres must be chiral
   (d) Prefix D-refers for dextrotatory nature of compound
3. In *sp*-hybridization of carbon, if $2s$ and $2p_x$ undergo hybridization, then the two *sp*-orbitals :
   (a) are perpendicular to p_y (b) are perpendicular to p_z
   (c) are perpendicular to p_x (d) are at 120° to p_y and p_z
4. Select the electrophiles :
   (a) $\ddot{N}F_3$ (b) PCl_3 (c) CCl_4 (d) $\ddot{C}Cl_2$
5. Which of the following has non-zero dipole moment?
   (a) HS—C$_6$H$_4$—SH (b) N≡C—C$_6$H$_4$—C≡N
   (c) HO—C$_6$H$_4$—OH (d) H_3CO—C$_6$H$_4$—C·CH_3
6. Which of the following represents the correct order ?
   (a) Stability : $\overset{+}{C}H_3 > CH_3—\overset{+}{C}H_2 < CH_3—\overset{+}{C}H—CH_3 < (CH_3)_3\overset{+}{C}$
   (b) Stability : $\overset{\bullet}{C}H_3 < CH_3—\overset{\bullet}{C}H_2 < CH_3—\overset{\bullet}{C}H—CH_3 < (CH_3)_3\overset{\bullet}{C}$
   (c) Hyperconjugation : $CH_3— < CH_3—CH_2— < (CH_3)_2CH— < (CH_3)_3C—$
   (d) Basic nature : $\bar{C}H_3 > \bar{N}H_2 > \bar{O}H > \bar{F}$
7. Which of the following represents the correct order ?
   (a) + *I* effect : $CH_3— < CH_3—CH_2— < (CH_3)_2CH— < (CH_3)_3C—$
   (b) – *I* effect : $NO_2 > SO_3H > F > NH_2$
   (c) Stability : Allyl carbocation > vinyl carbocation
   (d) Stability : $CH{\equiv}\bar{C} < CH_3—C{\equiv}\bar{C} < CH_2{=}\bar{C}H < CH_3—\bar{C}H_2$
8. Which are not the correct orders for C—Cl bond length in?
   I. $CH_3—CH_2—Cl$ II. $CH_2{=}CH—Cl$
   III. $C_6H_5—Cl$
   (a) I > III > II (b) I > II > III
   (c) III > I > II (d) III > II > I
9. Which of the following are correctly shown for conjugated compounds :
   (a) Stability of conjugated compounds ∝ No. of resonating structures
   (b) Bond energy of conjugated compounds ∝ No. of resonating structures
   (c) Bond length of a functional group $\propto \frac{1}{\text{Bond strength}}$
   (d) Reactivity of a functional group due to breaking of bond $\propto \frac{1}{\text{No. of resonating structures}}$
10. Which of the following are correct fot N-compounds?
    (a) Basic nature ∝ stability of cation
    (b) Stability of cation ∝ degree of solvation
    (c) Basic nature ∝ degree of solvation
    (d) Basic nature $\propto \frac{1}{\text{electronegativity of N}}$
11. Select the correct statements :
    (a) Carbocations are electrophiles
    (b) Carbocation is diamagnetic in nature
    (c) Triphenyl methyl carbocation in propeller in shape
    (d) Carbocation are trigonal planar
12. Which hybridizations are present in pyrolle :
    (a) *sp* (b) sp^2
    (c) sp^3 (d) sp^3d
13. Which of the following will not show S_N1 reactions ?
    (a) $CH_3—\overset{O}{\overset{\|}{C}}—CH_2—Cl$ (b) C$_6$H$_4$(CH$_2$Cl)
    (c) H_3CO—C$_6$H$_3$(CH$_2$Cl) (d) $H—\overset{O}{\overset{\|}{C}}—CH_2Cl$
14. Which of the following will give S_N reactions ?
    (a) $R—NH_2$ (b) $R—OH$
    (c) $R—N_3$ (d) $R—Br$
15. Which of the following on subjecting for S_N2 reaction will show Walden inversion ?
    (a) CH_3CHDBr (b) CH_3CH_2Br
    (c) $C_6H_5CH_2Br$ (d) $C_2H_5—CHDBr$
16. Which of the following reactions do not represent trans-esterification?
    (a) $C_6H_5COOC_2H_5 + NaOH \longrightarrow C_6H_5COONa + C_2H_5OH$
    (b) $C_6H_5COOC_2H_5 + H_2O \longrightarrow C_6H_5COOH + C_2H_5OH$
    (c) $C_6H_5COOC_2H_5 + CH_3OH \longrightarrow C_6H_5COOCH_3 + C_2H_5OH$
    (d) $C_6H_5COCl + CH_3OH \longrightarrow C_6H_5COOCH_3$
17. Which statements are correct for the given reaction, if it takes place?

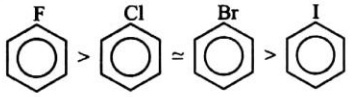
$$R-\overset{O}{\overset{\|}{C}}-L+\overset{\ominus}{N}u \longrightarrow R-\overset{O}{\overset{\|}{C}}-Nu+\overset{\ominus}{L}$$

(a) Basic nature of $\overset{\ominus}{Nu}$ should be greater than $\overset{\ominus}{L}$
(b) Basic nature of $\overset{\ominus}{L}$ should be greater than $\overset{\ominus}{Nu}$
(c) Acyl carbon is nucleophile
(d) Acyl carbon is electrophile

18. Which of the following will not give reaction according to benzyne mechanism on treating with KNH_2/NH_3?

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

19. The correct orders of reactivity are represented in :
(a) Halobenzenes S_E reactions :



(b) Activating nature of groups in benzene :
$-NH_2 > -OH > -CH_3 > -Cl$
(c) Reactivity following S_N2 :
$R-I > R-Br > R-Cl > R-F$
(d) Reactivity following S_N1 :
$RI > RBr > RCl > RF$

20. Which of the following will give alkene ?
(a) $CH_3-CHBr-CHBr\cdot CH_3 \xrightarrow{NaI/Acetone}$
(b) $CH_3\cdot CHBr\cdot CHBr\cdot CH_3 \xrightarrow{Zn/CH_3COOH}$
(c) $CH_3\cdot CHBr-CH_2\cdot CH_3 \xrightarrow{NaI/Acetone}$
(d) $CH_3CHBr\cdot CH_2CH_3 \xrightarrow{KOH\ alc.}$

21. Select the correct statements :
(a) According to Markownikoff's rule—"Richer becomes richer".
(b) Markownikoff's rule can be used for addition of unsymmetrical alkenes.
(c) Markownikoff's rule can be used if substituents present on doubly bonded carbons have $+I$ groups.
(d) Addition of HCl on $C_6H_5-CH=C\begin{matrix}CH_3\\CH_3\end{matrix}$ follows Markownikoff's rule.

22. Select the correct reactions :
(a) $CH_2=CH-N(CH_3)_3 \xrightarrow{HBr} \overset{Br}{\overset{|}{C}}H_2CH_2N(CH_3)_3$
(b) $CH_2=CH-N(CH_3)_3 \xrightarrow{HBr} CH_3-\overset{Br}{\overset{|}{C}}H-N(CH_3)_3$
(c) $CH_2=CH-CF_3 \xrightarrow{HBr} \overset{Br}{\overset{|}{C}}H_2-CH_2-CF_3$
(d) $CH_2=CH-CH_3 \xrightarrow[peroxide]{HCl} CH_3-\underset{Cl}{\overset{|}{C}}HCH_3$

23. Select the correct statements about : $CH_3CH=CH_2 \xrightarrow[NaCl]{Br_2}$
(a) $CH_3\cdot CHCl\cdot CH_2Br$ is major product and $CH_3CHBr\cdot CH_2Br$ is minor product
(b) $CH_3\cdot CHCl\cdot CH_2Br$ is minor product and $CH_3CHBr\cdot CH_2Br$ is major product
(c) Formation of cyclobromium cation takes place as an intermediate
(d) Formation of cyclochloronium cation takes place as an intermediate

24. Which statements are correct for the following reaction ?
$CH_3-CH=CH_2 + HBr \xrightarrow{\text{dibenzoyl peroxide}} CH_3CH_2\cdot CH_2Br$
(a) Initiation step involves formation of $C_6H_5\overset{O}{\overset{\|}{C}}-\dot{O}$, $\dot{H}$ and $\dot{Br}$ radicals
(b) In propagation step $\dot{Br}$ attacks first to react with π system of alkene
(c) In propagation step $\dot{H}$ attacks first to react with π system of alkene
(d) Initiation step starts with formation of $C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O}$

25. About a reaction producing more than one product, through common intermediate, the :
(a) product formed most rapidly is called kinetic product
(b) product formed most stable is called thermodynamic product
(c) process giving kinetic product in excess is called kinetically controlled process
(d) process giving thermodynamic product in excess is called thermodynamically controlled process

26. Which of the following are nucleophilic additions ?
(a) $CH\equiv CH + HCN \longrightarrow$
(b) $CH\equiv CH + HCl \longrightarrow$
(c) $CH\equiv CH + ROH \xrightarrow{KOH}$
(d) $CH\equiv CH + :\dot{C}H_2 \longrightarrow$

27. Hexa-1,3,5-triene on reaction with 1 equivalent of HBr gives:
(a) $CH_3\cdot \overset{Br}{\overset{|}{C}}H-CH=CH-CH=CH_2$

(b) $CH_3 \cdot CH{=}CH{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH{=}CH_2$

(c) $CH_3{-}CH{=}CH{-}CH{=}CH{-}\underset{\displaystyle Br}{\underset{|}{CH_2}}$

(d) $CH_2{=}CH{-}CH{=}CH{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH_3$

28. Select the correct statements about addition of Br_2 on *cis*-but-2-ene:
(a) It is stereospecific reaction
(b) Stereochemistry of product depends upon stereochemistry of substrate
(c) Br_2 always shows antiaddition
(d) *Cis*-2-butene with Br_2 gives enantiomers of 2,3-dibromobutane

29. Which of the following will produce geometrical isomers on treating with NH_2OH :
(a) CH_3COCH_3 (b) HCHO
(c) $CH_3CO \cdot CH_2CH_3$ (d) CH_3CHO

30. Select of correct reactivity orders for nucleophilic addition of carbonyl compounds :
(a) cyclopropanone > cyclobutanone > cyclopentanone > cyclohexanone
(b) $FCH_2{-}CHO > CH_3CHO > C_6H_5CHO > CH_3COCH_3$
(c) $ClCH_2CHO > HCHO > CH_3COCH_2Cl > CH_3COCH_3$
(d) $C_2H_5COC_2H_5 > C_2H_5{-}CO \cdot CH_2 \cdot CH(CH_3)_2$

$> C_2H_5 \cdot \underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CO{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}C_2H_5$

$> C_2H_5{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CO{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}C_2H_5$ (CH₃ groups on both C)

31. Select the correct statements about reactions of carbonyl compounds with alcohols :
(a) These reactions are addition reactions and reversible in nature
(b) Aldehydes form hemi-acetal and acetal in acid medium
(c) Ketone forms hemi-ketal and ketal in basic medium
(d) Hemi-acetal and hemi-ketal are formed when pH > 7 whereas acetal and ketals when pH < 7

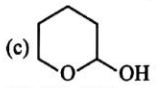
32. Which of the following gives iodoform test with NaOI?
(a) Δ–$COCH_3$ (b) $C_6H_5CHOHCH_3$
(c) $CH_2BrCOCH_3$ (d) $H_2C(COCH_3)_2$

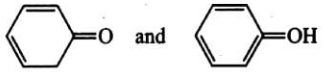
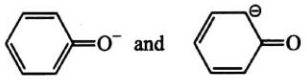
33. Which of the following will decarboxylate on heating?
(a) CH_3COCH_2COOH (b) $HOOC \cdot CH_2CH_2COOH$
(c) $CH_3CO \cdot CH_2 \cdot COCH_3$ (d) $CH_3 \cdot CH_2COCH_2COOH$

34. Which are correct about the reaction :

$$CH_3CHO + CH_3 \cdot CH_2CHO \xrightarrow[10^{\circ}C]{OH^-} :$$

(a) The reaction is crossed aldol addition
(b) The reaction is mixed aldol addition
(c) The reaction gives four aldols
(d) The products formed can be separated easily

35. Which of the following compounds will give positive Tollens reagent test?
(a) $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(OH)OCH_3$
(b) $CH_3CH_2C(OCH_3)_2$
(c) 
(d) CH_3CHO

36. Which of the following are tautomers?
(a) 
(b) 
(c) $CH_2{=}N^+(O^-)(O^+)$ and $CH_2{=}N^+(O)(O^-)$
(d) $CH_3{-}N^+(O)(O^-)$ and $CH_2{=}N^+(OH)(O^-)$

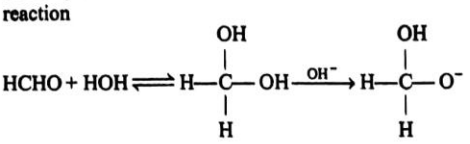
37. Which of the following form stable hemi-ketal?
(a) $C_6H_5{-}C(=O){-}C_6H_5$
(b) $HO(CH_2)_3 \cdot C(=O){-}CH_3$
(c) $CH_2OH{-}C(=O){-}(CHOH)_3CH_2OH$
(d) $HO{-}CH_2{-}(CH_2)_4{-}C(=O){-}CH_3$

38. Which of the following will show Dieckmann condensation reactions?
(a) $C_2H_5O{-}C(=O){-}(CH_2)_4 \cdot C(=O){-}OC_2H_5$
(b) $C_2H_5O{-}C(=O){-}(CH_2)_5 \cdot C(=O){-}OC_2H_5$
(c) $C_2H_5O{-}C(=O){-}(CH_2)_6 \cdot COC_2H_5$
(d) $C_2H_5O{-}C(=O){-}(CH_2)_3 \cdot C(=O){-}OC_2H_5$

39. When an aldehyde is treated with formaldehyde in presence of an aqueous base, the formaldehyde is always oxidised and the other aldehyde is reduced. The reasons for this are :

(a) Formaldehyde is a better reductant than the other aldehyde

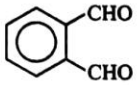
(b) In an aqueous basic solution it exists as a conjugate base of its hydrate which is one of the intermediates of the reaction



(c) It has two α-H-atoms on carbonyl group whereas other aldehydes have only one α-H-atom

(d) The reaction is called crossed Cannizzaro reaction

40. Which of the following will show intramolecular Cannizzaro reaction ?

(a) 

(b) $C_2H_5-\overset{O}{\overset{\|}{C}}-CHO$

(c) $C_6H_5-\overset{O}{\overset{\|}{C}}-CHO$

(d) $CH_3-\overset{O}{\overset{\|}{C}}-CHO$

41. Which of the following alcohols are not oxidised by MnO_2 ?

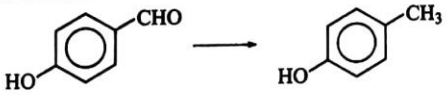
(a) $C_6H_5CH_2OH$

(b) $CH_3\cdot CH=CH\cdot \underset{OH}{\underset{|}{C}}H\cdot CH_3$

(c) $C_6H_5CH_2CH_2OH$

(d) $CH_3CH=CHOH$

42. The reductants used for are :



(a) Zn-Hg/conc. HCl

(b) NH_2NH_2/alc. KOH

(c) $HS-(CH_2)_3-SH/H^+$, Ni/H_2

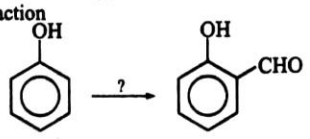
(d) red P + HI

43. Which of the following will yield a hydrocarbon when treated with CH_3MgBr?

(a) $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-C_6H_5$

(b) $CH\equiv CH$ (c) $R-OH$ (d) H_2SO_4

44. The reaction



can be made by :

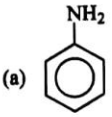
(a) $CHCl_3$/alc. KOH followed by hydrolysis

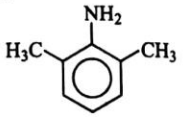
(b) HCN/HCl/anhy. $AlCl_3$

(c) $(CH_2)_6N_4$/OH followed by hydrolysis

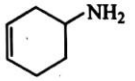
(d) CrO_3

45. Which of the following gives carbylamine test?

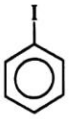
(a) 

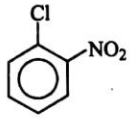
(b) 

(c) $CH_2=CH-CH_2NH_2$

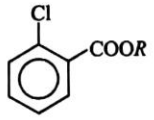
(d) 

46. Which of the following will give Ullmann reaction :

(a) 

(b) 

(c)

(d) 

47. Nitration of salicylic acid gives :

(a) 3-nitro phenol

(b) Picric acid

(c) 2,4,6-tri nitro phenol

(d) 2,4,6-tri nitro benzoic acid

48. Which of the following will give white ppt. with $AgNO_3$ in presence of HNO_3?

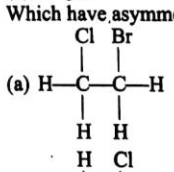
(a) $C_6H_5NH_3^+Cl^-$

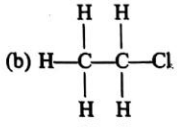
(b) C_6H_5Cl

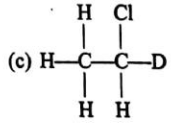
(c) 2,4,6-tri nitro chloro benzene

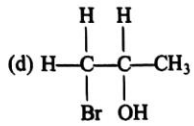
(d) CH_3SH

49. Which have asymmetric carbon atoms?

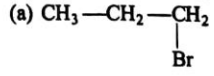
(a) 

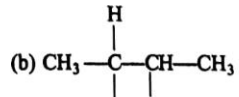
(b) 

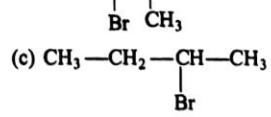
(c) 

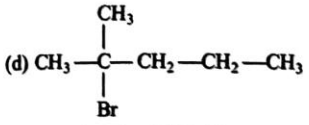
(d) 

50. Which of the following have asymmetric carbon atoms?

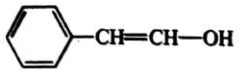
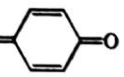
(a) 

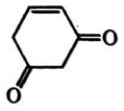
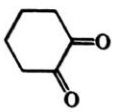
(b) 

(c) 

(d) 

51. Tautomerism is exhibited by :

(a)  (b) 

(c)  (d) 

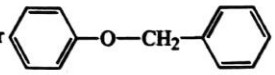
52. Which of the following compounds will show geometrical isomerism ?
(a) 2-butene (b) Propene
(c) 1-phenyl propene (d) 2-methyl-2-butene

53. Which of the following will give yellow precipitate with I_2/NaOH?
(a) $ICH_2COCH_2CH_3$ (b) $CH_3COOCOCH_3$
(c) CH_3CONH_2 (d) $CH_3CH(OH)CH_2CH_3$

54. Reaction of $R-\overset{O}{\overset{\|}{C}}-NH_2$ with a mixture of Br_2 and KOH gives $R-NH_2$ as the main product. The intermediate involved in this reaction are :

(a) $R-\overset{O}{\overset{\|}{C}}-NHBr$ (b) $R-NHBr$

(c) $R-N=C=O$ (d) $R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}Br\\Br\end{matrix}$

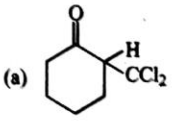
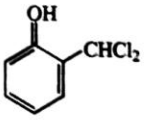
55. The ether 

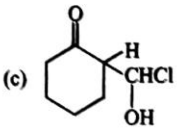
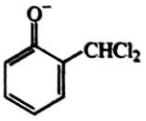
when treated with HI produces :
(a) $C_6H_5CH_2I$ (b) $C_6H_5CH_2OH$
(c) C_6H_5I (d) C_6H_5OH

56. Which of the following will undergo aldol condensation?
(a) Acetaldehyde (b) Propanaldehyde
(c) Benzaldehyde (d) Trideutero acetaldehyde

57. Which will react with acetone to give a product containing $\rangle C=N$, linkage?
(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$
(c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$

58. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates :

(a)  (b) 

(c)  (d) 

59. A new carbon-carbon bond formation is possible in :
(a) Cannizzaro reaction (b) Friedel-Crafts alkylation
(c) Clemmensen reduction (d) Reimer-Tiemann reaction

60. *p*-chloroaniline and anilinium hydrochloride can be distinguished by :
(a) Sandmeyer reaction (b) $NaHCO_3$
(c) $AgNO_3$ (d) Carbylamine test

61. Toluene when treated with Br_2/Fe, gives *p*-bromotoluene as the major product because the CH_3 group :
(a) is para directing
(b) is meta directing
(c) activates the ring by hyperconjunction
(d) deactivates ring

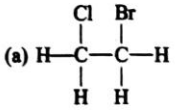
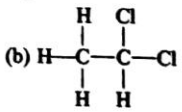
62. Resonance structure of a molecule should have :
(a) identical arrangement of atoms
(b) nearly the same energy content
(c) the same number of paired electrons
(d) identical bonding

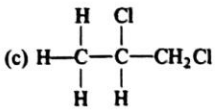
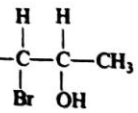
63. Phenol is less acidic than :
(a) acetic acid (b) *p*-methoxyphenol
(c) *p*-nitrophenol (d) ethanol

64. Dipole moment is shown by :
(a) 1, 4-dichlorobenzene
(b) *cis*-1, 2-dichloroethane
(c) *trans*-1, 2-dichloroethene
(d) *trans*-1, 2-dichloro-2-pentene

65. Only two isomeric monochloro derivatives are possible for :
(a) *n*-butane (b) 2, 4-dimethylpentane
(c) benzene (d) 2-methylpropane

66. Which of the following have asymmetric carbon atom ?

(a)  (b) 

(c)  (d) 

67. The compound in which C uses its sp^3-hybrid orbitals for bond formation is :
(a) HCOOH (b) $(H_2N)_2CO$
(c) $(CH_3)_3COH$ (d) CH_3CHO

68. Among the following compounds, which will react with acetone to give a product containing > C=N— bond ?
(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$
(c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$

69. An aromatic molecule will :
(a) have $4n\pi$ electrons
(b) have $(4n + 2)\pi$ electrons
(c) be planar
(d) be cyclic

70. Aryl halide are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to :
(a) the formation of less stable carbonium ion
(b) resonance stabilization
(c) longer carbon halogen bond
(d) sp^2-hybridized carbon attached to the halogen

71. The compound used as refrigerant are :
(a) NH_3 (b) CCl_4
(c) CF_4 (d) CF_2Cl_2

72. Which of the following compounds will give a yellow precipitate with iodine and alkali ?
(a) 2-Hydroxypropane (b) acetophenone
(c) methyl acetate (d) acetamide

73. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$ the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer are ?
(a) The electron density on *meta* carbon is more than that on *ortho* and *para* positions
(b) The intermediate carbonium ion formed after initial attach of Br^+ at the *meta* position is least destablished
(c) Loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position
(d) Easier loss of H^+ to regain aromaticity from the *meta* position than from *ortho* and *para* position

74. Base catalysed aldol condensation occurs with :
(a) Propionaldehyde
(b) Benzaldehyde
(c) 2-methylpropionaldehyde
(d) 2, 2-dimethylpropionaldehyde

75. Which of the following compounds will react with ethanolic KCN ?
(a) ethyl chloride (b) acetyl chloride
(c) chlorobenzene (d) benzaldehyde

76. Keto-enol tautomerism is observed in :
(a) $H_5C_6-\overset{\overset{O}{\|}}{C}-H$
(b) $H_5C_6-\overset{\overset{O}{\|}}{C}-CH_3$
(c) $H_5C_6-\overset{\overset{O}{\|}}{C}-C_6H_5$
(d) $H_5C_6-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

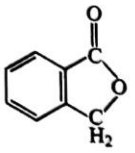
77. Which of the following are example of aldol condensation ?
(a) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$
(b) $2CH_3COCH_3 \xrightarrow{\text{dil. NaOH}} CH_3COH(CH_3)CH_2COCH_3$
(c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH$
(d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$

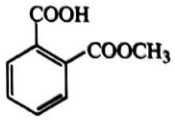
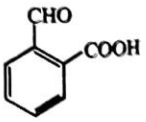
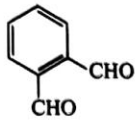
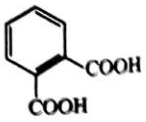
78. The smallest ketone and its next homologue are reacted with NH_2OH to from oxime : **(IIT 2006)**
(a) Two different oximes are formed
(b) Three different oximes are formed
(c) Two oximes formed are optically active
(d) All oximes formed are optically active

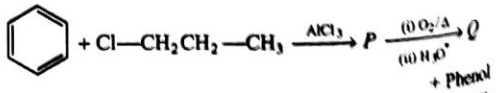
79. The product of reaction of alcoholic silver nitrite with ethyl bromide are :
(a) ethane (b) ethene
(c) nitroethane (d) ethyl nitrite

80. A positive carbylamine test is given by :
(a) *N*, *N*-dimethylaniline
(b) 2, 4-dimethylaniline
(c) *N*-methyl-*o*-methylaniline
(d) *p*-methylbenzylamine

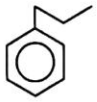
81. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following : **(IIT 2006)**

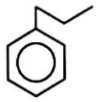


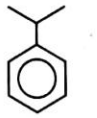
(a) 
(b) 
(c) 
(d) 

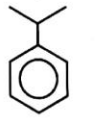
82. 
+ Phenol **(IIT 2006)**

The major products *P* and *Q* are :

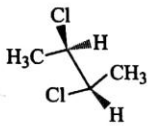
(a)  and CH_3CH_2CHO

(b)  and CH_3COCH_3

(c)  and CH_3COCH_3

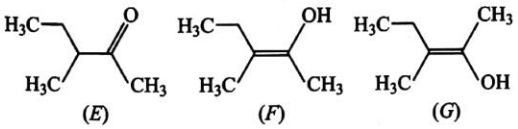
(d)  and CH_3CH_2CHO

83. The correct statement(s) about the compound given below is (are): **(IIT 2008)**



(a) The compound is optically active
(b) The compound possesses centre of symmetry
(c) The compound possesses plane of symmetry
(d) The compound possesses axis of symmetry

84. The correct statement(s) concerning the structures *E*, *F* and *G* is (are): **(IIT 2008)**



(a) *E*, *F* and *G* are resonance structures
(b) *E*, *F* and *E*, *G* are tautomers
(c) *F* and *G* are geometrical isomers
(d) *F* and *G* are diasteromers

85. The correct statement(s) about the compound

$H_3C(HO)HC—CH=CH—CH(OH)CH_3$ (*X*) is(are): **(IIT 2009)**

(a) The total number of stereoisomers possible for *X* is 6
(b) The total number of diastereomers possible for *X* is 3
(c) If the stereochemistry about the double bond in *X* is *trans*, the number of enantiomers possible for *X* is 4
(d) If the stereochemistry about the double bond in *X* is *cis*, the number of enantiomers possible for *X* is 2

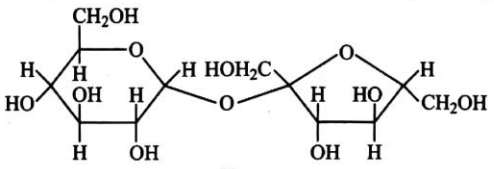
86. In the reaction

$$2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+[BH_4]^-$$

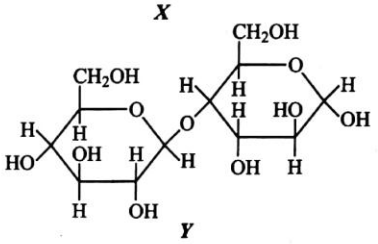
the amine(s) *X* is(are): **(IIT 2009)**

(a) NH_3 (b) CH_3NH_2
(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

87. The correct statement(s) about the following sugars *X* and *Y* is(are): **(IIT 2009)**



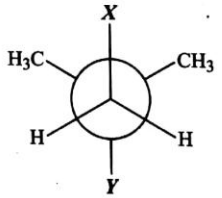
X



Y

(a) *X* is a reducing sugar and *Y* is a non-reducing sugar
(b) *X* is a non-reducing sugar and *Y* is a reducing sugar
(c) The glucosidic linkages in *X* and *Y* are α and β, respectively
(d) The glucosidic linkages in *X* and *Y* are β and α, respectively

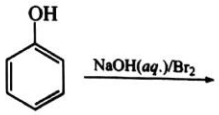
88. In the Newmann projection for 2,2-dimethylbutane.



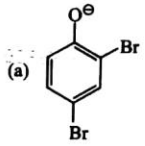
X and *Y* can respectively be: **(IIT 2010)**

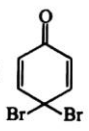
(a) H and H (b) H and C_2H_5
(c) C_2H_5 and H (d) CH_3 and CH_3

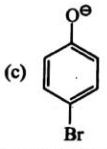
89. In the reaction

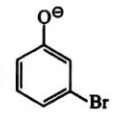


the intermediate(s) is(are): **(IIT 2010)**

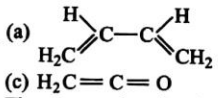
(a) 

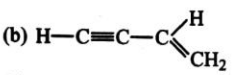
(b) 

(c) 

(d) 

90. Amongst the give options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are): **(IIT 2011)**

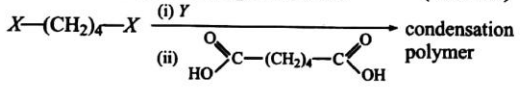
(a) 

(b) 

(c) $H_2C=C=O$

(d) $H_2C=C=CH_2$

91. The correct functional group X and the reagent/reaction condition Y in the following scheme are: **(IIT 2011)**



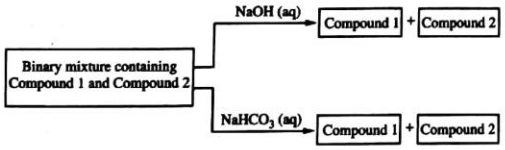
(a) $X = COOCH_3$, $Y = H_2$ / Ni / heat

(b) $X = CONH_2$, $Y = H_2$ / Ni / heat

(c) $X = CONH_2$, $Y = Br_2$ / NaOH

(d) $X = CN$, $Y = H_2$ / Ni / heat

92. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. **(IIT 2012)**



(a) C_6H_5OH and C_6H_5COOH

(b) C_6H_5COOH and $C_6H_5CH_2OH$

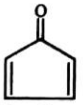
(c) $C_6H_5CH_2OH$ and C_6H_5OH

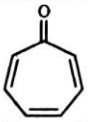
(d) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

93. Which of the following molecules, in pure form, is(are) **unstable** at room temperature? **(IIT 2012)**

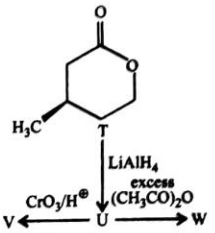
(a)

(b)

(c) 

(d) 

94. With reference to the scheme given, which of the given statement(s) about **T**, **U**, **V** and **W** is(are) correct? **(IIT 2012)**



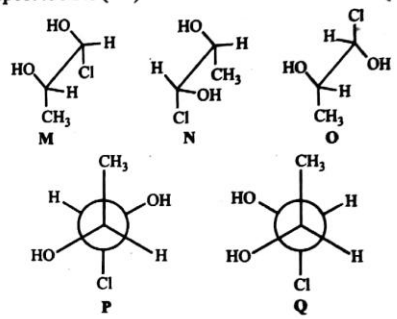
(a) **T** is soluble in hot aqueous NaOH.

(b) **U** is optically active.

(c) Molecular formula of **W** is $C_{10}H_{18}O_4$.

(d) **V** gives effervescence on treatment with aqueous $NaHCO_3$.

95. Which of the given statement(s) about **N**, **O**, **P** and **Q** with respect to **M** is (are) correct? **(IIT 2012)**



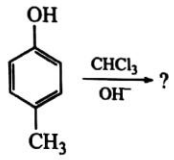
(a) M and N are non-mirror image stereoisomers.

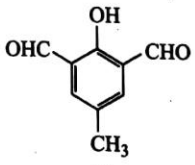
(b) M and O are identical.

(c) M and P are enantiomers.

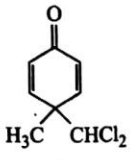
(d) M and Q are identical.

96. In the following reaction, the product(s) formed is (are): **[JEE (Advanced) II 2013]**

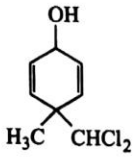




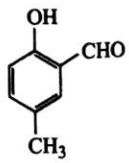
P



Q



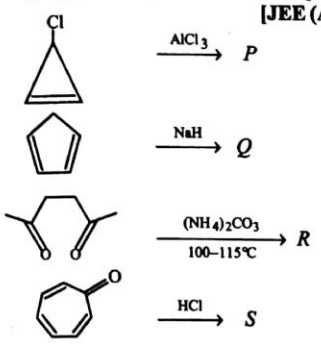
R



S

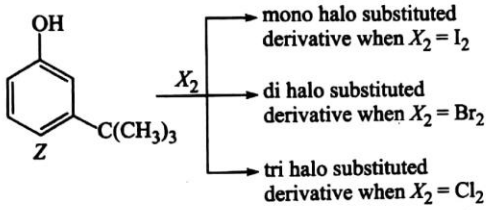
(a) *P* (Major) (b) *Q* (Minor)
(c) *R* (Minor) (d) *S* (Major)

97. Among *P*, *Q*, *R* and *S*, the aromatic compound(s) is/are : **[JEE (Advanced) I 2013]**



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

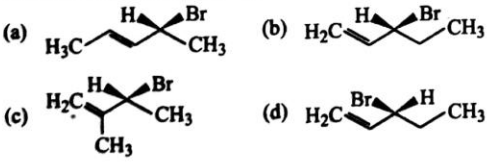
98. The reactivity of compound *Z* with different halogens under appropriate conditions is given below : **[JEE (Advanced) I 2014]**



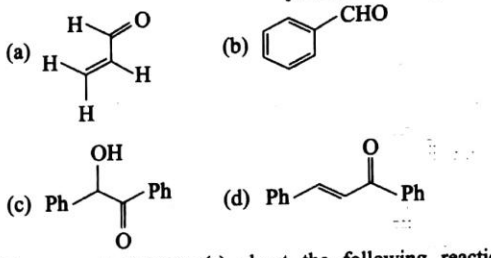
The observed pattern of electrophilic substitution can be explained by
(a) the steric effect of the halogen
(b) the steric effect of the *tert*-butyl group
(c) the electronic effect of the phenolic group
(d) the electronic effect of the *tert*-butyl group

99. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are : **[JEE (Advanced) I 2014]**
(a) *tert*-butanol and 2-methylpropan-2-ol
(b) *tert*-butanol and 1,1-dimethylethan-1-ol
(c) *n*-butanol and butan-1-ol
(d) isobutyl alcohol and 2-methylpropan-1-ol

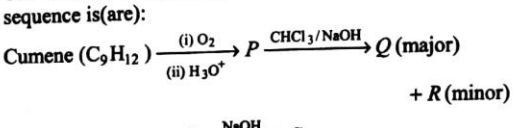
100. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) :

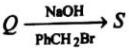


101. Positive Tollens' test is observed for: **[JEE (Advanced) I 2016]**



102. The correct statement(s) about the following reaction sequence is(are):

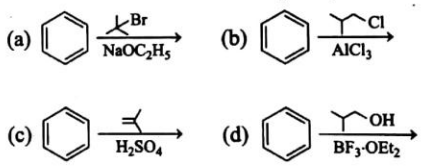




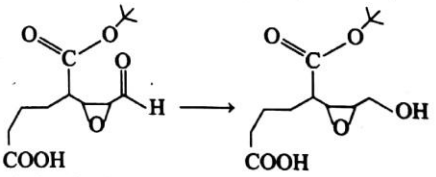
[JEE (Advanced) I 2016]

(a) ***R*** is steam volatile
(b) ***Q*** gives dark violet coloration with 1% aqueous $FeCl_3$ solution
(c) ***S*** gives yellow precipitate with 2, 4-dinitrophenyl-hydrazine
(d) ***S*** gives dark violet coloration with 1% aqueous $FeCl_3$ solution

103. Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are) : **[JEE (Advanced) II 2016]**

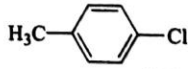


104. Reagent(s) which can be used to bring about the following transformation is(are) : **[JEE (Advanced) II 2016]**



(a) $LiAlH_4$ in $(C_2H_5)_2O$ (b) BH_3 in THF
(c) $NaBH_4$ in C_2H_5OH (d) Raney Ni/H_2 in THF

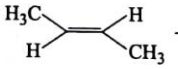
105. The IUPAC name(s) of the following compound is (are):

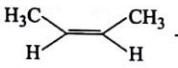


[JEE (Advanced) I 2017]

(a) 4-methylchlorobenzene
(b) 4-chlorotoluene
(c) 1-chloro-4-methylbenzene
(d) 1-methyl-4-chlorobenzene

106. The correct statement(s) for the following addition reactions is (are): **[JEE (Advanced) I 2017]**

(i)  $\xrightarrow{Br_2/CHCl_3}$ **M and N**

(ii)  $\xrightarrow{Br_2/CHCl_3}$ **O and P**

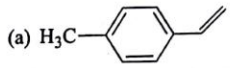
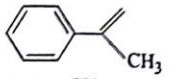
(a) (M and O) and (N and P) are two pairs of diastereomers
(b) Bromination proceeds through *trans*-addition in both the reactions
(c) O and P are identical molecules
(d) (M and O) and (N and P) are two pairs of enantiomers

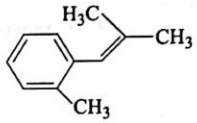
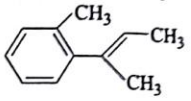
107. Compounds P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is C_8H_8O. Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction. **[JEE (Advanced) II 2017]**

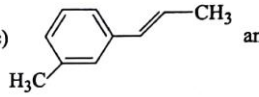
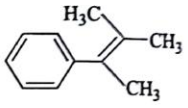
(i) $P \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3/CH_2Cl_2} Q\ (C_8H_8O)$

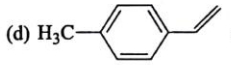
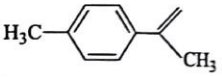
(ii) $R \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3/CH_2Cl_2} S\ (C_8H_8O)$

The option(s) with suitable combination of P and R, respectively, is (are):

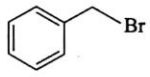
(a)  and 

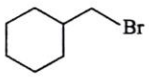
(b)  and 

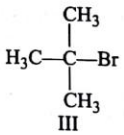
(c)  and 

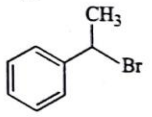
(d)  and 

108. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is (are):


I


II


III

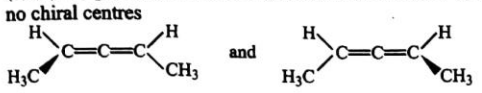

IV

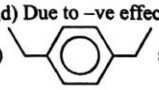
[JEE (Advanced) II 2017]

(a) I and II follow $S_{N}2$ mechanism
(b) the order of reactivity for I, III and IV is : IV > I > III
(c) I and III follow $S_{N}1$ mechanism
(d) compound IV undergoes inversion of configuration

SOLUTIONS (More Than One Answer Correct)

1. (a,c,d) 2,3-pentadiene has two stereo centres C^1 and C^3, but no chiral centres



2. (a,b,c) Prefix D-refers for configuration of the compound.
3. (a,b) p_x, p_y and p_z are at 90° and *sp*-orbitals are linear.
4. (a,b,c,d) Due to –ve effect of halogen atoms.
5. (a,c,d)  structure has non-zero dipole moment.
6. (a,b,c) Increase in electronegativity (along the period) gives rise to increase in basic nature

$$\bar{C}H_3 < \bar{N}H_2 < \bar{O}H < \bar{F}$$

7. (a,b,c) More is the *s* character on adjacent carbon to $\bar{C}$, more is stability

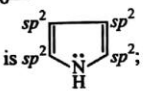
$$\underset{sp}{CH\equiv\bar{C}} > CH_3-C\equiv\bar{C} > CH_2=\bar{C}H > CH_3-\bar{C}H_2$$

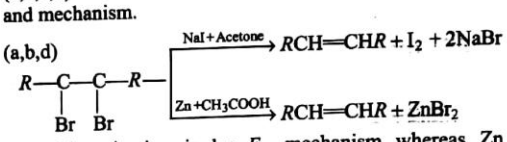
8. (a,c,d)

CH_3-CH_2-Cl	No resonance
$CH_2=CH-Cl$	2 resonating structures
C_6H_5-Cl	4 resonating structures

Bond length of functional group

$$\propto \frac{1}{\text{No. of resonating structures}}$$

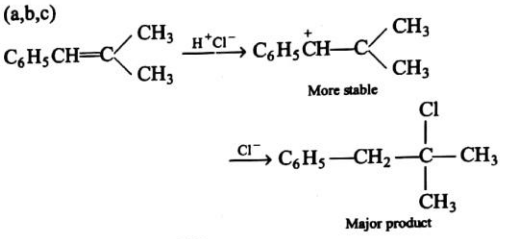
9. (a,b,c,d) These are facts.
10. (a,b,c,d) —do—
11. (a,b,c,d) —do—
12. (b,c) Pyrolle is  ; N has sp^3-hybridisation
13. (a,d)
    S_N1 reactions are favoured if unsaturation is at β-carbon
    S_N2 reactions are favoured if unsaturation is at α-carbon and substrate containing carbonyl group at β-carbon does not give S_N1 reaction.
14. (b,c,d) $R-NH_2$ does not give S_N reactions as $-NH_2$ is poor leaving group.
15. (a,d) Only optically active compounds show Walden inversion.
16. (a,b,d) *Trans* esterification is the reaction of ester with alcohol.
17. (a,d) If $\overset{\ominus}{L}$ is the best leaving group, a nucleophile (*i.e.*, less basic nature) then only the reaction is possible.
18. (b,d) Aryl halides having no H-atom at ortho position do not show benzyne mechanism.
19. (a,b,c,d) All the facts are based on electronic displacement and mechanism.
20. (a,b,d)

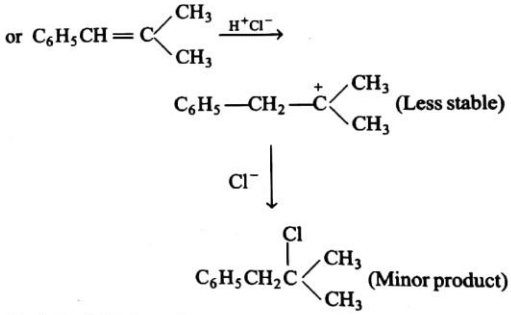


The debromination is by E_2 mechanism whereas Zn behaves as a nucleophile.

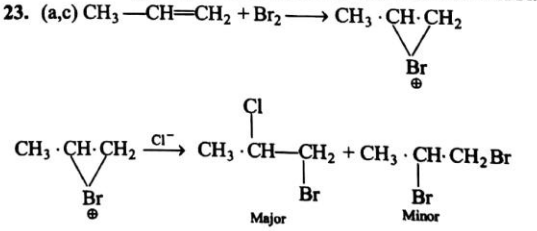
$$R\underset{Br}{\underset{|}{C}}-\underset{Br}{\underset{|}{C}}-R \xrightarrow{KOH\ alc.} RCH=CHR + HBr$$

21. (a,b,c)



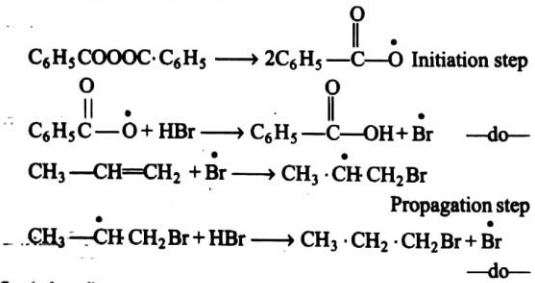


22. (a,c) Anti Markownikoff addition is observed when one doubly bonded carbon is attached with powerful electron withdrawing group. Kharash effect is not observed in HCl.
23. (a,c)

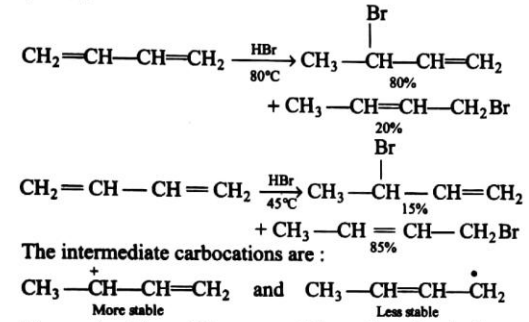


(Cl⁻ is more reactive than Br⁻)

24. (b,d) The mechanism is :



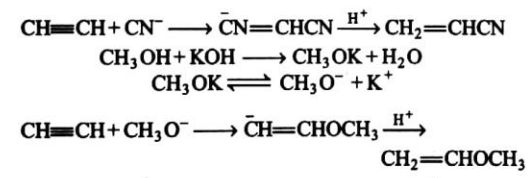
25. (a,b,c,d)



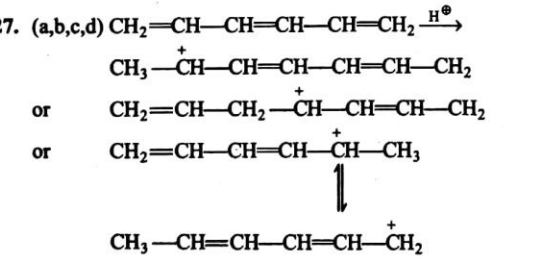
The intermediate carbocations are :

The product formed by more stable carbocation is always kinetically controlled and by less stable carbocation is thermodynamically controlled.

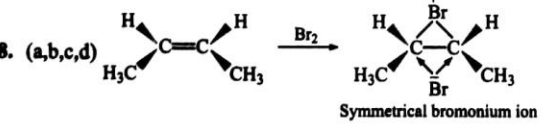
26. (a,c)



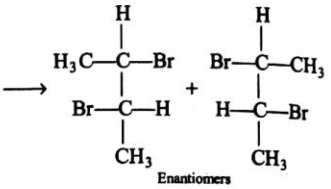
27. (a,b,c,d)



28. (a,b,c,d)



Symmetrical bromonium ion



Enantiomers

29. (c,d) Unsymmetrical carbonyl compounds form syn and anti oximes.

30. (a,b,c,d) Follow mechanism of . Notice more the +ve charge on C^+ centre, more is its reactivity.

31. (a,d) Hemi-acetal and hemi-ketals are given in basic medium, whereas acetal and ketal in acid medium.

32. (a,b,c) Each has or unit. In (d) halogen attacks on H of CH_2 as it has reactive methylene H-atoms.

33. (a,b,d) Dicarboxylic acids show decarboxylation on heating. Also, β-oxocarboxylic acids also undergo decarboxylation.

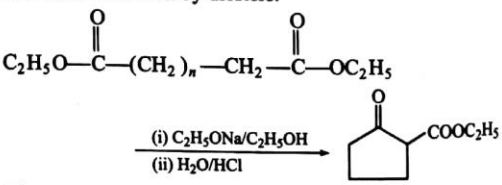
34. (a,b,c) If both the carbonyl compounds have α-H-atoms, four products are formed. If one of the carbonyl compounds has an α-H-atom, two products are formed. The products formed have similar physical and chemical properties and thus their separation is difficult.

35. (a,c,d) Tollens reagent is a mild oxidant. It converts CHOH to CHO and then COOH as well as hemi-acetals are also converted to aldehyde and then —COOH.

36. (a,d) Follow tautomerism.

37. (b,c,d) Simple ketals are less stable.

38. (a,b,c) Dieckman condensation is an intramolecular condensation shown by diesters.



The reaction is given by 1, 6; 1, 7 and 1,8 dibasic esters.

39. (a,b,c,d) All are facts.

40. (a,c) α-keto aldehydes lacking with α-H-atom also show Cannizzaro reaction. Keto group is reduced and aldehyde is oxidised.

41. (a,b,c) MnO_2 oxidises only alcohols with allyl group and benzyl alcohol.

42. (b,c) In others —OH will also be reduced.

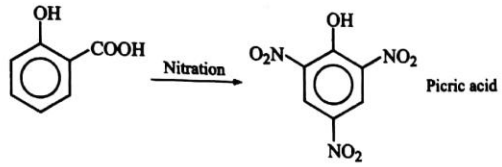
43. (a,b,c,d) Compounds having an acidic or active H-atom give alkane with Grignard reagent.

44. (a,b,c) The reaction made by hexamethylene tetraamine followed by hydrolysis is called Duff reaction.

45. (a,c,d) Stearic hindrance in (b) does not allow to give the test.

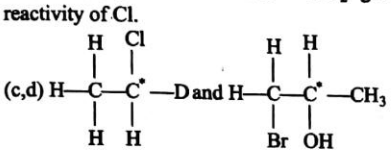
46. (a,b,d) Aryl fluoride does not give Ullmann's reaction.

47. (b,c)



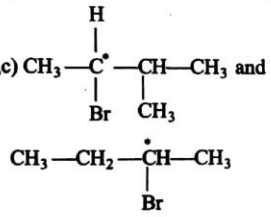
48. (a,c) In (c) presence of three $-NO_2$ groups increases reactivity of Cl.

49. (c,d)



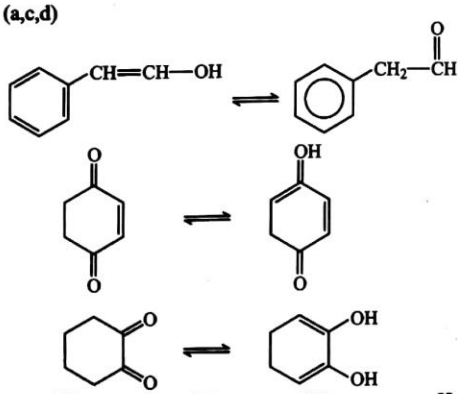
(C^* are asymmetric carbon atoms)

50. (b,c)

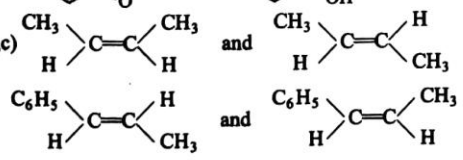


(C^* are asymmetric carbon atoms)

51. (a,c,d)



52. (a,c)

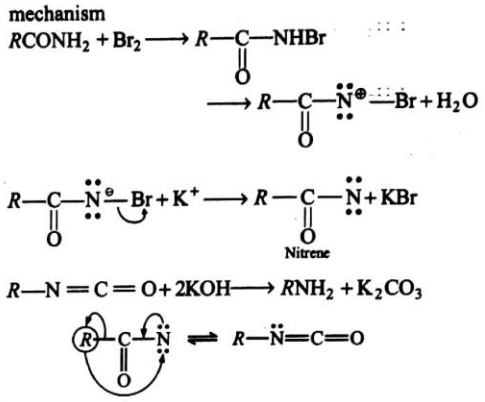


53. (a,d) Both have $CH_3-\overset{O}{\overset{\|}{C}}-$ and $CH_3-\underset{|}{CHOH}$ groups.

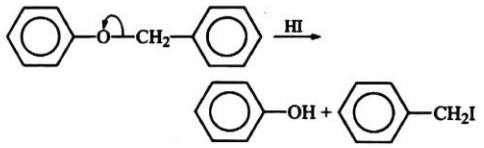
54. (a,c) This is Hoffmann bromide reaction

$$R\text{CONH}_2 + Br_2 + 4KOH_{(aq.)} \longrightarrow R\text{NH}_2 + 2KBr + 2H_2O + K_2CO_3$$

mechanism

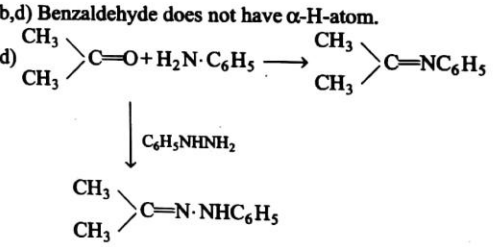


55. (a,d)



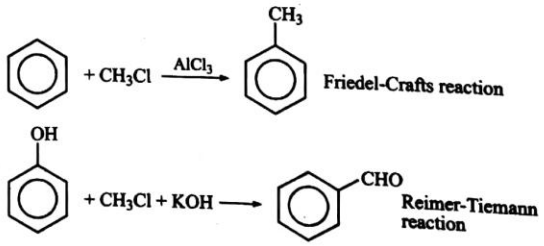
56. (a,b,d) Benzaldehyde does not have α-H-atom.

57. (a,d)



58. (a,b) Follow mechanism or Reimer-Tiemann reaction.

59. (b,d)

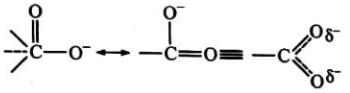


60. (b,c) $C_6H_5NH_3Cl$ gives effervescences with $NaHCO_3$ and white ppt. with $AgNO_3$.

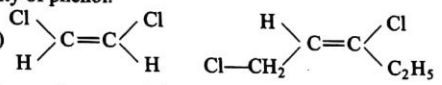
61. (a,c) These are facts.

62. (a,b,c) These are the facts

63. (a,c) Carboxylic acids are more acidic than phenol because carboxylate anion is more resonance stabilised than phenoxide ion.



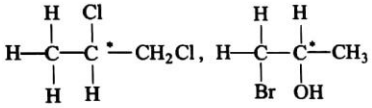
$-NO_2$ gp. is an electron withdrawing and increases the acidity of phenol.

64. (b,d) 

65. (a,d) *n*-butane and 2-methyl propane have two isomeric monochloro derivatives :

$CH_3-CH_2-CH_2-CH_2Cl$ (1-chloro butane (i)) $\quad CH_3-CH_2-\underset{Cl}{CH}-CH_3$ (2-chloro butane (ii))

$CH_3-\underset{CH_3}{CH}-CH_2Cl$ (2-methyl, 1-chloro-butane) $\quad CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3$ (2-methyl, 2-chloropropane)

66. (c,d) 

A chiral carbon atom or an asymmetric C-atom is that C-atom which contains four different gps at its four valencies.

67. (c,d) In saturated state, carbon forms four σ-bonds and has sp^3-hybridisation.

68. (a,d) Aniline and phenyl hydrazine both undergo condensation reaction to form hydrazones.

$$C_6H_5N\boxed{H_2+O}=C(CH_3)_2 \longrightarrow C_6H_5N=C(CH_3)_2+H_2O$$

$$C_6H_5NH\cdot N\boxed{H_2+O}=C(CH_3)_2 \longrightarrow C_6H_5NH\cdot N=C(CH_3)_2+H_2O$$

69. (b,c,d) An aromatic molecule may have

(i) $(4n+2)\pi$ electrons (Huckel rule)
$n = 0, 1, 2, 3.....$

(ii) Molecule should be flat *i.e.*, all the should lie in one plane.

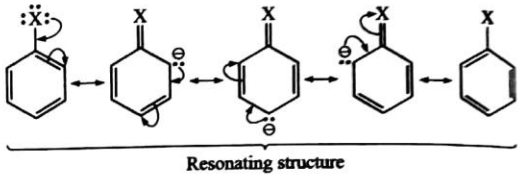
(iii) The compound must be cyclic and having a extended conjugated π system.

70. (b,d) The halogen atom in Aryl halide is comparatively less reactive towards nucleophilic substitution reaction than alkyl halide due to :

(i) Resonance stabilization

(ii) sp^2-hybridized carbon attached to the halogen.

(iii) development of partial double bond character in C—Cl bond.



Resonating structure

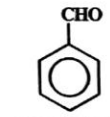
71. (a,d) NH_3 and dichlorodifluoro methane are used as refrigerant.

72. (a,b) Iodoform reaction is given by those compounds which contains $COCH_3$ gp. (methyl ketone), all sec. alcohols and ethyl alcohol (only *p*-alcohol).
Exceptions CH_3CO $CH_2COOC_2H_5$ (ethylacetoacetate), CH_3CONH_2 (acetamide), although contain $-COCH_3$ gp. yet do not give iodoform test.

73. (a,b,d) $-NO_2$ gp. is an electron withdrawing gp. and have $-I$ and $-M$ effects, therefore decreases the electron density at *o*- and *p*- position and, electrophilic attacks at *m*-position.

74. (a,c) Aldehydes having α-H atom undergo aldol condensation.

$CH_3\overset{\alpha}{C}H_2CHO$ Propionaldehyde



Benzaldehyde (no α-hydrogen atom)

$CH_3-\underset{CH_3}{\overset{\alpha}{C}H}-CHO$ 2-methylpropionaldehyde

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO$ 2,2-dimethylpropionaldehyde (no α-hydrogen atom)

75. (a,b,d) Ethyl chloride and acetyl chloride undergo nucleophilic substitution reaction with alc. KCN while benzaldehyde undergoes benzoin condensation and chlorobenzene does not react.

$$C_2H_5Cl \xrightarrow{KCN\ (alc.)} C_2H_5CN+KCl$$

$$CH_3COCl \xrightarrow{KCN\ (alc.)} CH_3COCN+KCl$$

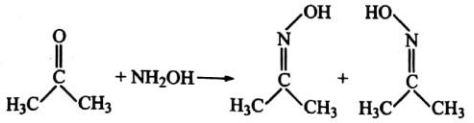
$$2C_6H_5CHO \xrightarrow{KCN\ (alc.)} C_6H_5CHOHCOC_6H_5$$

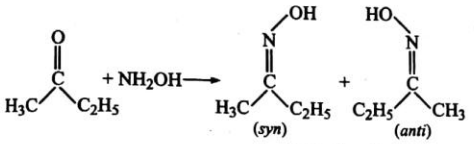
76. (b,d) Keto-enol tautomerism is shown by those compounds which have α-hydrogen to the CO group.

77. (a,b) The compounds containing α-Hydrogen atom undergo aldol condensation. In aldol condensation, two molecules of

aldehydes or ketones combine to form the α-hydroxy aldehyde or ketone.

78. (b,c) Acetone reacts with hydroxyl amine to form oxime of two types *i.e.*, *syn* and *anti* form

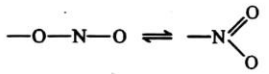




79. (c,d)

$$2C_2H_5Br + 2AgNO_2 \rightarrow \underset{\text{(Major)}}{C_2H_5NO_2} + \underset{\text{(Minor)}}{C_2H_5ONO} + AgBr$$

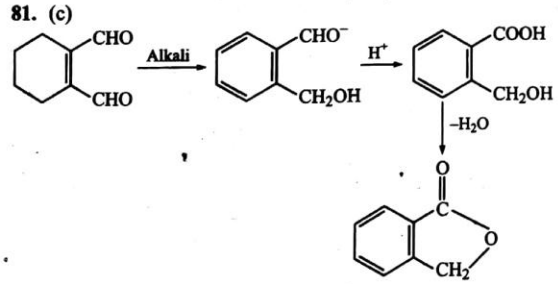
$-NO_2$ gp. exists into two tautomeric forms.



80. (b,d) Carbylamine test is given by primary amines.

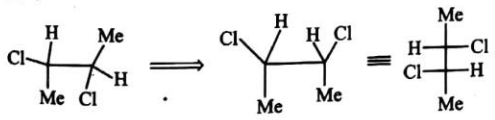
$$R\text{—}NH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Alkyl isocyanide}}{R\text{—}N \equiv C} + 3KCl + 3H_2O$$

81. (c)

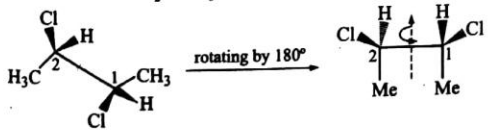


82. (c) It is cumene hydroperoxide rearrangement reaction.

83. (a,d)



The molecule is optically active.



The molecule passes an axis of symmetry (C_2) perpendicular to the C—C bond.

84. (b), (c), (d)

85. (a,d) The molecule has $C_{abcd}\,C_{(ab)_2}\cdot C_{abcd}$.

i.e., $n = 2$ (asymmetric carbon)

∴ **Optical isomer**

$$\text{Enantiomer} = 2^{n-1} = 2^{2-1} = 2$$

$$\text{meso} = 2^{\frac{2n-2}{2}} = 2^1 = 2$$

Geometrical = 2 due to one double lined

86. (a,b,c) Trimethyl amine does not have H atom on N

$$\rangle N\text{—}H + B_2H_6 \longrightarrow [BH_2(N\langle)_2]^+[BH_4]^-$$

87. (b,c) These are facts for given sugars.

88. (b,d) Follow text

89. (b,c) Follow mechanism.

90. (a,b) Buta-1-3-diene has sp^2-sp^2 bond and belong to conjugated system, hence such bonds posses double bond character. The molecule is planar and exists in two conformations, transoid (*s-trans*) and cisoid (*s-cis*).

Alkynes are planar.

In ketenes and allenes (even no. of double bonds) H-atoms are out of plane.

91. (c,d) If *X* is-$CONH_2$ it will be converted to —CH_2NH_2 only either on reduction with $Na + C_2H_5OH$ or $LiAlH_4$ by Br_2 / OH^- (Hoffmann Bromamide Reaction).

$$H_2NCO\text{—}(CH_2)_4\text{—}CONH_2 \xrightarrow{Br_2/OH^-} H_2N\text{—}(CH_2)_4\text{—}NH_2$$

If *X* is –COOMe it will form diol only on catalytic reduction with $Na + C_2H_5OH$ or $LiAlH_4$ (ether). If *X* is –CN it will form $-CH_2NH_2$ on reduction with H_2 / Ni

$$NC\text{—}(CH_2)_4\text{—}CN \xrightarrow{H_2/Ni} H_2N\text{—}CH_2(CH_2)_4CH_2\text{—}NH_2$$

All these will form condensation polymer with dicarboxylic acid.

$$H_2N\text{—}CH_2(CH_2)_4CH_2\text{—}NH_2 \xrightarrow{HOOC\text{—}(CH_2)_4COOH} \text{Polyamide}$$

$$H_2N\text{—}(CH_2)_4\text{—}NH_2 \xrightarrow{HOOC\text{—}(CH_2)_4COOH} \text{Polyamide}$$

92. (b,d)

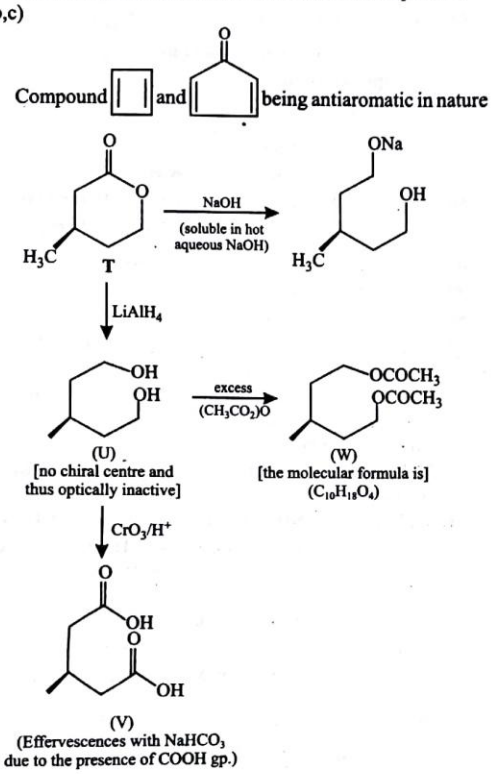
(a) Both are soluble in NaOH, hence can not be separated by NaOH.

(b) Benzoic acid (C_6H_5COOH) is soluble in NaOH and $NaHCO_3$, while benzyl alcohol ($C_6H_5CH_2OH$) is not soluble in $NaHCO_3$ and thus mixtures can be separated.

(c) Benzyl alcohol ($C_6H_5CH_2OH$) and phenol (C_6H_5OH) can be separated by NaOH as only the later is soluble in NaOH. However, in $NaHCO_3$, both are insoluble. Hence, can not be separated.

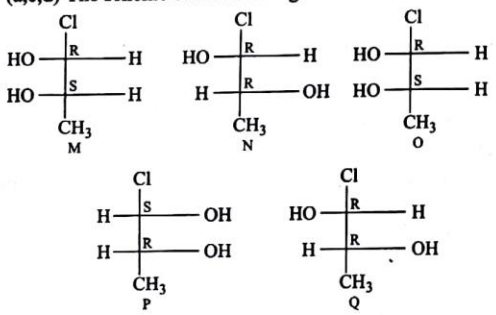
(d) α-phenyl acetic acid ($C_6H_5CH_2COOH$) is soluble in NaOH and $NaHCO_3$. Whereas benzyl alcohol ($C_6H_5CH_2OH$) is not. Hence, mixture can be separated.

93. (b,c)



and therefore unstable at room temperature.

94. (a,c,d) The scheme of reaction is given below



95. (a,b,c) The Fischer projections of M, N, O, P and Q are shown below

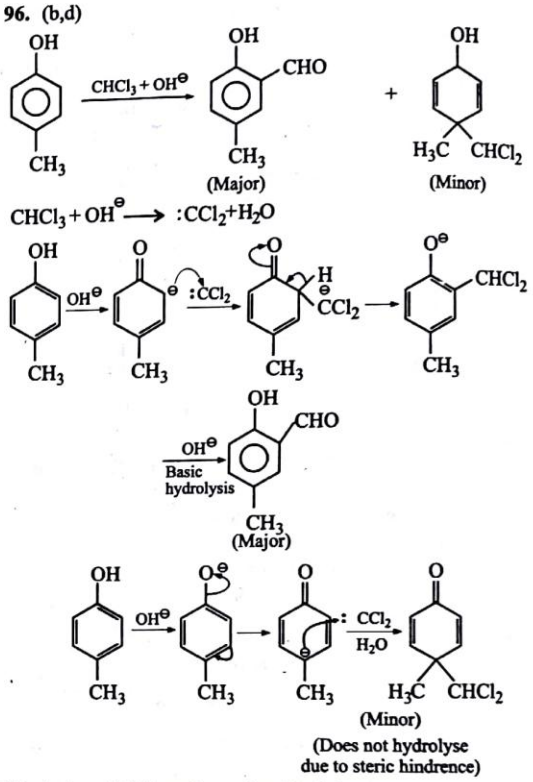
M and N are diastereoisomers

M and O are identical

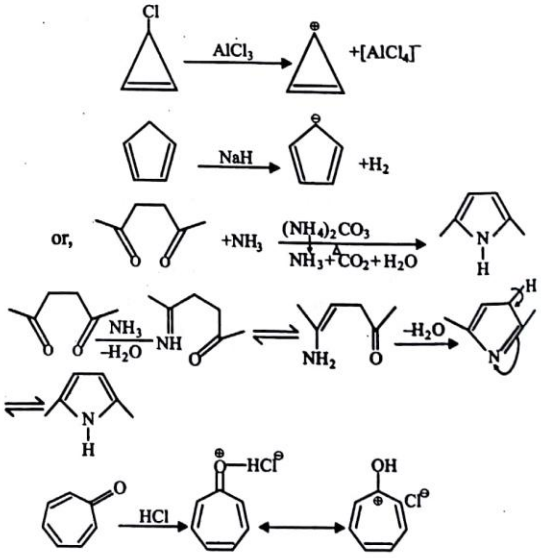
M and P are enantiomers

M and Q are diastereoisomers

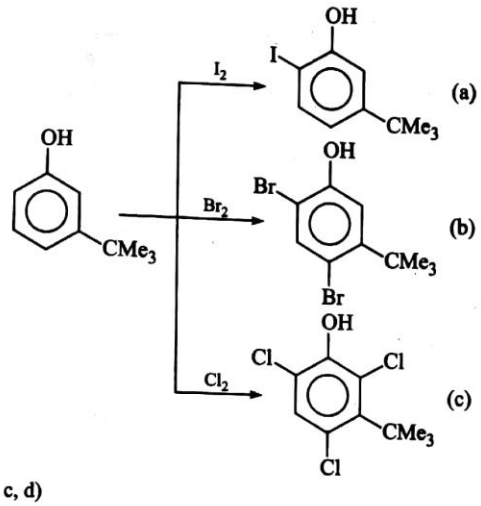
96. (b,d)



97. (a, b, c, d) All products obey Huckel rule for aromaticity.



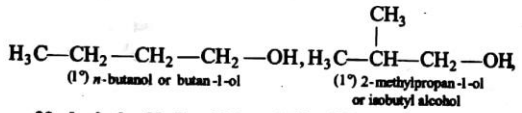
98. (a, b, c)



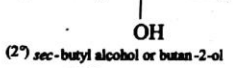
99. (a, c, d)

Isomeric alcohols of molecular formula, $C_4H_{10}O$ are

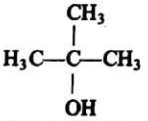
Primary or 1° alcohol



(1°) *n*-butanol or butan-1-ol (1°) 2-methylpropan-1-ol or isobutyl alcohol

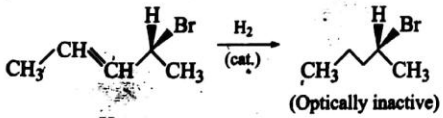
2° alcohol 

(2°) *sec*-butyl alcohol or butan-2-ol

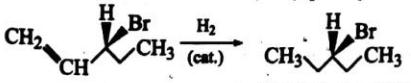
3° alcohol 

(3°) *tert*-butanol or 2-methylpropan-2-ol

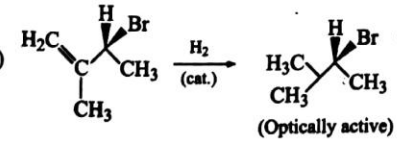
100. (b, d)

(a) 

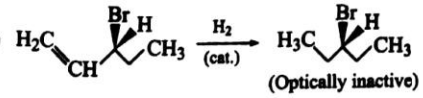
(Optically inactive)

(b) 

(Optically inactive)

(c) 

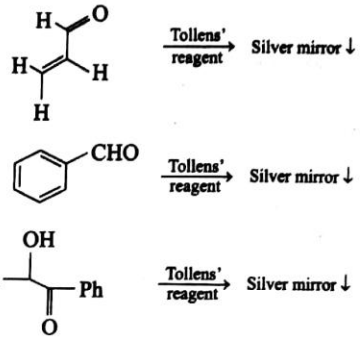
(Optically active)

(d) 

(Optically inactive)

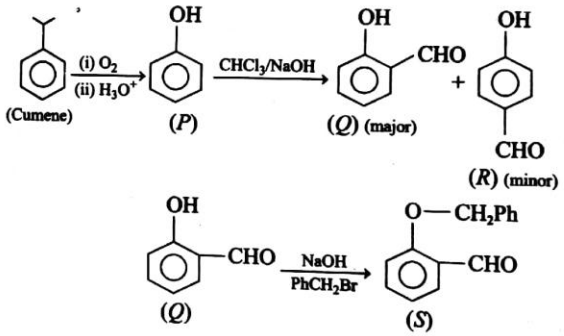
101. (a, b, c)

Aldehydes, formic acid, formic esters and α-hydroxy attached to a powerful electron withdrawing gp. such as ketons, carboxylic acid, amide, esters, cyanide show positive Tollens' test.



α, β dicarbonyl compounds also respond Tollens' test on warming slightly.

102. (b, c)

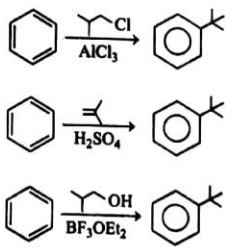


Q is steam volatile because of intra molecular H-bonding not *R*.

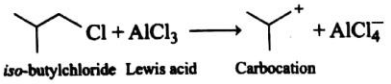
Q and *R* give positive test with 1% aqueous $FeCl_3$ solution.

Q, *R*, *S* give positive 2, 4-dinitrophenyl hydrazine.

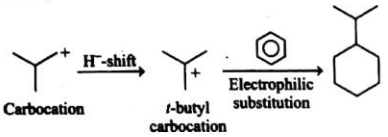
103. (b, c, d)



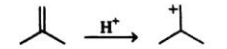
Note : Benzene neither reacts with sod. ethoxide nor with *t*-bromide. *t*-butyl bromide reacts with sodium ethoxide show E_1 and E_2 elemination to give isobutylene and ethanol. Neither of these two reacts with C_6H_6.

(b) 

iso-butylchloride Lewis acid Carbocation

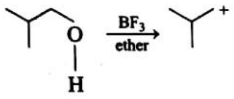


Carbocation *t*-butyl carbocation

(c) 

Isobutylene Carbocation

(d) BF_3(gas) dissolved in ether

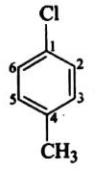


OH being poor leaving gp. but due to lone pair on O, it becomes good leaving gp. and leads to carbocation.

104. (c, d)

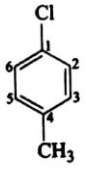
$NaBH_4/C_2H_5OH$ and Raney Ni/H_2 in T.H.F. do not reduce acid (—COOH), ester (—COO*R*) and epoxide

105. (b, c)



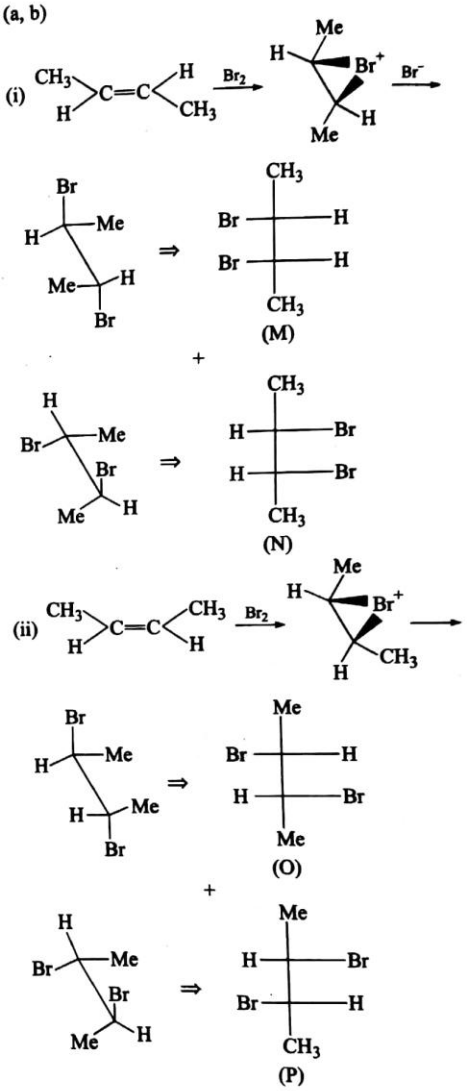
1-Chloro-4-methylbenzene

Since "Toluene" is accepted by IUPAC as a name of parent carbon chain, therefore



can also be named as 4-chlorotoluene.

106. (a, b)



(O) and (P) are enantiomers

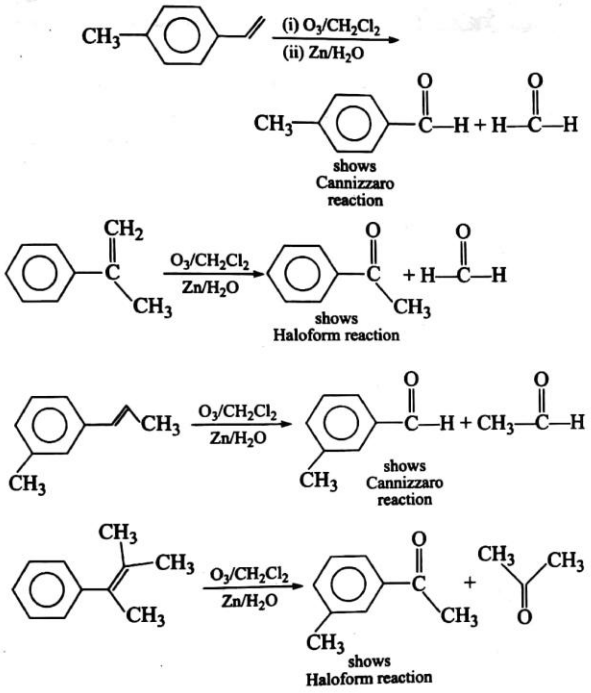
(a) (M) and (O) are distereomers of each other
(N) and (P) are distereomers of each other

(b) Addition of Br_2 on alkene follows non-classical carbocation mechanism. It is anti or trans addition

(c) (O) and (P) are enantiomers

(d) (M) and (N) are identical and (O) and (P) are enantiomers
(M and O) are distereomers and (N and P) are distereomers

107. (a, c)



108. (a, c, d)

When medium is highly polar and protic

S_{N^1} order :

benzyl > allyl > 3° > 2° > 1° > methyl > phenyl halide

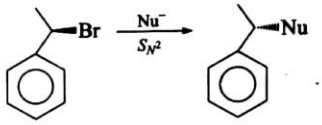
Hence options (c) is correct.

S_{N^2} order :

phenyl > methyl > 1° > 2° > 3° > allyl > benzyl halide

(I) and (II) will follow S_{N^2} when medium is polar aprotic and nucleophile is strong and in high concentration.

Option (d) is correct as



Inversion in case of S_{N^2}.

Option (b) is incorrect for both S_{N^1} and S_{N^2} conditions.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Organic molecules show chemical reaction on account of homolytic bond fission or heterolytic bond fission in addition to inductive effect, electromeric effect, resonance and hyperconjugation. The usual reactions shown by organic molecules are substitution (S_N1) and (S_N2) addition (syn and anti) and elimination (E_1 and E_2) reactions along with rearrangement reactions. In addition to these, various oxidation and reduction reactions are also given. The species which attacks a +ve centre is called nucleophile and the species capable of attacking –ve centres are called electrophile.

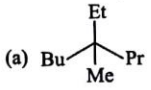
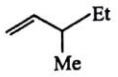
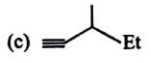
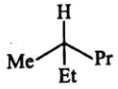
[1] Which is not formed during homolytic or heterolytic fission of covalent bond?
(a) Free radical (b) Carbocation
(c) Carbanion (d) Bridged carbocation

[2] The electromeric effect in a molecule occurs only of it has atleast one :
(a) σ-bond (b) lone pair
(c) π-bond (d) three centred bond

[3] The most stable carbocation among the following is :
(a) $C_6H_5^+$ (b) $C_6H_5\overset{+}{C}HCH_2$ (CH_3 branch)
(c) $C_6H_5-\overset{+}{C}(CH_3)_2$ (d) $C_6H_5\overset{+}{C}H_2$

[4] During nitration of an organic compound, HNO_3 acts as :
(a) acid (b) base
(c) neutral (d) salt

[5] Dextro 2-bromobutane on treatment with NaOH(*aq*) will not give :
(a) racemic mixture of 2-butanol if S_N1 is obeyed
(b) laevo form of 2-butanol if S_N2 is obeyed
(c) dextro form of 2-butanol if S_N2 is obeyed
(d) 100% inversion if S_N2 is obeyed

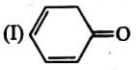
[6] Which does not represent the simplest chiral alkane, alkene or alkyne?
(a) 
(b) 
(c) 
(d) 

[7] Which of the following is neither a nucleophile or electrophile?
(a) NO_2^+ (b) Cl^+
(c) CN^- (d) $(CH_3)_4N^+$

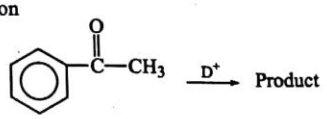
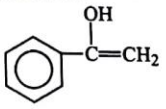
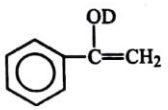
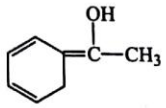
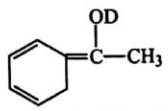
Comprehension 2 : Two molecules having same molecular formula but different structural formula due to migration of mobile H-atom between two polyvalent atoms is called tautomerism. The two isomers possess different functional groups and show interconversion of one into other giving rise to a dynamic equilibrium. These show such rapid interconversion that they cannot be independently isolated, *e.g.*,

$$CH_3\cdot CHO \rightleftharpoons CH_2=CHOH$$

[1] The compound cyclohex-1-en-ol-1 can be distinguished from cyclohexanol by :
(I) NH_2OH (II) Neutral $FeCl_3$ (III) $Ag(NH_3)_2OH$
(IV) Br_2 water
(a) I, II, IV (b) I, III
(c) II, III (d) II, IV

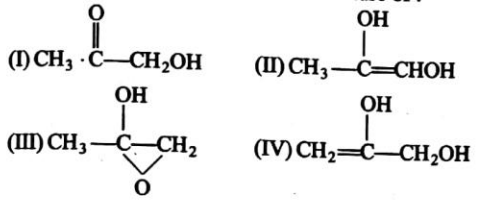
[2] Tautomerism is possible in :
(I)  (II) $F_3C-\overset{O}{\overset{\|}{C}}-CF_3$
(III) $CH_3\overset{O}{\overset{\|}{C}}\cdot CH_2\cdot\overset{O}{\overset{\|}{C}}\cdot CH_3$ (IV) $CH_3CH_2NO_2$
(a) I, III, IV (b) I, II, III
(c) I, II, IV (d) II, III, IV

[3] Enolic form of acetyl acetone is stabilized by :
(a) van der Waals' forces
(b) intermolecular H-bonding
(c) intramolecular H-bonding
(d) dipole-dipole repulsion

[4] In the reaction

the product is :
(a)  (b) 
(c)  (d) 

[5] The solubility of methyl acetoacetate in dilute NaOH solution is due to the formation of :
(a) $NaCH_2\cdot CO\cdot CH_2COOCH_2Na$
(b) $CH_3COCH_2COOCH_2Na$
(c) $CH_3-\overset{ONa}{\overset{|}{C}}=CHCOOCH_3$
(d) $CH_3CO\cdot CH_2\cdot COONa$

[6] 1-hydroxy acetone is a tautomeric mixture of :

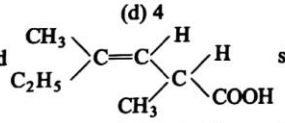


(a) I, III
(b) I, IV
(c) I, II
(d) It does not show tautomerism

Comprehension 3: Organic compounds having same molecular formula and same structure formula but different spatial arrangements of atoms or groups are known as stereo-isomers. The atom in a molecule round which positions of atoms are to be changed is called stereo-centre. In geometrical isomerism, it represents for a doubly bonded atom whereas in optical isomerism it represents for a chiral centre. *cis* and *trans* are two common forms of geometrical isomerism whereas enantiomers (a pair of *d* and *l*) are common forms of optical isomers :

[1] Select the set of incorrect statements :
(a) A *cis*-isomer has lower b.pt. than *trans*-isomer
(b) A *cis*-isomer has lower m.pt. than *trans*-isomer
(c) Butan-2-ol has chiral carbon
(d) 3-methyl-3-ethyl octane is simplest chiral alkane

[2] The number of stereo-centres in fumaric acid :
(a) 1 (b) 2
(c) 3 (d) 4

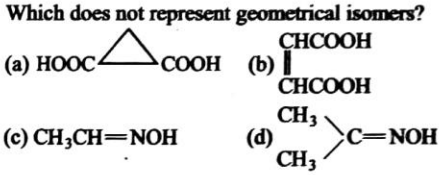
[3] The compound  shows :
(I) geometrical isomerism (II) optical isomerism
(III) stereo-isomerism (IV) none of these
(a) I, II, III (b) II
(c) I (d) IV

[4] The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane are :
(a) 2 (b) 3
(c) 4 (d) 1

[5] The number of structural and configurational isomers of a bromocompound C_5H_9Br formed by the addition of HBr on 2-pentyne respectively are :
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

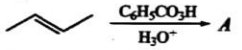
[6] Total number of isomers shown by C_4H_8 are :
(a) 3 (b) 4
(c) 5 (d) 6

[7] Which does not represent geometrical isomers?

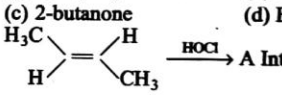


Comprehension 4: The carbon-carbon double bond in a molecule is capable of decolorizing Br_2/CCl_4 following free radical mechanism. The decolorization of Br_2/water solution however shows electrophilic addition. The addition of bromine to cyclopentene provides evidence for bromonium ion immediate in bromine addition. It follows ionic mechanism. When cyclopentene reacts with bromine in presence of CCl_4 anti addition occurs and gives *trans*-isomer so addition of halogen to an alkene is a stereospecific reaction. *cis*-alkene on addition with halogen gives *meso* products and *trans* alkene on addition gives racemic mixture.

[1] In the reaction given below *A* is :

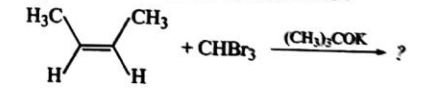


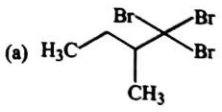
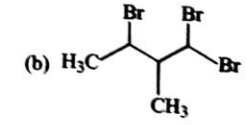
(a) 2,3-epoxy butane (b) 2,3-butane diol
(c) 2-butanone (d) Epoxy ethane

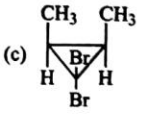
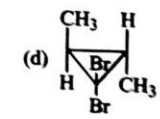
[2]  A Intermediate forms are :
(a) hydroxonium ion (b) chloronium ion
(c) hydronium ion (d) none of these

[3] *Trans*-2-butene on reacting with Br_2 in CCl_4 forms mainly :
(a) ± 2,3-dibromobutane (b) + 2,3-dibromobutane
(c) –2,3-dibromobutane (d) *Meso*-2,3-dibromobutane

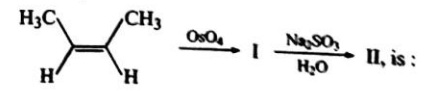
[4] The product obtained in the reaction is :



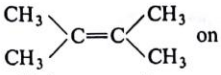
(a)  (b) 

(c)  (d) 

[5] The final product in



(a) *Meso*-2,3-butane diol (b) 2-butanol
(c) ±2,3-butandiol (d) 2-butanone

[6]  on passing through 5% Br_2/CCl_4 which seems to be correct :

(a) No colour change in Br_2/CCl_4 solution

(b) Addition product as 2,3-dibromo-2,3-dimethyl butane

(c) Colour of Br_2/CCl_4 is discharged

(d) The reaction occurs through electrophilic addition

[7] Which of the following statements are correct?

(1) Addition of Br_2 on 2,3-dimethyl butene is free radical addition in presence of H_2O

(2) Addition of Br_2 on ethene in presence of NaCl(*aq*) gives only 1,2-dibromo ethane

(3) Addition of Br_2 on alkene occurs at more faster rate in presence of polar or ionising medium

(4) Addition of Br_2 on alkene in a vessel coated with steric acid occurs at faster rate than in a bottle coated with wax

(a) 1, 2 (b) 1, 2, 4

(c) 2, 3, 4 (d) 3, 4

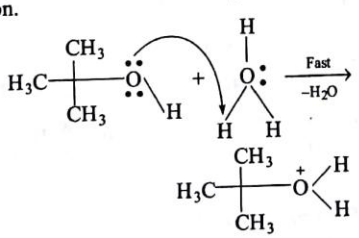
Comprehension 5: The dehydration of alcohols and the conversion of alcohols to alkyl halides by treatment of hydrogen halides are similar in two important ways suggesting the formation of carbocation as key intermediate.

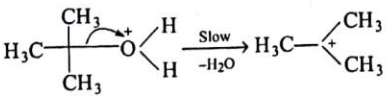
(a) Both reactions are protonated by acids.

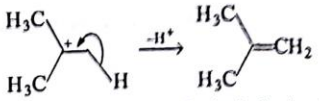
(b) The reactivity of alcohols decrease in the order, tertiary > secondary > primary due to the formation of stable carbocations, which is stabilized by hyperconjugation and +*I* effect. The dehydration of alcohol follows three steps mechanism for acid-base catalysed dehydration of least stable tertiary butyl alcohol, *i.e.*,

$$(CH_3)_3COH \xrightarrow[\Delta]{H_2SO_4} (CH_3)_2C{=}CH_2 + H_2O$$

In step I, protonation (acid catalysed) of *tert*-butyl alcohol takes place. In step II, dissociation of *tert*-butyloxenium ion takes place followed by formation of carbocation. Alkene is formed in step III by deprotonation (base catalysed) of *tert*-butyl cation.

Step I : 

Step II : 

Step III : 

Another important reaction of alcohols is iodoform reaction given by ethanol (in primary alcohols) and are secondary alcohols having 2-ol nature. Such alcohols give yellow ppt. of CHI_3 with NaOH and I_2 solution.

[1] Why dehydration of vinyl alcohols is not difficult?

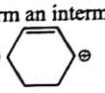
(a) Due to high enthalpy of vinylic —C—OH bond

(b) Due to unstable nature of =C—OH both by tautomerism

(c) Carbocation never forms in case of vinyl alcohol

(d) Both (a) and (b) are correct

[2] Which carbocation will not form an intermediate?

(a) $(C_6H_5)_3\overset{+}{C}$ (b) 

(c) (d) $CH_3{=}\overset{+}{C}H$

[3] Which will give iodoform test?

(a) 2-methylpropan-2-ol (b) Ethyl acetoacetate

(c) 2-methylbutan-2-ol (d) 3-methylpentan-2-ol

[4] Iodoform reaction is given by molecules having $CH_3—\underset{\underset{O}{\|}}{C}—$ unit or $CH_3—\underset{|}{CHOH}$ unit attached to carbon or H-atom. However and $CH_3 \cdot CO \cdot CH_2COOC_2H_5$ does not give iodoform reaction because :

(a) I_2 reacts at active H-atom

(b) I_2 reacts at α-methyl group

(c) I_2 does not react with these molecule

(d) Hydrolysis of iodide substituted molecule does not occur

[5] The reagent used to distinguish 1-cycloethanol and 2-cycloethanol is :

(a) Soda lime (b) $NaOI + H_2O$

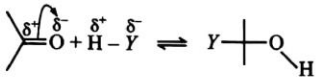
(c) Acidified $KMnO_4$ (d) (*Aq.*) $FeCl_3$

[6] An alcohol on iodoform reaction give iodoform and sodium salt of unsaturated acid containing 3 carbon atoms. The alcohol is :

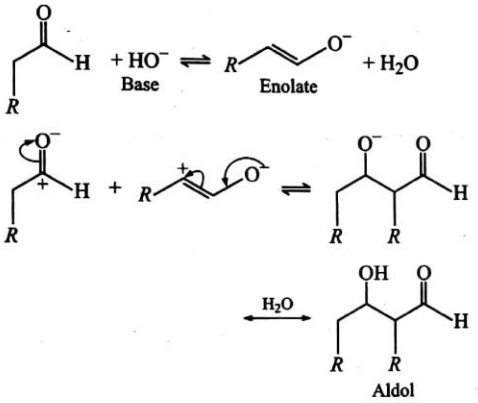
(a) But-3-en-2-ol (b) Prop-2-en-2-ol

(c) Pent-3-en-2-ol (d) 3-methyl-but-3-en-2-ol

Comprehension 6: Aldehydes and ketones are polar molecule. Nucleophiles attack on carbonyl group (>C=O) at carbon (positively charged) and electrophiles are attacked by oxygen. The characteristic reaction of aldehyde and ketone is nucleophilic addition to the carbon of carbonyl group.

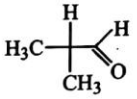
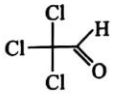
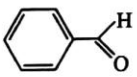
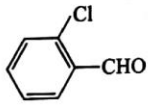


Aldehydes and ketones undergo condensation only when they consist α-hydrogen atom. The reaction takes place in presence of dilute alkali and one aldehyde molecule is partially converted to its enolate anion by the base. The enolate ion undergoes nucleophilic addition to the carbonyl group. The alkoxide formed in nucleophilic addition step, abstracts a proton from the solvent to give aldol, which consists aldehydic and hydroxyl group.

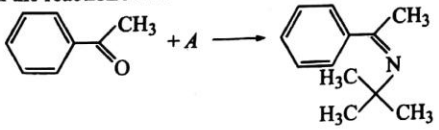


The reactivity of carbonyl compounds for nucleophilic addition reaction is inversely proportional to $+I$ effect. In absence of α-H atom, the aldehydes undergo Cannizzaro's reaction.

[1] Which of the following undergoes aldol condensation?

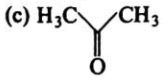
(a) 
(b) 
(c) 
(d) 

[2] In the reaction A is :



(a) $(CH_3)_2$—NH (b) $(CH_3)_3$—N
(c) $(CH_3)_3C$—NH_2 (d) none of these

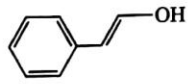
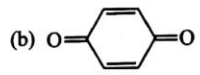
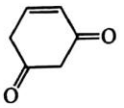
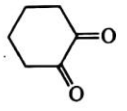
[3] Which one is most reactive for addition of alcohol on carbonyl group?

(a) C_6H_5CHO (b) HCHO
(c)  (d) $CH_3 \cdot CHO$

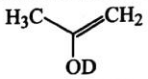
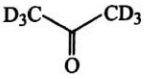
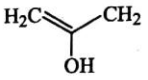
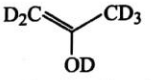
[4] How many aldol products can form when 2-butanone and propanaldehyde reacts in presence of dilute base?

(a) 4 (b) 5
(c) 6 (d) 7

[5] Tautomerism is not exhibited by :

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

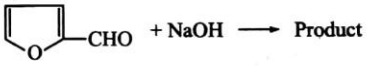
[6] The enol form of acetone after treatment with D_2O gives:

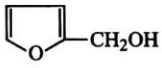
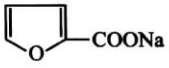
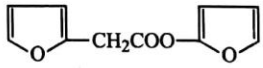
(a)  (b) 
(c)  (d) 

[7] Which does not undergo intermolecular Cannizzaro's reaction?

(a) *m*-chloro benzaldehyde (b) 2-methyl propanal
(c) Glyoxalic acid (d) Glyoxal

[8] The product formed in the reaction are :



(i)  (ii) 
(iii)
(iv) 

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

Comprehension 7 : Organic compounds having —COOH group are called carboxylic acid. An organic compound having —OH group and —COOH group both, are called hydroxy acid. Molecules with two carboxylic groups are dibasic and those having 3 carboxy group are tribasic acid. A dibasic acid having two —COOH group on adjacent carbon atoms looses H_2O to form inner anhydride. Hydroxy acids behave both as acids and alcohols and the hydroxyl and carboxyl groups do not interfere with each other when they are far apart. The heating of hydroxy acids however gives different products depending upon the nature of α-, β- or γ-hydroxy substituted acids.

[1] Which are correct for citric acid?
(I) It forms three series of salts
(II) It is α-hydroxy acid
(III) It is β-hydroxy acid
(IV) On heating to 150°C it gives aconitic acid
(V) It contains two —OH group
(a) I, II, IV, V (b) I, II, III, IV
(c) I, II, IV (d) I, III, IV

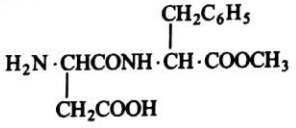
[2] α-hydroxy acids on heating forms :
(a) Lactides (b) Lactones
(c) Unsaturated acids (d) Either of these

[3] Which one is not correct for tartaric acid?
(I) It is an unsaturated acid
(II) It has two —OH group and two —COOH group
(III) It exist in four forms
(IV) It gives pyruvic acid on heating
(V) On heating it forms anhydride
(a) II, IV (b) II, III, IV
(c) I, II, V (d) II, V

[4] Which of the following does not forms its anhydride?
(I) Maleic acid (II) Tartaric acid
(III) Citric acid (IV) Fumaric acid
(V)Malic acid (VI) Malonic acid
(a) II, III, IV, VI (b) II, III, IV, V
(c) I, II, III, IV (d) III, IV, V, VI

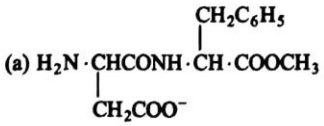
[5] Which one is not correct for fumaric and maleic acid?
(a) Both are dibasic acid
(b) pK_{a_1} for maleic acid is lesser than pK_{a_1} of fumaric acid
(c) pK_{a_2} for maleic acid is greater than pK_{a_2} for fumaric acid
(d) pK_{a_1} of maleic acid is more than fumaric acid

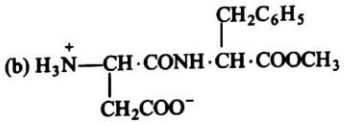
Comprehension 8 : Aspartame is an artificial sweetener having peptide bond in its structure given below :

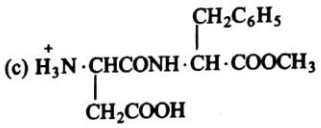


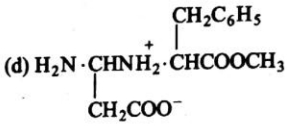
[1] It contains the functional groups :
(I) Amino (II) Carboxylic (III) Ester (IV) Amide
(V) Benzyl
(a) I, II, III, IV, V (b) I, II, III, IV
(c) I, II, III (d) I, II, IV, V

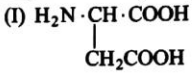
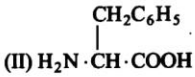
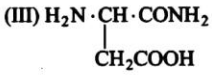
[2] Its zwitter ion structure is :

(a)


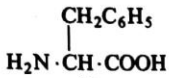
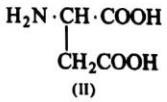
(b)


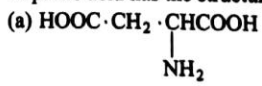
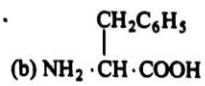
(c)


(d)


[3] Aspartame on hydrolysis forms two amino acids :
(I)

(II)

(III)

(IV)

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

[4] Which is correct for

(I)
and

(II)
(1) (I) is less hydrophobic
(2) (I) is more hydrophobic
(3) $C_6H_5 \cdot CH_2^-$ is more hydrophobic than CH_2COOH
(4) $C_6H_5—CH_2—$ is less hydrophobic than CH_2COOH
(a) 2, 3 (b) 1, 4
(c) 2, 4 (d) 1, 3

[5] Aspartic acid has the structure :
(a)

(b)


(c) $HOOH \cdot CH_2 \cdot CH_2 \cdot \underset{\displaystyle NH_2}{\underset{|}{CH}}COOH$

(d) $HOOC \cdot \underset{\displaystyle NH_2}{\underset{|}{\overset{\displaystyle CH_2C_6H_5}{\overset{|}{C}}}} \cdot COOH$

Comprehension 9: The term arene is used to benzene and its homologues. The term aromatic refers for the organic compounds which obey Huckel rule, *i.e.*, all aromatic compounds must possess π electrons equal to $(4n+2)$ where n is any positive integer. Due to aromatic nature benzene and its homologues show electrophilic substitution reactions producing *o*- and *p*-substituted derivatives or *m*-substituted derivatives. The orientation (new incoming group's substitution) in benzene nucleus is explained in terms of directive influence of the groups.

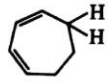
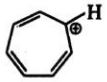
[1] Side chain of a nucleus can be oxidised to —COOH group only when it has atleast one :
(a) Vinylic H (b) Benzylic H
(c) Allylic H (d) Olefinic H

[2] The general formula for arenes having monocyclic nature where y represents number of 6-membered rings is :
(a) C_nH_{2n-6y} (b) C_nH_{2n-8y}
(c) C_nH_{2n-4y} (d) C_nH_{2n-5y}

[3] Which of the following are aromatic in nature?

(I) (II)

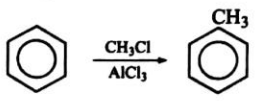
(III) (IV)

(V)  (VI) 

(a) II, III, IV, VI (b) I, II, III, IV
(c) III, IV, V, VI (d) IV, V, VI

[4] Which of the following are *m*-directing groups?
(I) $-NH_3^+$ (II) $-NH_2$ in acid
(III) $-CCl_3$ (IV) $-COO^-$
(V) —NC (VI) —CN
(a) I, II, III, VI (b) IV, V, VI
(c) III, IV, V (d) III, IV, VI

[5] Which of the following statements regarding S_E reaction in C_6H_6 is wrong?



(a) $AlCl_3$ acts as Lewis acid
(b) $AlCl_3$ acts to produce free radical
(c) $AlCl_3$ acts to produce electrophile
(d) $AlCl_3$ acts as halogen carrier

[6] Oxidation of which arene homologues does not produce benzoic acid with acidic $KMnO_4$ gives respectively :

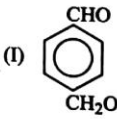
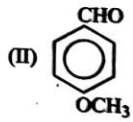
(a) (b)

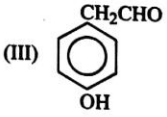
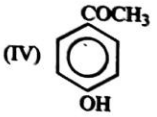
(c) (d)

Comprehension 10: Five isomeric para-disubstituted aromatic compounds (*A*) to (*E*) with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds :

(i) Both (*A*) and (*B*) form a silver mirror with Tollen's reagent; also, (*B*) gives a positive test with $FeCl_3$ solution but (*A*) not.
(ii) (*C*) gives positive iodoform test.
(iii) (*D*) is readily extracted in aqueous $NaHCO_3$ solution.
(iv) (*E*) on acid hydrolysis gives 1,4-dihydroxybenzene.

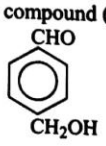
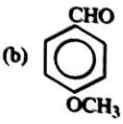
[1] The compound (*A*) is :

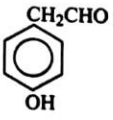
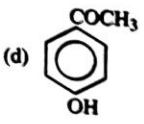
(I)  (II) 

(III)  (IV) 

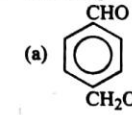
(a) I, II, III (b) I, II, III, IV
(c) I, II (d) I, IV

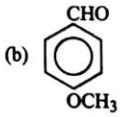
[2] The compound (*B*) is :

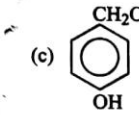
(a)  (b) 

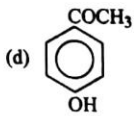
(c)  (d) 

[3] The compound (*C*) is :

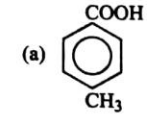
(a) 

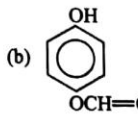
(b) 

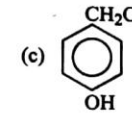
(c) 

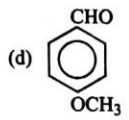
(d) 

[4] The compound (*D*) is :

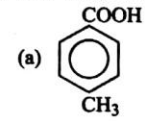
(a) 

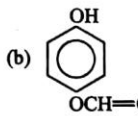
(b) 

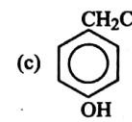
(c) 

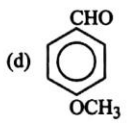
(d) 

[5] The compound (*E*) is :

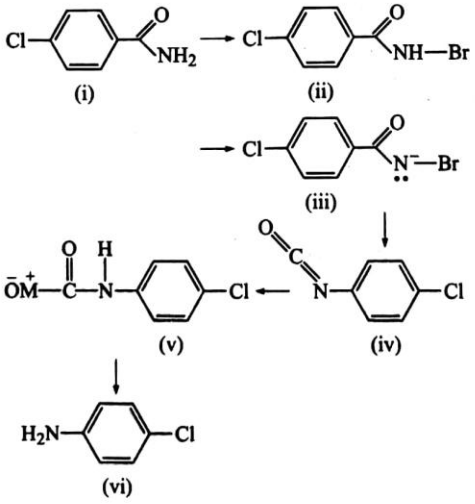
(a) 

(b) 

(c) 

(d) 

Comprehension 11: $RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation.

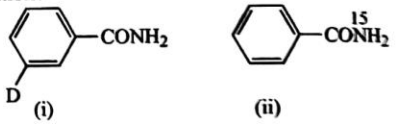


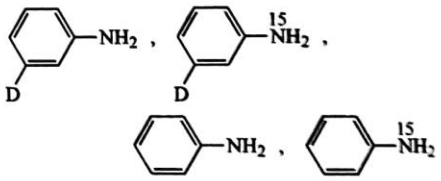
In this reaction, *R*CONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction. **(IIT 2006)**

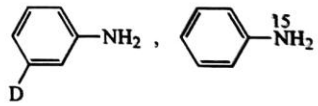
[1] How can the conversion of (i) to (ii) be brought about?
(a) KBr (b) $KBr + CH_3ONa$
(c) KBr + KOH (d) $Br_2 + KOH$

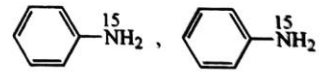
[2] Which is the rate determining step in Hofmann bromamide degradation?
(a) Formation of (i) (b) Formation of (ii)
(c) Formation of (iii) (d) Formation of (iv)

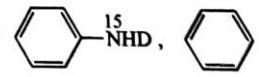
[3] What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?



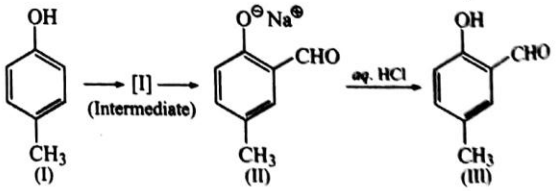
(a) 

(b) 

(c) 

(d) 

Comprehension 12 : Riemer-Tiemann reaction introduces an aldehyde group, into the aromatic ring of phenol, ortho to the hydroxyl group. The reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below. **(IIT 2007)**



[1] Which one of the following reagents is used in the above reaction?

(a) *aq*. NaOH + CH_3Cl (b) *aq*. NaOH + CH_2Cl_2

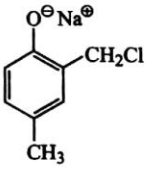
(c) *aq*. NaOH + $CHCl_3$ (d) *aq*. NaOH + CCl_4

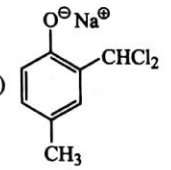
[2] The electrophile in this reaction is :

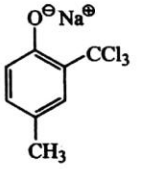
(a) $:CHCl$ (b) $+CHCl_2$

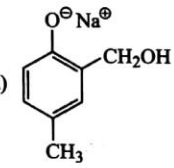
(c) $:CCl_2$ (d) $:CCl_3$

[3] The structure of the intermediate **I** is :

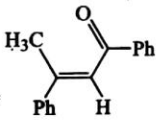
(a) 

(b) 

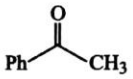
(c) 

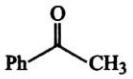
(d) 

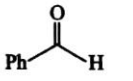
Comprehension 13: A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I.** Ozonolysis of **I** leads to compounds **J** and **K.** Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L,** whereas **K** on reaction with KOH gives only **M.** **(IIT 2008)**

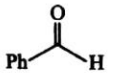
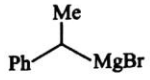
M = 

[1] Compound **H** is formed by the reaction of :

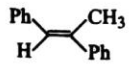
(a)  + PhMgBr

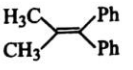
(b)  + $PhCH_2MgBr$

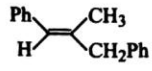
(c)  + $PhCH_2MgBr$

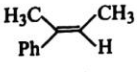
(d)  + 

[2] The structure of compound **I** is :

(a) 

(b) 

(c) 

(d) 

[3] The structure of compounds **J, K** and **L,** respectively, are :

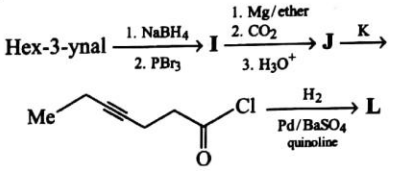
(a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

(b) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$

(c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

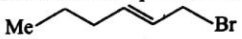
(d) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

Comprehension 14 : In the following reaction sequence, products, **I, J** and **L** are formed, **K** represents a reagent.

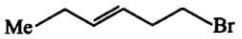


(IIT 2008)

[1] The structure of the product **I** is :

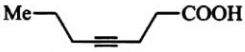
(a) 

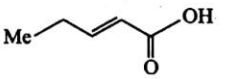
(b)

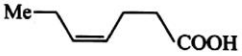
(c) 

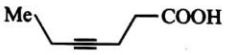
(d)

[2] The structure of compounds **J** and **K,** respectively, are :

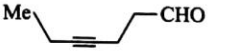
(a)  and $SOCl_2$

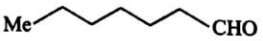
(b)  and SO_2Cl_2

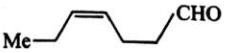
(c)  and $SOCl_2$

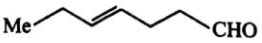
(d)  and CH_3SO_2Cl

[3] The structure of product **L** is :

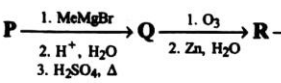
(a) 

(b) 

(c) 

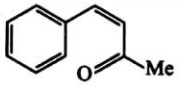
(d) 

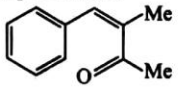
Comprehension 15: A carbonyl compound **P,** which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q.** Ozonolysis of **Q** leads to a dicarbonyl compound **R,** which undergoes intramolecular aldol reaction to give predominantly **S.**

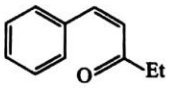


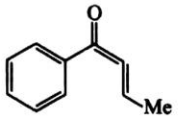
(IIT 2009)

[1] The structure of the carbonyl compound **P** is :

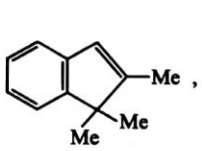
(a) 

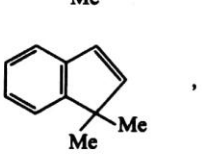
(b) 

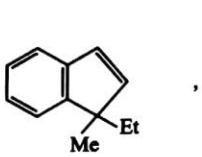
(c) 

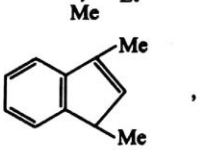
(d) 

[2] The structure of the products **Q** and **R**, respectively, are :

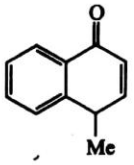
(a) 

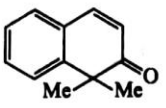
(b) 

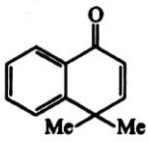
(c) 

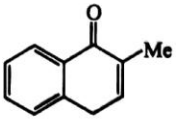
(d) 

[3] The structure of the product **S** is :

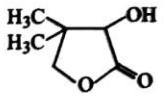
(a) 

(b) 

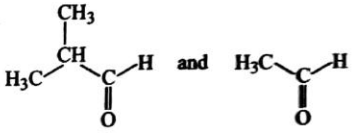
(c) 

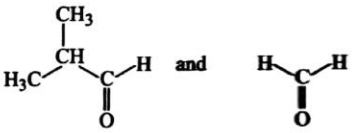
(d) 

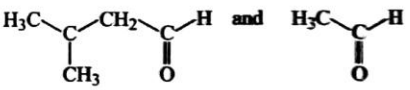
Comprehension 16: Two aliphatic aldehydes *P* and *Q* react in the presence of aqueous K_2CO_3 to give compound *R*, which upon treatment with HCN provides compound *S*. On acidification and heating, *S* gives the product shown below : **. (IIT 2010)**

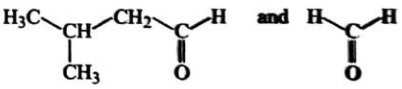


[1] The compounds *P* and *Q* respectively are :

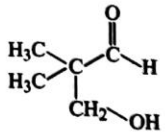
(a) 

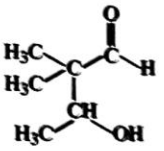
(b) 

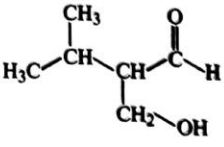
(c) 

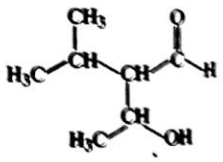
(d) 

[2] The compound *R* is :

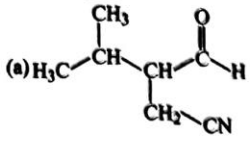
(a) 

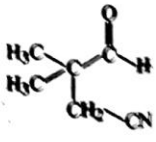
(b) 

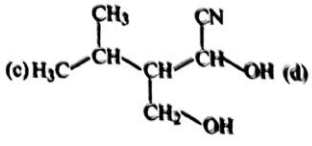
(c) 

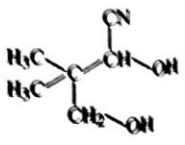
(d) 

[3] The compound *S* is :

(a) 

(b) 

(c) 

(d) 

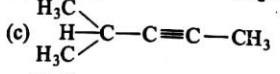
Comprehension 17 : An acyclic hydrocarbon *P*, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which *Q* is an intermediate organic compound. **(IIT 2011)**

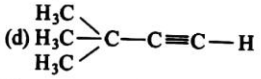
$$\underset{(C_6H_{10})}{P} \xrightarrow[\text{(iii) dil. acid}]{\text{(i) dil. } H_2SO_4/HgSO_4,\ \text{(ii) } NaBH_4/\text{ethanol}} Q \xrightarrow[(-H_2O)]{\text{(i) conc. } H_2SO_4,\ \text{(catalytic amount)}} \xrightarrow[\text{(iii) } Zn/H_2O]{\text{(ii) } O_3} 2CH_3COCH_3$$

[1] The structure of compound *P* is :

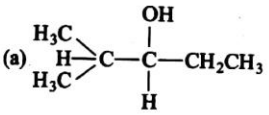
(a) $CH_3CH_2CH_2CH_2-C\equiv C-H$

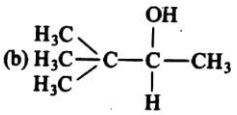
(b) $H_3CH_2C-C\equiv C-CH_2CH_3$

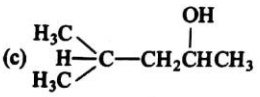
(c) 

(d) 

[2] The structure of the compound *Q* is :

(a) 

(b) 

(c) 

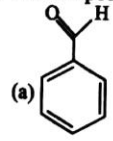
(d) $CH_3CH_2CH_2\underset{H}{\overset{OH}{C}}CHCH_2CH_3$

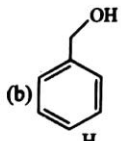
Comprehension 18 : In the following reaction sequence, the compound *J* is an intermediate :

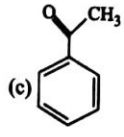
$$I \xrightarrow[CH_3COONa]{(CH_3CO)_2O} J \xrightarrow[\text{(ii) } SOCl_2,\ \text{(iii) anhyd. } AlCl_3]{\text{(i) } H_2,\ Pd/C} K$$

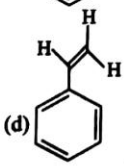
J ($C_9H_8O_2$) gives effervescence on treatment with $NaHCO_3$ and a positive Baeyer's test. **(IIT 2012)**

[1] The compound *I* is :

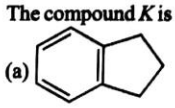
(a) 

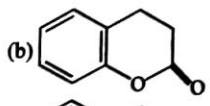
(b) 

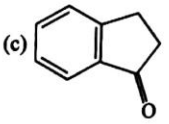
(c) 

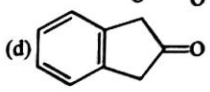
(d) 

[2] The compound *K* is :

(a) 

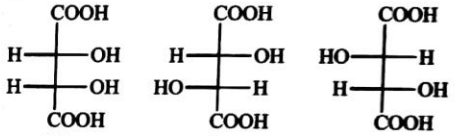
(b) 

(c) 

(d) 

Comprehension 19 : *P* and *Q* are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2 / H_2O. On heating, *P* forms the cyclic anhydride.

Upon treatment with dilute alkaline $KMnO_4$, *P* as well as *Q* could produce one or more than one from *S*, *T* and *U*.



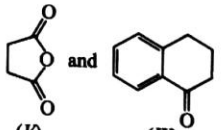
(*S*) (*T*) (*U*)

[JEE (Advanced) II 2013]

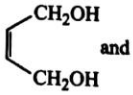
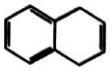
[1] In the following reaction sequences *V* and *W* are, respectively

$$Q \xrightarrow[\Delta]{H_2/Ni} V$$

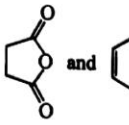
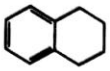
$$+ V \xrightarrow{AlCl_3\ (\text{anhydrous})} \xrightarrow[(ii)\ H_3PO_4]{(i)\ Zn\text{–}Hg/HCl} W$$

(a)  and

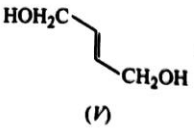
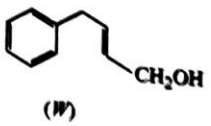
(*V*) (*W*)

(b)  and 

(*V*) (*W*)

(c)  and 

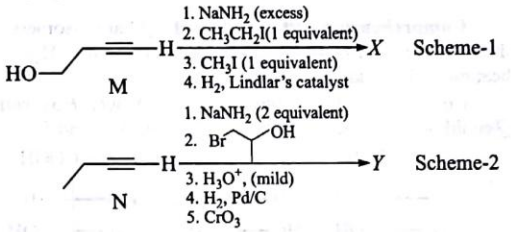
(*V*) (*W*)

(d)  and 

(*V*) (*W*)

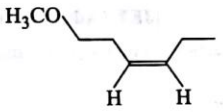
[2] Compounds formed from P and Q are, respectively :
[JEE (Advanced) II 2013]
(a) Optically active S and optically active pair (T, U)
(b) Optically inactive S and optically inactive pair (T, U)
(c) Optically active pair (T, U) and optically active S
(d) Optically inactive pair (T, U) and optically inactive S

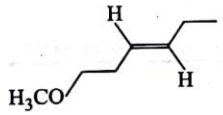
Comprehension 20 : Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both schemes.

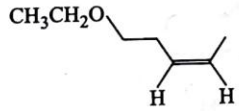


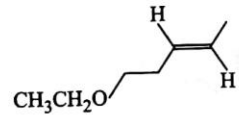
[JEE (Advanced) II 2014]

[1] The product X is :

(a) 

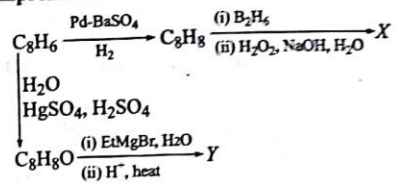
(b) 

(c) 

(d) 

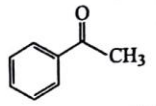
[2] The correct statement with respect to product Y is :
(a) It gives a positive Tollens test and is a functional isomer of X.
(b) It gives a positive Tollens test and is a geometrical isomer of X.
(c) It gives a positive iodoform test and is a functional isomer of X.
(d) It gives a positive iodoform test and is a geometrical isomer of X.

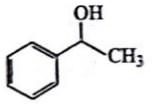
Comprehension 21 : In the following reaction

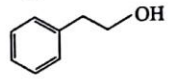


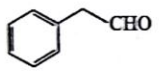
[JEE (Advanced) II 2015]

[1] Compound X is :

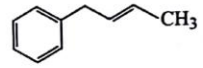
(a) 

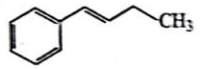
(b) 

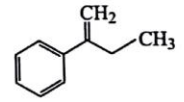
(c) 

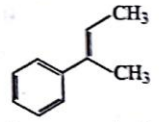
(d) 

[2] The major compound Y is :

(a) 

(b) 

(c) 

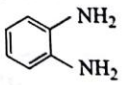
(d) 

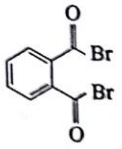
Comprehension 22 : Treatment of compound O with $KMnO_4$ / H^+ gave P, which on heating with ammonia gave Q. The compound Q on treatment with Br_2/NaOH produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T.

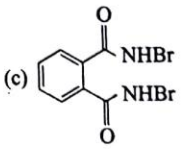
(O)

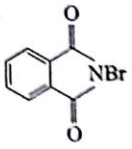
[JEE (Advanced) II 2016]

[1] The compound R is :

(a) 

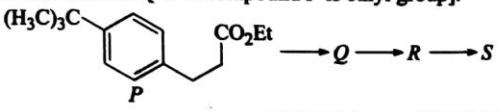
(b) 

(c) 

(d) 

[2] The compound T is :
(a) glycine
(b) alanine
(c) valine
(d) serine

Comprehension 23 : The reaction of compound *P* with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives *Q*. The compound *Q* on treatment with H_2SO_4 at 0°C gives *R*. The reaction of *R* with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces comound *S*. [Et in compound *P* is ethyl group].



[JEE (Advanced) II 2017]

[1] The reactions, *Q* to *R* and *R* to *S*, are :

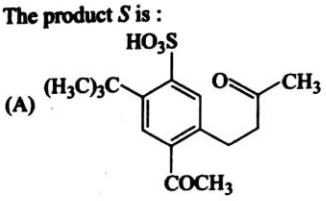
(a) Dehydration and Friedel-Crafts acylation

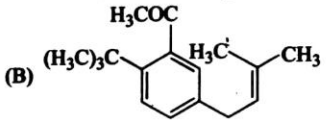
(b) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation

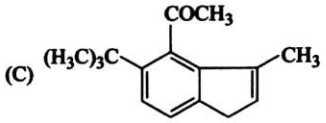
(c) Aromatic sulfonation and Friedel-Crafts acylation

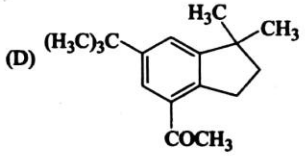
(d) Friedel-Crafts alkylation and Friedel-Crafts acylation

[2] The product *S* is :

(A) 

(B) 

(C) 

(D) 

SOLUTIONS

Comprehension 1

[1] (d) $\rangle C-C\langle \xrightarrow{\text{bond fission}} \rangle C^{+} + \rangle C^{-}$ Heterolytic

$\rangle \dot{C} + \dot{C}\langle$ Homolytic

[2] (c) $\rangle C=O \rightleftharpoons \rangle \overset{+}{C}-\overset{-}{O}$ or $\rangle C=C\langle \rightleftharpoons \rangle \overset{+}{C}-\overset{-}{C}\langle$

[3] (c) Resonance and $+I$ effect in $C_6H_5C^{+}(CH_3)_2$

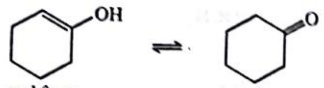
[4] (b) $\underset{\text{Base}}{HNO_3} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow NO_2^{+} + HSO_4^{-} + H_3\overset{+}{O}$

[5] (c) This is against the characteristics of S_N2

[6] (a) The simplest alkane with chirality is $C_3H_7-\underset{\displaystyle C_2H_5}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}}$

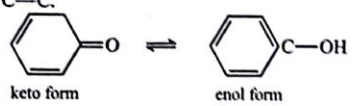
[7] (d) It can neither accept electron pair nor can donate.

Comprehension 2

[1] (a) 

enol form ⇌ keto form

$FeCl_3(aq)$ gives +ve test with enol form; NH_2OH gives +ve test with keto form. Br_2 water shows decolorisation due to C=C.

[2] (a) 

keto form ⇌ enol form

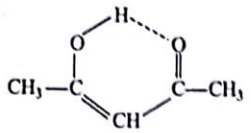
$CH_3-\underset{\text{keto form}}{\underset{\|}{\overset{O}{C}}}-CH_2-\underset{\|}{\overset{O}{C}}-CH_3 \rightleftharpoons$

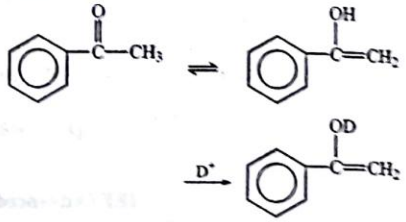
$CH_3-\underset{\|}{\overset{O}{C}}-CH=\underset{|}{\overset{OH}{C}}-CH_3$ (enol form)

$CH_3CH_2-N\overset{O}{\underset{O}{<}} \rightleftharpoons CH_3CH=N\overset{OH}{\underset{O}{<}}$

nitro form ⇌ acinitro form

[3] (c) $CH_3-\underset{\|}{\overset{O}{C}}-CH_2-\underset{\|}{\overset{O}{C}}-CH_3 \rightleftharpoons$



[4] (b) 

[5] (c) Enol form reacts with Na to form sodium salt.

$CH_3CO\cdot CH_2\cdot COOCH_3 \rightleftharpoons CH_3\cdot \underset{|}{\overset{OH}{C}}=CH\cdot COOCH_3$

$\xrightarrow{NaOH} CH_3-\underset{|}{\overset{ONa}{C}}=CHCOOCH_3$

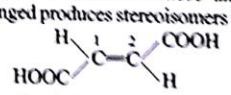
[6] (a) $CH_3-\underset{\|}{\overset{O}{C}}-CH_2OH \rightleftharpoons CH_3-\underset{\diagdown\,\diagup\ O}{\overset{OH}{\underset{|}{C}}}-CH_2$:

It is ring chain tautomerism.

Comprehension 3

[1] (d) *cis* being usually more polar and thus high b.pt. Also *trans*-shows more asymmetry in close packing, thus low m.pt. 3-methyl hexane is simplest chiral alkane.

[2] (b) An atom in a molecule whose any two groups when interchanged produces stereoisomers is called stereocentre.



[3] (a) It has C=C and one chiral centre.

[4] (a) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow{\text{Chlorination}}$

$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{*}{\underset{Cl}{\underset{|}{CH}}}-CH_3$ *d* and *l*

$CH_2Cl\cdot\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$ *d* and *l*

[5] (b) $CH_3\cdot C\equiv CH-CH_2\cdot CH_3 \xrightarrow{HBr} CH_3\cdot CH_2-$

$CHBr\cdot CH_2\cdot CH_3$

It has *cis* and *trans* form. The other four are structural isomerism by allocating Br at carbon 1,2,4 and 5.

[6] (d) $CH_3\cdot CH_2\cdot CH=CH_2$, $\underset{\text{cis and trans}}{CH_3CH=CH\cdot CH_3}$,

$CH_3\diagdown\ \diagup CH_2$, ,

[7] (d) Acetone oxime has two similar gp round doubly bonded carbon.

Comprehension 4

[1] (a) $CH_3CH{=}CH{-}CH_3 \xrightarrow[\text{(Perbenzoic acid)}]{C_6H_5COOOH} CH_3CH(O)CHCH_3 + C_6H_5COOH$

[2] (b) $\underset{CH_3CH}{\overset{CH_3CH}{\|}} \xrightarrow{HOCl} \underset{CH_3CHOH}{\overset{CH_3CHCl}{|}}$

$HOCl + H^+ \rightleftharpoons ClOH_2^+ \rightleftharpoons Cl^+ + H_2O$ (Chloronium ion)

[3] (d) $\underset{H}{\overset{CH_3}{>}}C{=}C\underset{H}{\overset{CH_3}{<}} \xrightarrow{Br_2} \underset{H}{\overset{CH_3}{>}}\overset{Br^+}{C}{-}C\underset{CH_3}{\overset{H}{<}}$

$\xrightarrow[\text{anti addition}]{Br^-}$ $\begin{matrix} CH_3 \\ H{-}C{-}Br \\ H{-}C{-}Br \\ CH_3 \end{matrix}$ *Meso* product

[4] (c) $\underset{H}{\overset{CH_3}{>}}C{=}C\underset{H}{\overset{CH_3}{<}} + CHBr_3 \xrightarrow{(CH_3)_3COK}$

$\begin{matrix} CH_3 & & CH_3 \\ H & C{-}C & H \\ & Br\ \ Br & \\ & C & \\ & Br & \end{matrix}$

[5] (a) $\underset{CH_3CH}{\overset{CH_3CH}{\|}} + OsO_4 \longrightarrow \underset{CH_3CH{-}O}{\overset{CH_3CH{-}O}{|}}OsO_2$

$\xrightarrow[H_2O]{Na_2SO_3}$ $\begin{matrix} CH_3CH{-}OH \\ | \\ CH_3CH{-}OH \end{matrix}$ *Meso*-2,3-butandiol

[6] (a) The given alkene has no olefinic H-atom and thus no reaction.

[7] (d) $CH_2{=}CH_2 \xrightarrow{Br_2} + Br\overset{+}{<}\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \xrightarrow[\text{or}]{Br^-} CH_2Br{-}CH_2Br$

$\xrightarrow{Cl^-} CH_2Br{-}CH_2Cl$

Comprehension 5

[1] (d) These are facts.

[2] (c) Rest all will form carbocation.

[3] (d) $CH_3{-}\underset{CH_3}{CH}{-}\underset{OH}{CH}{-}CH_3$ has $CH_3{-}\underset{|}{CHOH}$ unit responsible for iodoform reaction.

[4] (a) Both have $H_2C<$ group attached to electron withdrawing groups and thus H-atom of $>CH_2$ become reactive and such a $H_2C<$ group is called reactive methylene gp.

$>CH_2 + I_2 \longrightarrow >CI_2 \xrightarrow{OH^-} >C(OH)_2 \longrightarrow >C{=}O$

[5] (b) 1-cycloethanol will give iodoform reaction.

[6] (a) $CH_2{=}CH{\cdot}\underset{OH}{CH}{\cdot}CH_3 \xrightarrow[[O]]{I_2} CH_2{=}CH{\cdot}CO{\cdot}CH_3$

But-3-en-2-ol

$CH_2{=}CHCOCH_3 \xrightarrow{I_2} CH_2{=}CH{\cdot}CO{\cdot}CI_3$

$CH_2{=}CHCOCI_3 \xrightarrow{NaOH} CH_2{=}CHCOONa + CHI_3$

Comprehension 6

[1] (a) Rest all do not have α-H-atom.

[2] (c) $(CH_3)_3C{-}N\boxed{H_2 + O}{=}\underset{CH_3}{\overset{|}{C}}{-}C_6H_5 \longrightarrow$

$(CH_3)_3CN{=}\underset{CH_3}{\overset{|}{C}}{-}C_6H_5$

[3] (a) C_6H_5 give rise to $-I$ effect and thus nucleophilic addition is favoured.

[4] (c) $\underset{C_2H_5}{\overset{CH_3}{>}}C{=}O + \underline{CH_3}COC_2H_5$;

$\underset{C_2H_5}{\overset{CH_3}{>}}C{=}O + CH_3\underline{CH_2}COCH_3$;

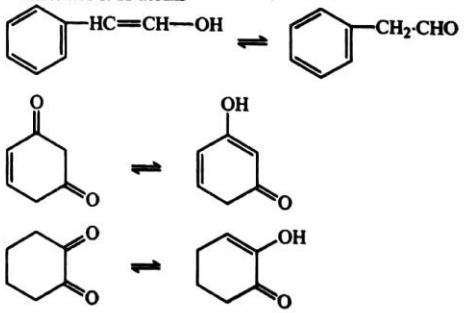
$\underset{C_2H_5}{\overset{CH_3}{>}}C{=}O + CH_3\underline{CH_2}CHO$;

$CH_3CH_2CH{=}O + CH_3\underline{CH_2}CHO$;

$CH_3CH_2CH{=}O + \underline{CH_3}COC_2H_5$;

$CH_3CH_2CH{=}O + \underline{CH_3}CH_2COCH_3$;

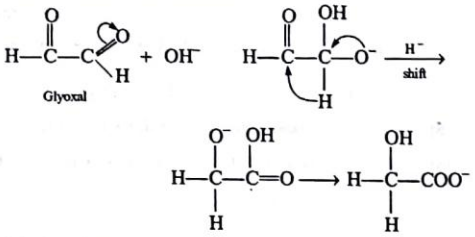
— indicates α-H-atoms

[5] (b) 

[6] (a) $CH_3{-}\underset{O}{\overset{|}{C}}{-}CH_3 \longrightarrow CH_3{-}\underset{OH}{\overset{|}{C}}{=}CH_2 \xrightarrow{D_2O}$

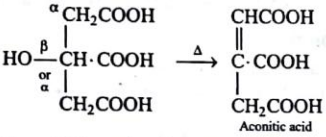
$CH_3{-}\underset{OD}{\overset{|}{C}}{=}CH_2$

[7] (d) Rest all show intermolecular Cannizzaro reaction.

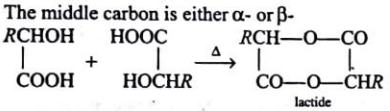


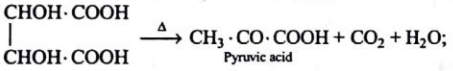
[8] (d) It is Cannizzaro reaction.

Comprehension 7

[1] (b) 

The middle carbon is either α- or β-

[2] (a) 

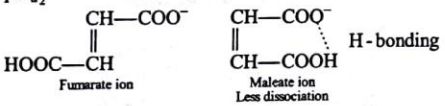
[3] (b) 

D-, *L*-, *DL*- and *meso* forms are isolated.

[4] (a) Rest all forms anhydrides.

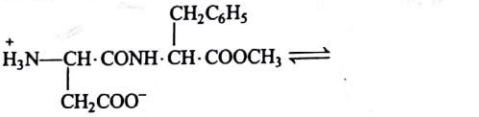
[5] (d)

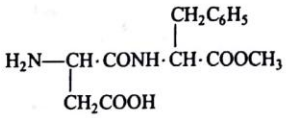
	Maleic	Fumaric
pK_{a_1}	1.92	3.02
pK_{a_2}	6.23	4.38

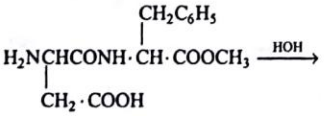


Comprehension 8

[1] (b) Benzyl is not functional gp.

[2] (b) 



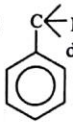
[3] (a) 

[4] (a) $C_6H_5 \cdot CH_2$— is more hydrophobic

[5] (a) Aspartic acid is 2-amino butan-dioic acid

Comprehension 9

[1] (b) C← Benzylic carbon; H-atom attached on carbon joined directly to an aromatic ring.



Side chain must have at least one H or C (benzylic carbon)

[2] (a) $y = 1$ for monocyclic, thus, C_nH_{2n-6}.

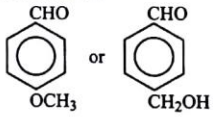
[3] (a) I has 4π electrons, II has 6π electrons, III has 2π electrons, IV has 6π electrons, V has 6π electrons but delocalised over six carbon atom and not over entire ring. VI has 6π electrons and localised over entire cyclic system.

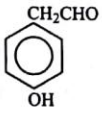
[4] (a) A positive charge makes the last gp *m*-directing whereas a –ve charge makes a gp *o*- and *p*-directing. In CCl_3, follow Hammick Illing worth rule.

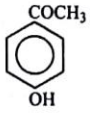
[5] (b) $AlCl_3 + CH_3Cl \longrightarrow [AlCl_4]^- + CH_3^+$ (Acid)

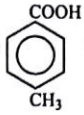
[6] (d) Side chain in *t*-butyl benzene does not have benzylic H-atom

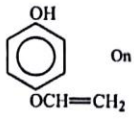
Comprehension 10

[1] (c)  Presence of —CHO group and thus reduces Tollen's reagent.

[2] (c)  Presence of —CHO group and thus reduces Tollen's reagent. Phenolic group gives positive test with $FeCl_3$ (*aq.*).

[3] (d)  Presence of methyl ketone group and thus gives positive iodoform test.

[4] (a)  Presence of carboxylic group and thus forms sodium salt of acid.

[5] (b)  On acid hydrolysis gives 1, 4-dihydroxy benzene.

Comprehension 11

[1] (d) Hofmann bromamide reaction takes place with $Br_2 + KOH$.

[2] (d) Also read mechanism of reaction.

[3] (b) —do—

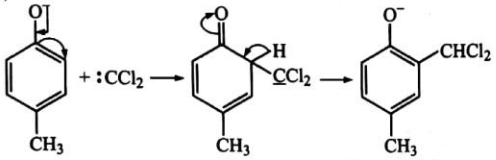
Comprehension 12

[1] (c) The reagent used in the given Reimer-Tiemann reaction is *aq*. NaOH + $CHCl_3$.

[2] (c) The electrophile in the given reaction is $:CCl_2$ generated from $CHCl_3$ by *aq*. NaOH.

$$CHCl_3 + OH \rightleftharpoons CCl_3 + H_2O$$
$$CCl_3 \rightleftharpoons :CCl_2 + Cl$$

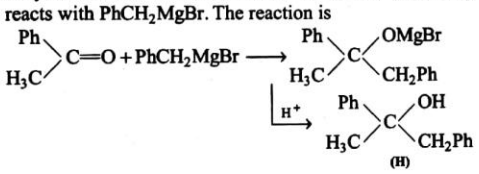
[3] (b)



(Intermediate)

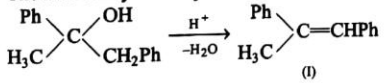
Comprehension 13

[1] (b) A tertiary alcohol (**H**) which can undergo acid catalysed dehydration will be formed when the ketone $PhCOCH_3$ reacts with $PhCH_2MgBr$. The reaction is



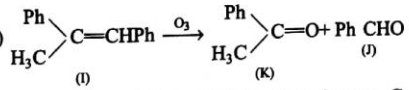
(H)

[2] (a) The acid catalysed dehydration reaction is



(I)

[3] (d)

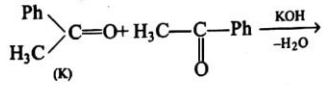


(I) (K) (J)

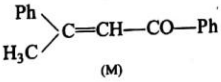
The compound **J** is PhCHO. It undergoes Cannizzaro reaction.

$$2PhCHO \xrightarrow[H_2O]{KOH} PhCH_2OH + \underset{(L)}{PhCOO^-K^+}$$

The compound K undergoes aldol condensation.



(K)



(M)

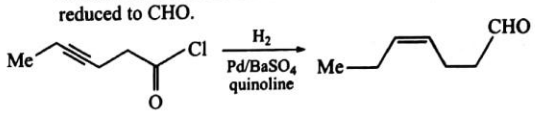
Comprehension 14

[1] (d) $H_3C-CH_2-C\equiv C-CH_2-CHO$ (Hex-3-ynal) $\xrightarrow[2.\ PBr_5]{1.\ NaBH_4}$ $H_3C-CH_2-C\equiv C-CH_2-CH_2Br$ (I)

[2] (c) (I) $\xrightarrow[3.\ H_3O^+]{1.\ Mg/ether\ \ 2.\ CO_2}$ $CH_3-CH_2-C\equiv C-CH_2-CH_2-COOH$ (J)

(J) $\xrightarrow[(K)]{SOCl_2}$ $CH_3-CH_2-C\equiv C-CH_2-CH_2-\underset{O}{\overset{}{C}}-Cl$

[3] (c) The use of Lindlar catalyst leads to *syn* addition. This causes the formation *cis* isomer. Besides this, —COCl is reduced to CHO.

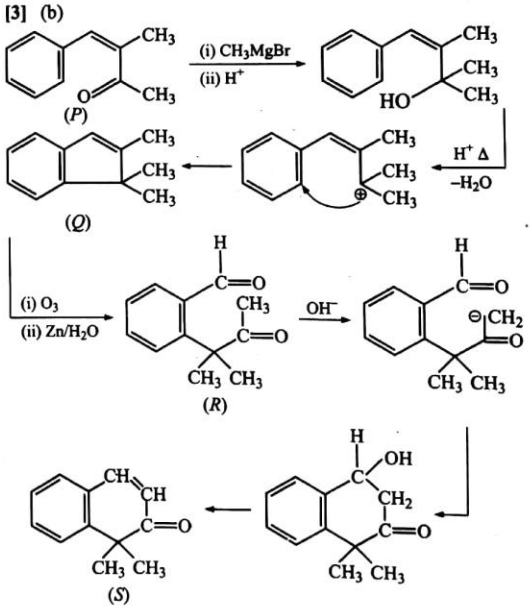


Comprehension 15

[1] (b)

[2] (a)

[3] (b)

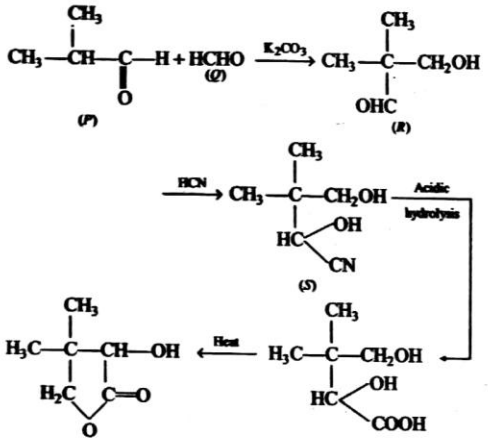


Comprehension 16

[1] (b)

[2] (a)

[3] (d)

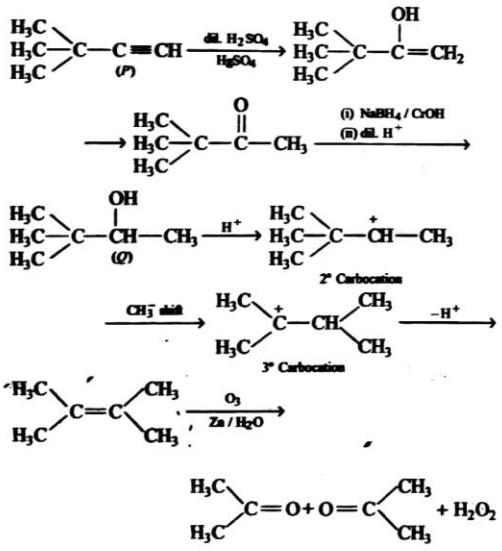


Comprehension 17

[1] (d)

[2] (b)

Explanation :

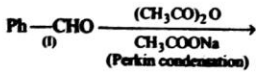


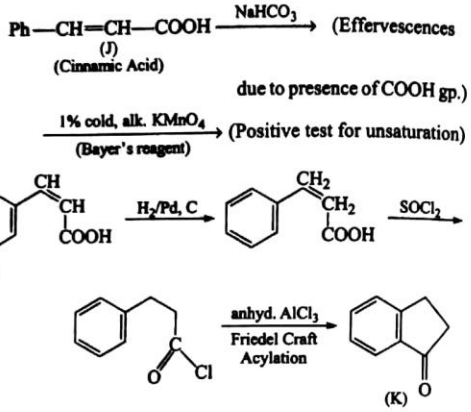
Comprehension 18

[1] (a)

[2] (c)

Explanation :





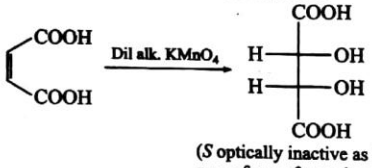
Comprehension 19

[1] (a)

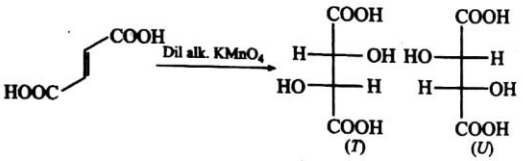
$C_4H_4O_4$ is a dicarboxylic acid and thus it may be HOOC—CH = CH—COOH

The two isomers are :

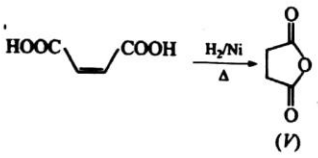
Maleic acid Fumaric acid



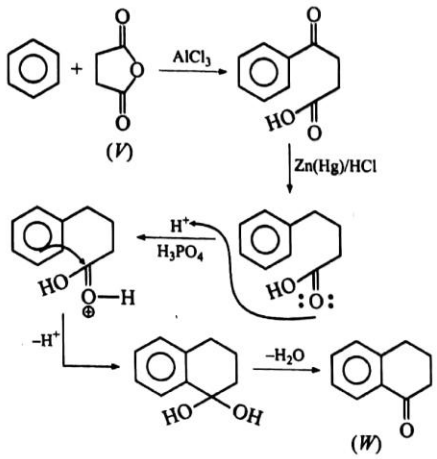
(*S* optically inactive as it is meso form of tartaric acid)



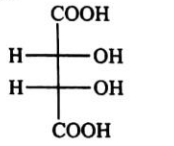
(optically active compounds but racemic mixture is optically inactive)



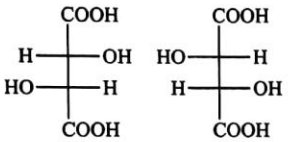
(*V*)



[2] (b)



(S is optically inactive as it is meso form of tartaric acid having symmetry)



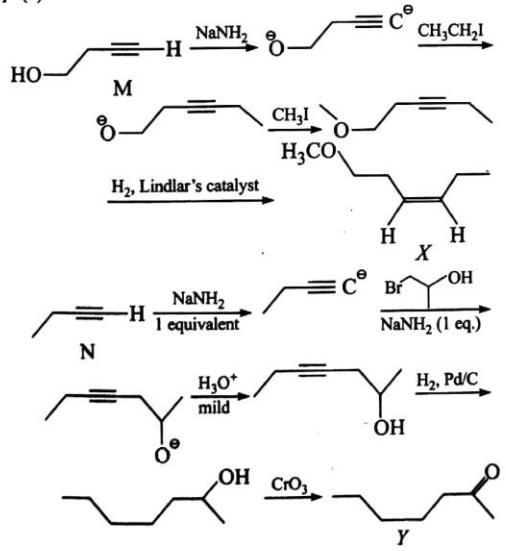
(T) (optically active) (U) (optically active)

Racemic mixture is optically inactive

Comprehension 20

[1] (a)

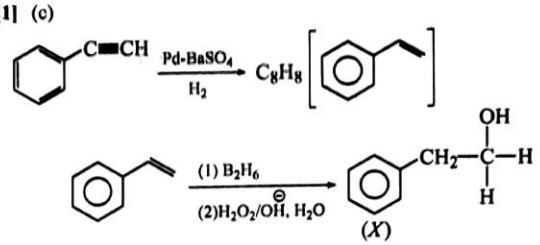
[2] (c)



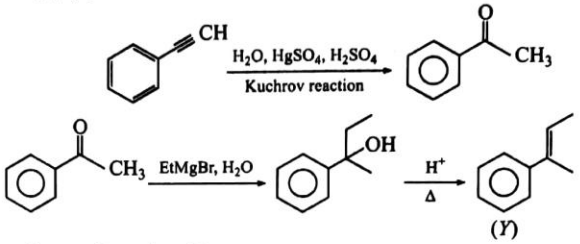
X and *Y* are functional isomers of each other and *Y* gives iodoform test.

Comprehension 21

[1] (c)

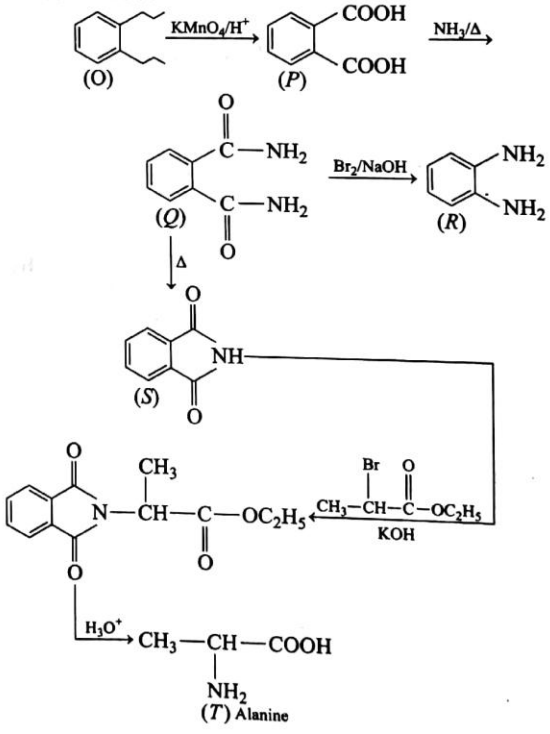


[2] (d)



Comprehension 22

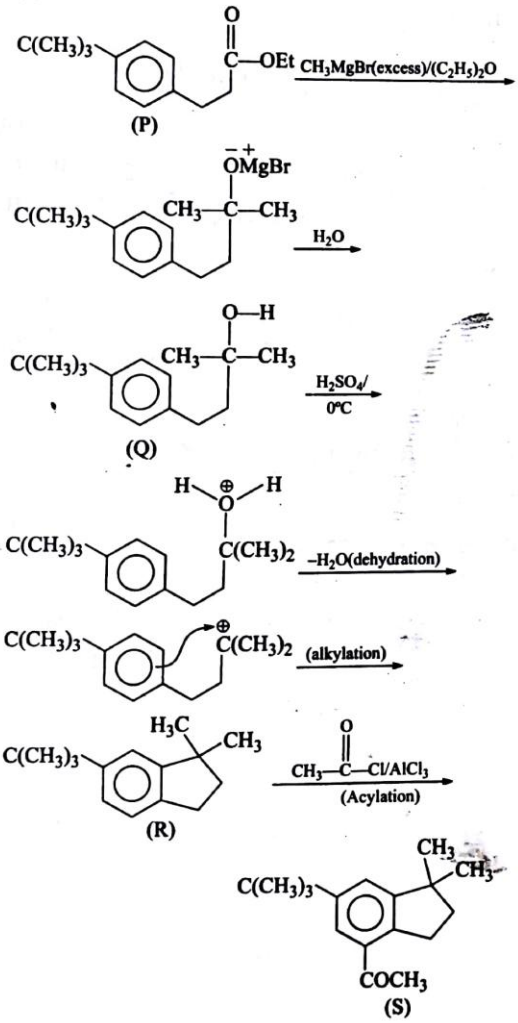
[1] (a) and [2] (b)



Comprehension 23

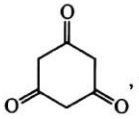
[1] (b)

[2] (d)

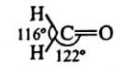


In each sub question below, a statement **S** and an explanation **E** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question.

(a) **S** is correct but **E** is wrong.
(b) **S** is wrong but **E** is correct.
(c) Both **S** and **E** are correct and **E** is correct explanation of **S.**
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S.**

1. **S :** Solubility of *n*-alcohol in water decreases with increases in molar mass.
   E : The hydrophobic nature of alkyl chain increases.
2. **S :** The yield in organic reactions are 100%.
   E : The organic reactions take place along with side reaction.
3. **S :** Ethane is much less reactive than ethene.
   E : Bond angles in ethane are less than those in ethene.
4. **S :** 2, 3-dimethyl but-2-ene decolourize Br_2 water.
   E : 2, 3- dimethyl but-2-ene is an unsaturated compound.
5. **S :** C_6H_6 does not decolourize Br_2 water.
   E : All the six carbon atoms have delocalized π-electrons.
6. **S :** C_6H_5Cl on treating with NaOH does not show replacement of Cl atom by OH.
   E : The resonance in chlorobenzene stabilizes the molecule.
7. **S :** Nitrobenzoic acid is more acidic than benzoic acid.
   E : Presence of electron repelling group decreases the acidic character in molecule.
8. **S :** *p*-dimethoxybenzene is polar.
   E : The different orientations of methoxy group in ring results in to produce dipole.
9. **S :** H atoms of ethyne are acidic in nature.
   E : The *sp*-hybridization of carbon atoms makes C atoms more electronegative.
10. **S :** Acetate ion is more basic than formate ion.
    E : The *+IE* methyl group in acetate ion intensifies electron density on oxygen atom.
11. **S :** C_2H_5I is more reactive than C_2H_5Cl.
    E : I being less electronegative than Cl.
12. **S :** 1-butene on reaction with HBr in the presence of per oxide produces 1-bromobutane.
    E : It involves the formation of primary radical.
13. **S :** Phenol is more reactive than benzene towards electrophilic substitution reaction.
    E : In the case of phenol, the intermediate carbocation is more resonance stabilised.
14. **S :** Ethyl acetoacetate gives reddish violet colour with $FeCl_3$ (*aq*).
    E : Ethyl acetoacetate shows keto-enol isomerism.
15. **S :** Acetate ion is more basic than methoxide ion.
    E : Acetate ion is resonance stabilised.
16. **S :** The unpaired electron of CH_3 free radical occupies *p*-orbital.
    E : $\overset{\bullet}{C}H_3$ possesses sp^2 hybridisation.
17. **S :** Acetic acid does not undergo haloform reaction.
    E : Acetic acid has no α-hydrogen.
18. **S :** Benzo nitrile is prepared by the reaction of chlorobenzene with potassium cyanide.
    E : Cyanide (CN^-) is a strong nucleophile.
19. **S :** Addition of Br_2 to 1-butene gives two optical isomers.
    E : The product contains one asymmetric carbon atom.
20. **S :** $CH_3COCH_2COOC_2H_5$ will give iodoform test.
    E : It contains $CH_3-\overset{\overset{O}{\|}}{C}-$ unit linked to carbon atom.
21. **S :**  , will show tautomerism.
    E : It contains α-hydrogen atom near keto group.
22. **S :** Addition of Br_2 on maleic acid gives *d* and *l* isomers of product.
    E : The addition of Br_2 on maleic acid follow anti addition.
23. **S :** Benzaldehyde forms two oximes on reacting with NH_2OH
    E : The two oximes are formed due to geometrical isomerism arised in product.
24. **S :** Aniline does not undergo Friedel-Craft's reaction.
    E : $-NH_2$ gp. of aniline reacts with $AlCl_3$ (Lewis acid) to give acid-base reaction.
25. **S :** Cannizzaro's reaction is a disproportionation reaction.
    E : One molecule of aldehyde is oxidised on the cost of other.
26. **S :** All enzymes are proteins but all proteins are not enzymes.
    E : Enzymes are biocatalyst and possess a stable configuration having active sites.
27. **S :** Borazole is less reactive than benzene.
    E : Both borazole and benzene have same structure (three π bonds) but borazole has polar bonds.
28. **S :** Addition of H_2 in presence of catalyst on *trans*-2, 3-diphenyl but-2-ene gives *meso* form of 2, 3-diphenyl butane.
    E : Addition of H_2 in presence of catalyst is *syn*-addition and the product formed is racemic mixture.

29. **S :** HCHO has sp^2-hybridised carbon and the following geometry :



E : The bond angles are changed due to multiple bond-bond pair repulsion.

30. **S :** Tertiary butyl benzene on oxidation gives benzoic acid.
E : A side chain containing benzylic hydrogen atom is oxidised to —COOH group.

31. **S :** Ethanol is more viscous than glycerol.
E : Both possess H-bonding.

32. **S :** The presence of Ag^+ ion enhances the solubility of alkenes in water.
E : Ag^+ co-ordinates with the alkene by *p-d* π bonding giving an ion and thus solubility increases.

33. **S :** The central carbon-carbon bond in 1, 3-butadiene is shorter than *n*-butane.
E : In butadiene the central bond has sp^2-sp^2 nature whereas in butane it is sp^3-sp^3.

34. **S :** 2, 3-dichloropentene has four stereoisomers.
E : It contains two chiral carbon atoms.

35. **S :** Chlorine deactivates the C_6H_6 ring for S_E reaction yet it is *o*-, *p*-directing.
E : —*M* effect is greater than –*I* effect in chlorobenzene.

36. **S :** S_N2 reactions take place through transition state formation.
E : Primary carbocation is more stable than secondary carbocation.

37. **S :** Addition of bromine on *trans*-2-butene yields *meso*-2, 3-dibromobutane.
E : Br_2 shows electrophilic addition.

38. **S :** $CH \equiv C-CH_2-CH=CH_2$ adds up HBr to give $CH \equiv C-CH_2CHBr \cdot CH_3$ while $CH \equiv C-CH=CH_2$ adds up HBr to give $CH_2=CBrCH=CH_2$.
E : An isolated double bond is more reactive than triple bond but in later case conjugate molecule is formed.

39. **S :** A mixture of HNO_3 and H_2SO_4 is used for the nitration of benzene.
E : H_2SO_4 works as an acid and HNO_3 as a base to produce NO_2^+ ion.

40. **S :** Cyclohexane floats over water.
E : Cyclohexane always has boat like structure.

41. **S :** Iodination of alkane is carried out in presence of iodic acid.
E : Iodine is an oxidizing agent.

42. **S :** Reaction of *tert.* butyl chloride with Na gives 2,2,3,3-tetramethyl butane.
E : *Tert.* butyl chloride on Wurtz reaction gives alkene.

43. **S :** A small amount of ethanol is added to $CHCl_3$ bottles.
E : It acts as negative catalyst for the oxidation of $CHCl_3$ to $COCl_2$.

44. **S :** The *p*-isomer of dichlorobenzene has higher m.p. than *o*-and *m*-isomer.
E : *p*-isomer is symmetrical and thus shows more closely packed structure.

45. **S :** *n*-butyl chloride has lower b.p. than *n*-butyl bromide.
E : The b.p. increases with increase in molar mass.

46. **S :** CHI_3 gives a precipitate with $AgNO_3$ solution on heating but $CHCl_3$ not.
E : C—I bond is quite weak as compared to C—Cl bond.

47. **S :** Alcohols cannot be dried by $CaCl_2$.
E : $CaCl_2$ forms solvated molecules with alcohols.

48. **S :** Methanol is stronger acid than water.
E : All alcohols are stronger acid than water.

49. **S :** Acid catalysed dehydration of *t*-butanol is faster than *n*-butanol.
E : The order of stability of carbocation is $3^\circ > 2^\circ > 1^\circ$.

50. **S :** Acetone forms one oxime whereas acetophenone forms two oximes.
E : In acetophenone *syn* and *anti* form of geometrical isomers are possible.

51. **S :** The boiling point of nitro-alkanes is higher than their corresponding alkyl nitrites.
E : Nitro-alkanes show strong dipole-dipole interaction.

52. **S :** Acylation of aniline increases the reactivity of C_6H_6 ring.
E : Acylation of aniline decreases the electron density at C_6H_6 ring.

53. **S :** Sulphanilic acid is insoluble in water and organic solvents.
E : Sulphanilic acid is typical dipolar salt.

54. **S :** Nitromethane and acinitromethane are tautomers to each other.
E : Migration of H atom from α-C atom to electronegative atom which is bonded with multiple bond develops this phenomenon.

55. **S :** Alcohols give only substitution products with HX and not elimination product.
E : $\bar{X}$ is a very weak base which cannot abstract proton from alcohol.

56. **S :** Salicyldehyde is less soluble in water than *p*-hydroxy benzaldehyde.
E : The former shows intermolecular H-bonding.

57. **S :** $R-CH=CH_2 \xrightarrow[\text{Peroxide}]{CCl_3Br} R\underset{\displaystyle Br}{\underset{|}{C}}H-CH_2CCl_3$
E : The addition obey free radical addition on alkenes in presence of peroxide.

58. **S :** 2,3-dimethyl but-2-ene is more stable than but-2-ene.

E : 2,3-dimethyl but-2-ene possesses 12 α-hydrogen atoms whereas but-2-ene possesses only 6 α-hydrogen atoms and therefore former shows more pronounced hyperconjugation.

59. S : Hydroxyl amine NH_2OH gives positive Lassaigne's test for nitrogen.

E : The formation of NaCN during preparation of sodium extract will give positive Lassaigne's test for nitrogen.

60. S : *R*I is more reactive than *R*Cl towards S_N reaction.

E : The rate of reaction for S_N1 or S_N2 mechanism is *R*I > *R*Cl.

61. S : Chloral hydrate $CCl_3CH(OH)_2$ is a stable molecule.

E : An organic compound having two —OH gps. on one carbon atom is unstable.

62. S : Addition of KCN solution to carbonyl compounds decreases the pH of solution.

E : KCN in aqueous solution forms a basic solution due to hydrolysis of CN^-. The nucleophilic addition on carbonyl and brings in a decrease in H^+ ions or an increase in OH^- ions.

63. S : In strongly acidic medium, aniline becomes less reactive towards electrophilic reagent.

E : —NH_2 group is *o*-and *p*-directing.

64. S : *Trans*-2-chloro propene has higher dipole moment than *cis*-2-chloro propene.

E : The resultant vector sum of all the vectors in *trans*-2-chloro propene is more than *cis*-2-chloro propene.

65. S : Aryl halides undergo nucleophilic substitution with ease.

E : The carbon halogen bond in aryl halides has partial double bond character.

66. S : Benzene removes butter stain from a table cloth.

E : Butter has an affinity towards benzene.

67. S : β-keto carboxylic acids lose CO_2 when heated to about 370 K.

E : An enol is first formed by loss of CO_2, but it readily tautomerize to give more stable ketone.

68. S : S_N2 reactions of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.

E : S_N2 reactions always proceed with inversion of configuration.

69. S : 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.

E : Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism whereas 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

70. S : *p*-nitrophenol is a stronger acid than *o*-nitrophenol.

E : Intramolecular hydrogen bonding makes the *o*-isomer weaker than the *p*-isomer.

71. S : Dimethyl sulphide is commonly used for the reduction of an ozonide of compound.

E : It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.

72. S : Ethyl alcohol reacts with HI to give ethyl iodide but it does not react with HCN.

E : HI being a strong acid and thus donate a proton to ethyl alcohol and thus Et OH_2^+ is formed readily. OH_2^+ being good leaving group and thus reaction Et $OH_2^+ + I^- \rightarrow EtI + H_2O$ occurs. HCN being weak acid does not form $CH_3OH_2^+$.

73. S : Phenyl group is known to exert negative inductive effect but each phenyl ring in biphenyl (C_6H_5—C_6H_5) is more reactive than benzene towards S_E reaction.

E : In biphenyl one of the phenyl group acts as electron donor and the other electron acceptor.

74. S : Enol form of $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$ is less stable than enol form of CH_3COCH_3.

E : H-bonding in enol form of CH_3COCH_3 is stronger than that of enol form of $CH_3 \cdot COCH_2COCH_3$.

75. S : A carboxylic acid on treatment with ammonia gives amide at room temperature.

E : Carboxylic acids do not undergo nucleophilic substitutions under basic conditions.

76. S : Energy of resonance hybrid is equal to the average of energies of all canonical forms.

E : Resonance hybrid can not be presented by a single structure.

77. S : Pent-2-one and pent-3-one are position isomers.

E : Keto group is divalent group.

78. S : Cyclooctane using the structure is cyclic and have conjugated 8 π-electron system but not an aromatic compound.

E : $(4n+2)\pi$ electron rule does not hold good and ring is not planar.

79. S : Optically active 2-iodobutane on treatment with NaI in acetone undergoes recemisation.

E : Reaction involves multiple walden inversion and the product contains mixture of dextro and laevo forms.

80. S : Presence of nitro group at ortho or para position increases the reactivity of haloarenes towards S_N reaction.

E : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

81. S : Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

E : The reaction proceeds through the formation of a carbocation.

82. S : *o*-Nitrophenol is less soluble in water than *m*- and *p*-isomers.

E : *m*- and *p*- nitrophenol exist as associated liquid.

83. S : The α-H atom in carbonyl compounds is less acidic.

E : The anion formed after the loss of α-H atom is resonance stabilized.

84. S : Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromo butane.

E : Bromine addition to an alkene is an electrophilic addition. **(IIT 2001)**

85. S : In strongly acidic solution aniline becomes more reactive towards electrophilic reagents.

E : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. **(IIT 2006)**

86. S : Glucose gives a reddish-brown precipitate with Fehling's solution.

E : Reaction of glucose with Fehling's solution gives CuO and gluconic acid. **(IIT 2007)**

87. S : *p*-hydroxy benzoic acid has a lower boiling point than *o* -hydroxy benzoic acid.

E : *o*-hydroxy benzoic acid has intramolecular hydrogen bonding. **(IIT 2007)**

88. S : Molecules that are not superimposable on their mirror images are chiral.

E : All chiral molecules have chiral centres. **(IIT 2007)**

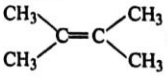
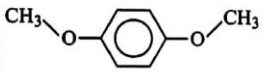
89. S : Aniline on reaction with $NaNO_2$ / HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate.

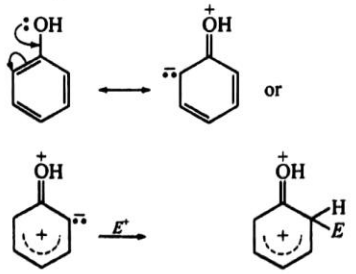
E : The colour of the compound formed in the reaction of aniline with $NaNO_2$ / HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation. **(IIT 2008)**

90. S : Bromobenzene upon reaction with Br_2 / Fe gives 1,4-dibromobenzene as the major product.

E : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. **(IIT 2008)**

ANSWERS (Statement Explanation Problems)

1. (c) The solubility of alcohols in water is due to H-bonding. As the molar mass of alcohol increases, the increase in hydrophobic nature of alkyl gp. results in decrease in solubility.
2. (b) The yield of organic reactions is not 100% because they take place with side reactions.
3. (d) Ethene is more reactive than ethane due to the presence of π-bond.
4. (b)  does not decolourise Br_2 water as it does not contain olefinic H atom, *i.e.*, all the olefinic H atoms are substituted by $-CH_3$ gp. No doubt it is an unsaturated compound.
5. (c) C_6H_6 does not decolourise Br_2 water because of resonance stabilization due to delocalisation of π-electrons.
6. (c) The given statement is true because of given explanation.
7. (d) Presence of electron attracting gp (here $-NO_2$) give rise to an increase in acidic character of benzoic acid.
8. (c) *p*-dimethoxybenzene is  a polar molecule because of different orientations of methoxy groups.
9. (c) Ethyne is acidic in nature due to given explanation.
10. (c) $CH_3 \rightarrow \underset{\underset{O}{\|}}{C} \rightarrow \overline{O}$ (The negative charge is intensified and thus basic character is more in CH_3COO^- than $HCOO^-$).
11. (d) C_2H_5I is more reactive than C_2H_5Cl due to lower bond energy of C—I bond than C—Cl bond.
12. (a) Addition of HBr in alkene in presence of peroxide takes place *via* free radical mechanism (secondary free radical).
13. (c) Presence of *o*-and *p*-directing group (except halogens) activates ring for S_E reactions.
Thus, both the reason and assertion are correct and reason is an explanation for assertion.



The more stabilized carbocation and thus facilitate attack of electrophile

14. (c) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2COOC_2H_5$ (keto) $\quad CH_3-\underset{\underset{OH}{|}}{C}=CHCOOC_2H_5$ (enol)

The enolic form gives characteristic test with $FeCl_3(aq.)$

15. (b) $CH_3-\underset{\underset{O}{\|}}{C}-\overline{O} \longleftrightarrow CH_3-\underset{\underset{O^-}{|}}{C}=O$

$CH_3-\overline{O}$, No resonance.

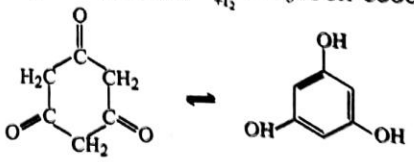
Also CH_3OH is less acidic than CH_3COOH ; thus CH_3COO^- is less basic than CH_3O^-. Stronger is acid, weaker is conjugate base.

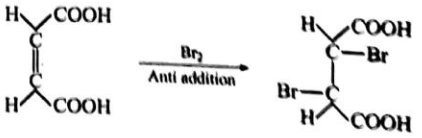
16. (c) Explanation is correct reason for statement.
17. (a) Compounds having $CH_3-\underset{\underset{O}{\|}}{C}-$ unit linked with C or H show haloform reaction. $CH_3-\underset{\underset{O}{\|}}{C}-OH$ has 3α-hydrogen atom but not above structure.
18. (b) No doubt CN^- is stronger nucleophile than Cl^-, but chlorine atom in chlorobenzene is firmly attached to ring due to resonance.
19. (c) $CH_3CH_2CH=CH_2 \xrightarrow{Br_2} CH_3CH_2\overset{\otimes}{\underset{\underset{Br}{|}}{C}}HCH_2Br$

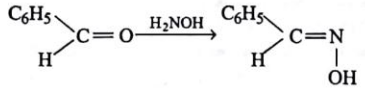
⊗ is asymmetric carbon and thus optical isomerism.

20. (b) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2COOC_2H_5$ does not give iodoform test inspite of $CH_3-\underset{\underset{O}{\|}}{C}-$ unit linked to atom because halogen reacts at acidic H atom in place of CH_3 unit of $CH_3-\underset{\underset{O}{\|}}{C}-$

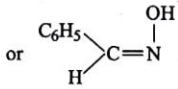
$$CH_3CO\cdot CH_2COOC_2H_5 \xrightarrow[+I_2]{NaOH} CH_3CO\overset{\underset{I}{|}}{C}H\cdot COOC_2H_5$$

21. (c) 
22. (c) The term *anti*-addition represents for the addition of Br_2 *trans*-position to available sites.



23. (c) 

(*Syn*)

or 

(Anti form)

24. (c) Aniline is Lewis base and thus consumes $AlCl_3$ which therefore cannot provide electrophile to develop Friedel-Craft's reaction.

25. (c) In Cannizzaro's reaction,

$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5COONa + C_6H_5CH_2OH$$

26. (c) Explanation is correct reason for statement.

27. (b) Explanation is correct and suggest that borazole is more reactive.

28. (b) Explanation is correct and thus assertion is wrong.

29. (c) Explanation is correct reason for statement.

30. (b) Tertiary butyl benzene has no benzylic hydrogen atom.

31. (b) Glycerol is more viscous than ethanol due to more extensive H-bonding.

32. (c) Explanation is correct reason for statement.

33. (c) Explanation is correct reason for statement.

34. (c) Explanation is correct reason for statement.

35. (c) Explanation is correct reason for statement.

36. (a) S_N1 reaction takes place with carbocation formation whereas S_N2 reactions proceed with transient state. Primary carbocation is less stable than secondary carbocation.

37. (d) Addition of Br_2 on *trans*-2-butene gives *meso*-2, 3-dibromobutane following *anti*-addition, which is however electrophilic one.

38. (c) Explanation is correct reason for statement.

39. (c) $2H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

40. (a) Cyclohexane is higher than water and has boat as well as chair structures.

41. (c) Explanation is correct reason for statement.

42. (b) $(CH_3)_3CBr \xrightarrow{Na} (CH_3)_2C=CH_2$

43. (c) Explanation is correct reason for statement.

44. (c) Explanation is correct reason for statement.

45. (c) Explanation is correct reason for statement.

46. (c) Explanation is correct reason for statement.

47. (c) Explanation is correct reason for statement.

48. (a) CH_3OH is stronger acid than water and rest all alcohols are weaker acids.

49. (c) Explanation is correct reason for statement.

50. (c) Explanation is correct reason for statement.

51. (c) Explanation is correct reason for statement.

52. (b) $-NHCOCH_3$ has lesser activating nature than $-NH_2$ group.

53. (c) Explanation is correct reason for statement.

54. (c) Explanation is correct reason for statement.

55. (c) Explanation is correct reason for statement.

56. (a) Salicyldehyde shows intramolecular H-bonding.

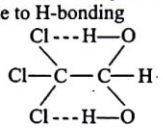
57. (c) Explanation is correct reason for statement.

58. (c) The phenomenon of displacement of electrons by conjugative mechanism involving σ and π-electron is called hyperconjugation. It is arised when alkyl groups having atleast one H atom on the α-carbon atom attached to an unsaturated carbon atom are able to release electrons due to delocalisation of σ and π bond. It is more pronounced if α-H atom are more in number. Thus, stability of alkenes has been explained in terms of hyper conjugation.

59. (b) Organic compounds (NH_2OH is inorganic) *i.e.*, compound of carbon also having nitrogen on fusion forms NaCN which gives violet colour during Lassaigne's test.

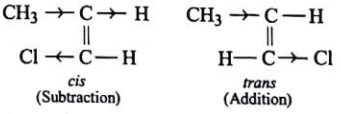
60. (c) The rate of reaction for alkyl halide is $RI > RBr > RCl > RF$ whether it obeys S_N1 or S_N2 mechanism due to steric hindrance of alkyl group.

61. (d) Chloral hydrate is stable inspite of two OH gps on one carbon atom due to H-bonding



62. (b) $KCN + H_2O \rightleftharpoons KOH + HCN$; the HCN formed now shows nucleophilic addition on carbonyl compounds and thus to have hydrolysis constant, the hydrolysis takes place more in forward direction and thus $[OH^-]$ increases or $[H^+]$ decreases, thus pH of solution increases.

63. (d) In presence of acid $-NH_2$ gp. forms $-NH_3^+$, *i.e.*, anilium ion and shows *m*-directing nature. Thus, ring is deactivated for S_E reactions.

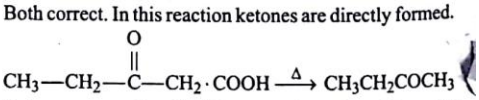
64. (c) 

cis (Subtraction) *trans* (Addition)

65. (b) In aryl halides the halo atoms decrease the electron density on benzene ring. But due to mesomeric effect it donates the electron pair to the benzene ring, therefore C—Cl bond gets partial double bond character.

66. (d) Both are correct. Benzene being non polar dissolves oils which are weak polar.

67. (d) Both correct. In this reaction ketones are directly formed.

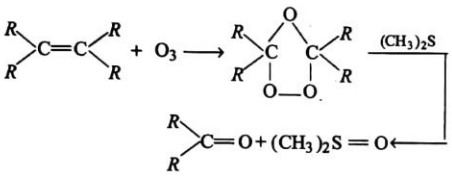


68. (b) Halogen atom of aryl halids cannot be replaced by —OH due to partial double bond character of C—Cl bond.

69. (d) As compared to chlorobenzene, the intermediate carbon ion resulting from 4-nitrochlorobenzene is stabilized by $-R$ effect of the $-NO_2$ gp.

70. (c) Both statement and reason are correct, and statement is an explanation of assertion.

71. (c) It is fact.



72. (c) Explanation is correct reason for statement.

73. (a) Both phenyl gps in biphenyl are of same nature.

74. (a) H-bonding in each forms provides stability.

75. (b) $RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{150\text{-}200} RCONH_2$

76. (b) Canonical forms do not have real existence and thus energy can not be obtained.

77. (b) Pent-2-one and pent-3-one are metamers.

78. (c) Explanation is correct reason for statement.

79. (c) —do—

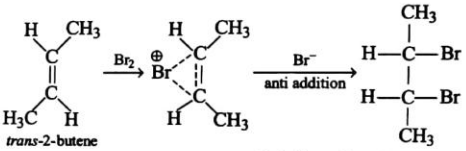
80. (c) —do—

81. (a) The reaction follows $S_{N}2$ mechanism.

82. (d) *o*-nitrophenol shows intramolecular H-bonding *m*- and *p*-isomers show intermolecular H-bonding.

83. (b) More is the stability of anion formed after loss of α-H atom by ketones, more is acidic nature of α-H atom.

84. (d) It is an *anti* addition of Br_2 to alkene.



trans-2-butene

meso-2, 3-dibromobutane

85. (b) $C_6H_5NH_2 + H^+ \longrightarrow C_6H_5NH_3^+$

86. (a) Cu_2O is formed.

87. (b) *p*-hydroxy benzoic acid has higher b.pt. than ortho benzoic acid.

88. (a) 2, 3-pentadiene has no chiral carbon but chiral molecule.

89. (b) Red dye is formed.

90. (a) Bromo group is *ortho*-and *para*-directing. Mesomeric effect is more dominant than the inductive effect.

MATCHING TYPE PROBLEMS

Type I Only One Match Possible

1.

List-A	List-B
(a) Nitrobenzene to hydrazobenzene	1. Sn/HCl
(b) Nitrobenzene to azoxybenzene	2. CH_3OH/CH_3ONa
(c) Nitrobenzene to aniline	3. Zn/NH_4Cl
(d) Nitrobenzene to phenyl hydroxyl amine	4. Zn/KOH

2.

List-A	List-B
(a) Heating glycerol with conc. H_2SO_4	1. Glyoxal as one of the products
(b) Hydrogenation of carbon	2. 2-hydroxy ethanoic acid
(c) Action of glyoxal with NaOH	3. Synthetic petrol
(d) Reductive ozonolysis of ethyne	4. Acrolein

3. (IIT 2007)

List-A	List-B
(A) Cellulose	(p) Natural polymer
(B) Nylon 6,6	(q) Synthetic polymer
(C) Protein	(r) Amide linkage
(D) Sucrose	(s) Glucoside linkage

4. (IIT 2003)

Acid	K_a
(A) Benzoic acid	(p) 6.4×10^{-5}
(B) O_2N—C$_6$H$_4$—COOH	(q) 30.6×10^{-5}
(C) Cl—C$_6$H$_4$—COOH	(r) 10.2×10^{-5}
(D) H_3CO—C$_6$H$_4$—COOH	(s) 3.3×10^{-5}
(E) H_3C—C$_6$H$_4$—COOH	(t) 4.2×10^{-5}

5.

X	*Y*
(A) Williamson's synthesis	(p) *tert*-alcohol
(B) Neutral $FeCl_3$ test	(q) Ether
(C) Lucas test	(r) Phenol

TYPE II More Than One Match Are Possible

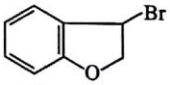
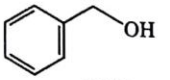
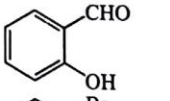
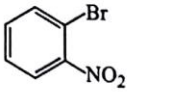
6. (IIT 2006)

Column-I	Column-II
(A) H_2N—$\overset{+}{N}H_3\,\overset{-}{Cl}$	(p) Sodium fusion extract of the compound gives prussion blue colour with $FeSO_4$
(B) HO—C$_6$H$_4$($\overset{+}{N}H_3I$)—COOH	(q) Gives positive $FeCl_3$ test
(C) HO—C$_6$H$_4$—$\overset{+}{N}H_3\bar{C}l$	(r) Gives white ppt with $AgNO_3$
(D) O_2N—C$_6$H$_3$(—NH$\overset{+}{N}H_3\bar{B}r$)—$NO_2$	(s) Reacts with aldehyde to form corresponding hydrazone derivative

7. Match the compounds/ions in Column I with their properties/reactions in Column II. (IIT 2007)

Column-I	Column-II
(A) C_6H_5CHO	(p) gives precipitate with 2, 4-dinitrophenylhydrazine
(B) $CH_3C\equiv CH$	(q) gives precipitate with $AgNO_3$
(C) CN^-	(r) is a nucleophile
(D) I^-	(s) is involved in cyanohydrin formation

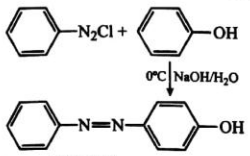
8. (IIT 2009)

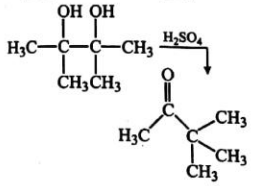
Column-I	Column-II
(A) 	(p) Nucleophilic substitution
(B) 	(q) Elimination
(C) 	(r) Nucleophilic addition
(D) 	(s) Esterification with acetic anhydride
	(t) Dehydrogenation

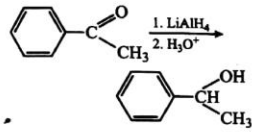
9. (IIT 2009)

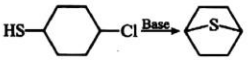
Column-I	Column-II
(A) $CH_3CH_2CH_2CN$	(p) Reduction with Pd–C/H_2
(B) $CH_3CH_2OCOCH_3$	(q) Reduction with $SnCl_2$/HCl
(C) CH_3—CH=CH—CH_2OH	(r) Development of foul smell on treatment with chloroform and alcoholic KOH
(D) $CH_3CH_2CH_2CH_2NH_2$	(s) Reduction with diisobutyl aluminium hydride (DIBAL-H)
	(t) Alkaline hydrolysis

10. **Column-I** **Column-II** **(IIT 2010)**

(A)  (p) Racemic mixture

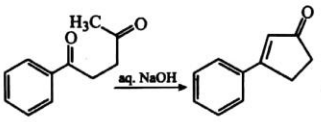
(B)  (q) Addition reaction

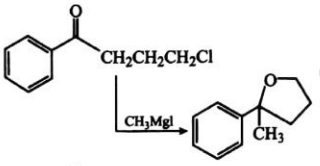
(C)  (r) Substitution reaction

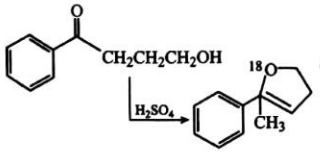
(D)  (s) Coupling reaction

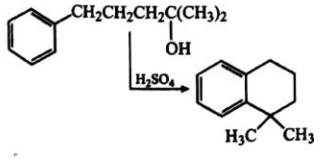
(t) Carbocation intermediate

11. **Column-I** **Column-II** **(IIT 2011)**

(A)  (p) Nucleophilic substitution

(B)  (q) Electrophilic substitution

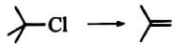
(C)  (r) Dehydration

(D)  (s) Nucleophilic addition

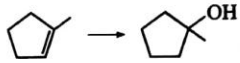
(t) Carbanion

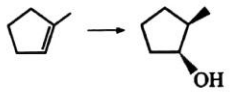
12. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists :

List I **List II**

(P)  (1) (i) $Hg(OAc)_2$; (ii) $NaBH_4$

(Q) (2) NaOEt

(R)  (3) Et—Br

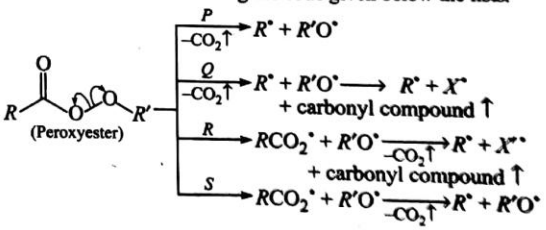
(S)  (4) (i) BH_3; (ii) H_2O_2/NaOH

[JEE (Advanced) II 2013]

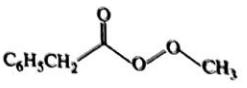
Codes:

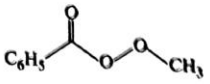
	P	*Q*	*R*	*S*
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

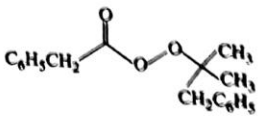
13. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from List-I with an appropriate structure from List-II and select the correct answer using the code given below the lists.

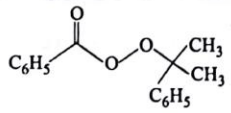


List- I **List-II**

P. Pathway *P* 1. 

Q. Pathway *Q* 2. 

R. Pathway *R* 3. 

S. Pathway *S* 4. 

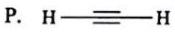
[JEE (Advanced) II 2014]

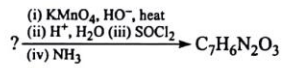
Codes:

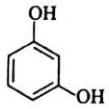
	P	*Q*	*R*	*S*
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

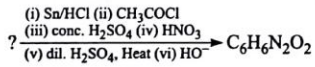
14. Match the four starting materials (P, Q, R, S) given in List-I with the corresponding reaction schemes (I, II, III, IV) provided in List-II and select the correct answer using the code given below the lists.

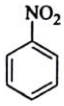
List-I **List-II**

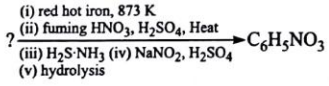
P.  1. Scheme I

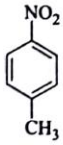


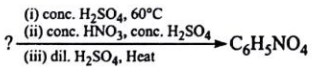
Q.  2. Scheme II



R.  3. Scheme III



S.  4. Scheme IV



Codes:

	P	*Q*	*R*	*S*
(a)	1	4	2	3
(b)	3	1	4	2
(c)	3	4	2	1
(d)	4	1	3	2

Q. 15, 16 and 17 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contains starting materials, reaction conditions, and type of reactions, respectively.

Column-1	Column-2	Column-3
(I) Toluene	(i) $NaOH/Br_2$	(P) Condensation
(II) Acetophenone	(ii) $Br_2/h\nu$	(Q) Carboxylation
(III) Benzaldehyde	(iii) $(CH_3CO)_2O/CH_3COOK$	(R) Substitution
(IV) Phenol	(iv) $NaOH/CO_2$	(S) Haloform

15. For the synthesis of benzoic acid, the only correct combination is :
(a) (III) (iv) (R) (b) (IV) (ii) (P)
(c) (I) (iv) (Q) (d) (II) (i) (S)

16. The only correct combination in which the reaction proceeds through radical mechanism is :
(a) (I) (ii) (R) (b) (II) (iii) (R)
(c) (III) (ii) (P) (d) (IV) (i) (Q)

17. The only correct combination that gives two different carboxylic acids is :
(a) (IV) (iii) (Q) (b) (III) (iii) (P)
(c) (II) (iv) (R) (d) (I) (i) (S)

ANSWERS

1. a – 4; b – 2; c – 1; d – 3
2. a – 4; b – 3; c – 2; d – 1
3. A – p; B – q; C – r; D – s
4. A – p; B – q; C – r; D – s; E – t
5. A – q; B – s; C – p.
6. A – r, s; B – p, q; C – p, q, r; D – p, s
7. A – p, s; B – q; C – q, r, s; D – q, r
8. A – p, q, t; B – p, s, t; C – r, s; D – p
9. A – p, q, s, t; B – s, t; C – p; D – r
10. A – r, s, t; B – t; C – p, q; D – r
11. A – r, s, t; B – p, s; C – r, s; D – q, r
12. (a) P – 2, Q – 3, R – 1, S – 4
13. (a) P – 1, Q – 3, R – 4, S – 2
14. (c) P – 3, Q – 4, R – 2, S – 1
15. (d) (II), (i), (S)
16. (a) (I), (ii), (R)
17. (b) (III), (iii), (P)

20 Qualitative Estimations

In order to identify a given inorganic compound, following tests characterise different radicals in it.

Test for acid radicals:

[A] Add dil. HCl or H_2SO_4 to a small amount of substance and warm gently, observe.

Carbonate or CO_3^{2-}:

(i) Brisk effervescences of colourless gas CO_2; may be carbonate.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2 \uparrow$$

(ii) The gas turns lime water milky.

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Milky}}{CaCO_3 \downarrow} + H_2O$$

(iii) Excess of passage of gas through lime water disappears milkyness.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2 \quad \text{(Soluble)}$$

Sulphite or SO_3^{2-}:

(i) Colourless gas with suffocating odour of burning sulphur; may be sulphite.

$$CaSO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + SO_2 \uparrow$$

(ii) The gas turns moistened paper with acidified $K_2Cr_2O_7$ green.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$$

(iii) The sulphites also give white ppt. with $BaCl_2$, soluble in dil. HCl.

$$Na_2SO_3 + BaCl_2 \longrightarrow 2NaCl + BaSO_3 \downarrow$$

Sulphide or S^{2-}:

(i) Colourless gas with rotten egg smell, may be sulphide.

$$CaS + H_2SO_4 \longrightarrow CaSO_4 + H_2S \uparrow$$

(ii) The gas turns lead acetate paper black.

$$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{Black}}{PbS \downarrow} + 2CH_3COOH$$

(iii) The sulphide also turns sodium nitroprusside solution violet.

$$Na_2S + Na_2[FeNO(CN)_5] \longrightarrow \underset{\text{Violet}}{Na_4[Fe(NOS)(CN)_5]}$$

Acetate or CH_3COO^-:

(i) Smell of vinegar comes out, may be acetate.

$$(CH_3COO)_2Ca + H_2SO_4 \longrightarrow \underset{\text{Vinegar smell}}{2CH_3COOH} + CaSO_4$$

(ii) The acetate gives blood red colour with neutral $FeCl_3$ solution.

$$3(CH_3COO)_2Ca + 2FeCl_3 \longrightarrow 2Fe(CH_3COO)_3 + 3CaCl_2$$

Nitrite or NO_2^-:

(i) Reddish, brown vapours of NO_2 comes out, may be nitrite.

$$2KNO_2 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_2$$
$$3HNO_2 \longrightarrow HNO_3 + 2NO \uparrow + H_2$$
$$2NO + O_2 \longrightarrow 2NO_2 \uparrow$$

(ii) The gas turns acidified KI + starch paper blue.

$$2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2 \uparrow$$
$$\text{Starch} + I_2 \longrightarrow \text{Blue colour}$$

[B] Add concentrated H_2SO_4 to a small amount of the substance and warm gently, observe.

Chloride or Cl^-:

(i) Colourless fuming gas (HCl) with pungent smell; may be chloride.

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl \uparrow$$

(ii) The chlorides give white precipitate with $AgNO_3$, soluble in NH_4OH.

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl \downarrow} + NaNO_3$$
$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{Ag(NH_3)_2Cl} + 2H_2O$$

(iii) Chlorides also give **chromyl chloride test**—On heating chloride salt with $K_2Cr_2O_7$ and concentrated H_2SO_4, orange-red vapours of chromyl chloride (CrO_2Cl_2) come out which on passing in NaOH gives yellow solution of Na_2CrO_4. Acidified solution of Na_2CrO_4 gives yellow precipitate with $(CH_3COO)_2Pb$.

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow 2CH_3COONa + \underset{\text{Yeilow ppt.}}{PbCrO_4\downarrow}$$

Note : Chlorides of Hg, Ag, Pb and Sn do not give chromyl chloride test.

Bromide or Br^-:

(i) Brown vapours come out; may be bromide or nitrate.

$$2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2\uparrow + 2H_2O + SO_2\uparrow$$

(ii) The bromides give light yellow precipitate, partially soluble in NH_4OH.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{Light yellow}}{AgBr\downarrow} + NaNO_3$$

(iii) Brown vapours of Br_2 on passing in H_2O give brown colour whereas of NO_2 does not impart colour to water.

Iodide or I^-:

(i) Dark violet fumes (I_2) come out; may be iodide.

$$2NaI + H_2SO_4 \longrightarrow Na_2SO_4 + 2HI$$

$$2HI + H_2SO_4 \longrightarrow I_2\uparrow + 2H_2O + SO_2\uparrow$$

(ii) Iodides give yellow precipitate with $AgNO_3$; insoluble in NH_4OH.

$$NaI + AgNO_3 \longrightarrow \underset{\text{Yellow}}{AgI\downarrow} + NaNO_3$$

Note : Sodium carbonate extract of bromide and iodide on addition of $CHCl_3$ and Cl_2 water gives brown or violet layer to $CHCl_3$ respectively.

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2;$$

$$Br_2 + CHCl_3 \longrightarrow \text{Brown colour}$$

$$2NaI + Cl_2 \longrightarrow 2NaCl + I_2;$$

$$I_2 + CHCl_3 \longrightarrow \text{Violet colour}$$

Nitrate or NO_3^-:

(i) Brown fumes come out; may be nitrate.

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

$$4HNO_3 \longrightarrow 2H_2O + O_2 + 4NO_2\uparrow$$

(ii) **Ring test:** An aqueous solution of salt (all nitrates are water soluble) is mixed with freshly prepared $FeSO_4$ and concentrated H_2SO_4 is poured in test tube from sides, brown ring is developed at the junction of two solutions.

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

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$FeSO_4 + NO \longrightarrow \underset{\text{Brown ring}}{Fe(NO)SO_4}$$

Oxalate or $C_2O_4^{2-}$:

(i) Colourless gases ($CO + CO_2$) come out.

$$Na_2C_2O_4 + H_2SO_4 \longrightarrow H_2O + CO + CO_2 + Na_2SO_4$$

(ii) These gases burn with blue flame at the mouth of test tube.

$$2CO + O_2 \longrightarrow 2CO_2$$

(iii) A solution of oxalates gives white precipitate with $CaCl_2$ solution. This precipitate gets dissolved in dil. H_2SO_4 and decolourises $KMnO_4$ (acidified) solution.

$$Na_2C_2O_4 + CaCl_2 \longrightarrow \underset{\text{White}}{CaC_2O_4\downarrow} + 2NaCl$$

$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

[C] Sulphate or SO_4^{2-}:

Add concentrated HNO_3 to a small amount of substance, heat and then add $BaCl_2$; white precipitate insoluble in any acid or alkali, sulphate is confirmed.

$$Na_2SO_4 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{White}}{BaSO_4\downarrow} + 2HCl$$

[D] Phosphate or PO_4^{3-}:

Add concentrated HNO_3 to a small amount of substance, heat and then add ammonium molybdate; canary yellow precipitate confirms the presence of phosphate.

$$Na_3PO_4 + 3HNO_3 \longrightarrow 3NaNO_3 + H_3PO_4$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{Yellow ppt.}}{(NH_4)_3PO_4.12MoO_3\downarrow} + 12H_2O + 21NH_4NO_3$$

Test for basic radicals:

[A] I group: Hg^+, Ag^+ and Pb^{2+}:

(i) Add dil. HCl to clear solution of substance. White precipitate indicates the presence of Hg^+, Ag^+ or Pb^{2+}.

$$2HgNO_3 + 2HCl \longrightarrow Hg_2Cl_2\downarrow + 2HNO_3$$

$$AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$$

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2\downarrow + 2HNO_3$$

(ii) Pb^{2+} ions give yellow precipitate with K_2CrO_4 and KI separately.

$$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{Yellow}}{PbCrO_4\downarrow} + 2KCl$$

$$PbCl_2 + 2KI \longrightarrow \underset{\text{Yellow}}{PbI_2\downarrow} + 2KCl$$

(iii) Hg^+ ions give black precipitate with NH_3.

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Black}}{Hg(NH_2)Cl} + Hg\downarrow + NH_4Cl + 2H_2O$$

(iv) Ag^+ ions give yellow precipitate with KI.

$$Ag^+ + I^- \longrightarrow \underset{\text{Yellow}}{AgI\downarrow}$$

[B] II group: Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, As^{3+}, Sb^{3+}, Sn^{2+} and Sn^{4+}:

(i) On passing H_2S in presence of HCl to a solution containing these ions give:

Yellow ppt. : CdS, As_2S_3, SnS_2
Orange ppt. : Sb_2S_3
Brown ppt. : SnS
Black ppt. : HgS, PbS, Bi_2S_3, CuS

(ii) Hg^{2+} ions in solution, on addition of $SnCl_2$, give white precipitate turning black.

$$2Hg^{2+} + SnCl_2 \longrightarrow Sn^{4+} + \underset{\text{White}}{Hg_2Cl_2\downarrow}$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{Black}}{Hg_2\downarrow}$$

(iii) (a) Pb^{2+} ions in solution give white precipitate with H_2SO_4.

$$Pb^{2+} + H_2SO_4 \longrightarrow PbSO_4 + 2H^+$$

(b) Pb^{2+} ions in solution give yellow precipitate with K_2CrO_4 and KI.

$$Pb^{2+} + CrO_4^{2-} \longrightarrow \underset{\text{Yellow}}{PbCrO_4\downarrow}$$

$$Pb^{2+} + 2I^{1-} \longrightarrow \underset{\text{Yellow}}{PbI_2\downarrow}$$

(iv) Cu^{2+} ions in solution give deep blue colour with excess of NH_4OH.

$$Cu^{2+} + 4NH_4OH \longrightarrow \underset{\text{Deep blue in colour}}{Cu(NH_3)_4^{2+}} + 4H_2O$$

(v) Cu^{2+} ions give chocolate precipitate with $K_4Fe(CN)_6$.

$$2Cu^{2+} + K_4Fe(CN)_6 \longrightarrow Cu_2[Fe(CN)_6] + 4K^+$$

(vi) Bi^{3+} ions in solution of HCl on addition of water give white cloudy precipitate.

$$BiCl_3 + H_2O \longrightarrow \underset{\text{White ppt.}}{BiOCl\downarrow} + 2HCl$$

(vii) Cd^{2+} ions in solution, with H_2S give yellow precipitate.

$$Cd^{2+} + H_2S \longrightarrow \underset{\text{Yellow}}{CdS} + 2H^+$$

(viii) As^{3+} ions in solution give yellow precipitate with ammonium molybdate and HNO_3.

$$As^{3+} \xrightarrow[\text{Oxidation}]{HNO_3} As^{5+} \text{ (as } H_3AsO_4)$$

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{Yellow ppt.}}{(NH_4)_3AsMo_{12}O_{40}\downarrow} + 21NH_4NO_3 + 12H_2O$$

(ix) Sn^{2+} ions in solution as $SnCl_2$ give white precipitate with $HgCl_2$, turning black on standing.

$$SnCl_2 + 2HgCl_2 \longrightarrow SnCl_4 + \underset{\text{White}}{Hg_2Cl_2\downarrow}$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl + \underset{\text{Black}}{Hg_2\downarrow}$$

(x) Sb^{3+} ions in solution as $SbCl_3$, on addition of water give white precipitate.

$$SbCl_3 + H_2O \longrightarrow \underset{\text{White}}{SbOCl\downarrow} + 2HCl$$

[C] III group: Fe^{3+}, Cr^{3+} and Al^{3+}:

(i) These ions are precipitated as hydroxides on addition of NH_4Cl and NH_4OH.

$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$ Red ppt.
$Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3$ Green ppt.
$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3$ White ppt.

(ii) White precipitate of $Al(OH)_3$ is soluble in NaOH.

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

(iii) Precipitate of $Cr(OH)_3$ is soluble in $NaOH + Br_2$ water and addition of $BaCl_2$ to this solution gives yellow precipitate.

$$Br_2 + H_2O \longrightarrow 2HBr + O$$
$$2Cr(OH)_3 + 4NaOH + 3O \longrightarrow 2Na_2CrO_4 + 5H_2O$$
$$Na_2CrO_4 + BaCl_2 \longrightarrow \underset{\text{Yellow ppt.}}{BaCrO_4\downarrow} + 2NaCl$$

(iv) Brown precipitate of $Fe(OH)_3$ is dissolved in HCl and addition of KCNS to this solution gives blood red colour.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$
$$FeCl_3 + 3KCNS \longrightarrow Fe(CNS)_3 + 3KCl$$

Also on addition of $K_4Fe(CN)_6$ to this solution, a prussian blue colour is obtained.

$$FeCl_3 + 3K_4Fe(CN)_6 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$

[D] IV group : Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}:

(i) These ions are precipitated as sulphides on passing H_2S in presence of NH_4OH.

$$MCl_2 + H_2S \longrightarrow MS\downarrow + 2HCl$$

CoS and NiS : Black Soluble in aqua regia
ZnS : White Soluble in HCl
MnS : Pink Soluble in HCl

(ii) Ni^{2+} and Co^{2+} ions in solution, on addition of $KHCO_3$ and Br_2 water give apple green colour if Co^{2+} is present and black precipitate if Ni^{2+} is present.

$$CoCl_2 + 6KHCO_3 \longrightarrow K_4[Co(CO_3)_3] + 2KCl + 3CO_2\uparrow + 3H_2O$$
$$2K_4[Co(CO_3)_3] + 2KHCO_3 + [O] \longrightarrow \underset{\text{Apple green colour}}{2K_3[Co(CO_3)_3]} + 2K_2CO_3 + H_2O$$
$$NiCl_2 + 2KHCO_3 \longrightarrow NiCO_3 + 2KCl + H_2O + CO_2\uparrow$$
$$2NiCO_3 + 4NaOH + [O] \longrightarrow \underset{\text{Black ppt.}}{Ni_2O_3\downarrow} + 2Na_2CO_3 + 2H_2O$$

(iii) Zn^{2+} ions in solution give white precipitate with NaOH, which dissolve in excess of NaOH.

$$Zn^{2+} + 2NaOH \longrightarrow \underset{\text{White}}{Zn(OH)_2\downarrow} + 2Na^+$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Soluble}}{Na_2ZnO_2} + 2H_2O$$

(iv) Mn^{2+} ions in solution give pink precipitate with NaOH turning black or brown on heating.

$$Mn^{2+} + 2NaOH \longrightarrow \underset{\text{Pink}}{Mn(OH)_2} + 2Na^+$$

$$Mn(OH)_2 + [O] \xrightarrow{\Delta} \underset{\text{Brown or black}}{MnO_2} + H_2O$$

[E] V group: Ba^{2+}, Sr^{2+} and Ca^{2+}.

(i) These ions are precipitated as carbonates on addition of $(NH_4)_2CO_3$ solution.

$$M^{2+} + (NH_4)_2CO_3 \longrightarrow MCO_3 + 2NH_4^+$$

$BaCO_3$, $CaCO_3$ and $SrCO_3$: White; Soluble in CH_3COOH

(ii) Ba^{2+} ions in solution give:

(a) Yellow precipitate with K_2CrO_4.

$$Ba^{2+} + K_2CrO_4 \longrightarrow \underset{\text{Yellow}}{BaCrO_4\downarrow} + 2K^+$$

(b) White precipitate with $(NH_4)_2SO_4$.

$$Ba^{2+} + (NH_4)_2SO_4 \longrightarrow \underset{\text{White}}{BaSO_4\downarrow} + 2NH_4^+$$

(c) White precipitate with $(NH_4)_2C_2O_4$.

$$Ba^{2+} + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White}}{BaC_2O_4\downarrow} + 2NH_4^+$$

(iii) Sr^{2+} ions give white precipitate with:

(a) $(NH_4)_2SO_4$

$$Sr^{2+} + (NH_4)_2SO_4 \longrightarrow \underset{\text{White ppt.}}{SrSO_4\downarrow} + 2NH_4^+$$

(b) $(NH_4)_2C_2O_4$

$$Sr^{2+} + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White ppt.}}{SrC_2O_4\downarrow} + 2NH_4^+$$

(iv) Ca^{2+} ions give white precipitate with only $(NH_4)_2C_2O_4$.

$$Ca^{2+} + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White}}{CaC_2O_4\downarrow} + 2NH_4^+$$

(F) VI group: Mg^{2+}

Mg^{2+} ions give white precipitate with NH_4OH and $(NH_4)_2HPO_4$.

$$Mg^{2+} + (NH_4)_2HPO_4 + NH_4OH \longrightarrow MgNH_4PO_4\downarrow + 2NH_4^+ + H_2O$$

(G) Zero group: NH_4^+

(i) All ammonium salts on treating with any alkali (say NaOH) give smell of NH_3.

$$NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3\uparrow + H_2O$$

(ii) The gas coming out (NH_3) shows white fumes with HCl.

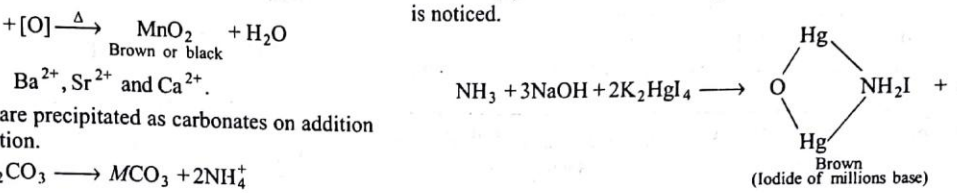
$$NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl\uparrow}$$

(iii) On passing this gas to:

(a) $Hg_2(NO_3)_2$, a black colour is formed.

$$Hg_2(NO_3)_2 + 2NH_3 \longrightarrow \underset{\text{Black}}{Hg + Hg(NH_2)\cdot NO_3} + NH_4NO_3$$

(b) With Nessler's reagent, a brown precipitate is noticed.



Some general hints on the basis of characteristics of anions and cations present in inorganic substances:

1. Physical appearance of inorganic salts :

(a) Cu^{2+} salts are blue in colour.

(b) Cr^{3+} and Cr^{6+} salts are generally dark green.

(c) Fe^{2+} salts are green Fe^{3+} salts are yellow or brown.

(d) Mn^{2+} salts are light pink.

(e) Co^{2+} salts are pink, Ni^{2+} salts are green or blue.

(f) HgO, HgI_2 and Pb_3O_4 are red in colour.

(g) Salts of Pb, Hg and Ba are relatively heavier.

(h) The colours of some important compounds are given below:

Colour	Examples
Blue	Copper salts, *e.g.*, $CuSO_4\cdot 5H_2O$, some anhydrous cobaltous salts and some complex salts : $[Co(SCN)_4]^{2-}$, $Fe_3[Fe(CN)_6]_2$, $Fe_4[Fe(CN)_6]_3$, $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]^{2+}$ etc.
Dark green	Chromium salts (Cr^{3+} and Cr^{6+}), *e.g.*, $Cr_2(SO_4)_3$ and some copper salts : $CuCl_2$, $Cu(C_2H_3O_2)_2$, $Cu_3(AsO_3)_2$; Manganese oxides : MnO, MnO_4^{2-}.
Yellow	Ferric salts : $FeCl_3$, $[Fe(CN)_6]^{4-}$; silver salts : AgBr, AgI, Ag_2S_3, Ag_2S_5, Ag_2CO_3, Ag_3PO_4, Ag_3AsO_3; PbO, PbI_2; S, As_2S_3, As_2S_5, CdS, SnS_2; $K_3[Co(NO_2)_6]$; Na_2CrO_4, $PbCrO_4$, $BaCrO_4$.
Red	HgO, HgI_2, Hg_2CrO_4; Ag_2CrO_4, Ag_3AsO_4; Cu_2O; SbI_3, Sb_2S_3; SnI_2; AsI_3; Fe_2O_3; Pb_3O_4; BiOI.
Black	FeO, FeS, Fe_3O_4; CoS; CuO, CuS, Cu_2S; Ag_2S; NiO, NiS; MnO_2; HgS; PbS; BiI_3.
Pink	Salts of CO, complex of Ni with dimethyl glyoxime.
Brown	$Fe_2(CrO_4)_3$; $CuCrO_4$; $Hg_2[Fe(CN)_6]$; Bi_2O_5; Bi_2S_3; $MnCO_3$; SnS; $SnCrO_4$; CdO; PbO_2; $Cu_2[Fe(CN)_6]$.

2. Solubility of salts:

(a) Nitrates and Nitrites of all the metals are water soluble.

(b) All sulphates except (Pb, Ba and Sr) are water soluble. $CaSO_4$ is slightly soluble in water.

(c) Halides of Ag, Pb, Hg(ous) and Cu(ous) are insoluble. The order of solubility is:

Fluoride > Chloride > Bromide > Iodide

(d) CaF_2 is insoluble, other halides of Ca are soluble.

(e) Some common insoluble substances with their colours are given below:

S.No.	Examples of some insoluble salts	Colour
1.	CaF_2, $BaSO_4$, $SrSO_4$, Sb_2O_3, Al_2O_3, SnO_2, SiO_2, AgCl, $PbSO_4$	White
2.	HgS	Black
3.	Fe_2O_3	Red
4.	$PbCrO_4$, AgBr, AgI	Yellow
5.	Cr_2O_3, $Cr_2(SO_4)_3$	Green
6.	$CrCl_3$	Violet

3. Action of heat:

(a) All carbonates except (Na, K, Rb and Cs) decompose on heating, giving CO_2.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$$

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2\uparrow$$

(b) All bicarbonates decompose to give carbonates and CO_2.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

(c) Halides are normally stable to heat, however some halides decompose as:

$$2FeCl_3 \xrightarrow{\Delta} 2FeCl_2 + Cl_2$$

$$AuCl_3 \xrightarrow{\Delta} AuCl + Cl_2$$

$$MgCl_2 \cdot 6H_2O \xrightarrow{\text{Strong heating}} MgO + 2HCl + 5H_2O$$

$$Hg_2Cl_2 \xrightarrow{\Delta} HgCl_2 + Hg$$

$$NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$$

(d) Nitrates decompose on heating.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

$$2MNO_3 \longrightarrow 2MNO_2 + O_2 \quad \text{(except Li)}$$

$$2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$$

$$\left.\begin{aligned} 2Mg(NO_3)_2 &\longrightarrow 2MgO + 4NO_2 + O_2 \\ 2Cu(NO_3)_2 &\longrightarrow 2CuO + 4NO_2 + O_2 \end{aligned}\right\}$$

(all bivalent nitrates except Hg)

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

$$Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2$$

(e) Silver salt on heating gives Ag.

$$Ag_2CO_3 \longrightarrow 2Ag + CO_2 + \frac{1}{2}O_2$$

(f) Some hydrated halides decompose to give oxy-salts.

$$2MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO \cdot MgCl_2 + 2HCl + 11H_2O$$

$$MgCl_2 \cdot 6H_2O \xrightarrow[\text{Heating}]{\text{Strong}} MgO + 2HCl + 5H_2O$$

$$2FeCl_3 \cdot 6H_2O \xrightarrow{\Delta} Fe_2O_3 + 6HCl + 9H_2O$$

$$\underset{\text{Pink}}{CoCl_2 \cdot 6H_2O} \xrightarrow{50^\circ C} \underset{\text{Pink}}{CoCl_2 \cdot 4H_2O} \xrightarrow{58^\circ C}$$

$$\underset{\text{Red-Violet}}{CoCl_2 \cdot 2H_2O} \xrightarrow{140^\circ C} \underset{\text{Blue}}{CoCl_2}$$

$$2CdI_2 + O_2 \xrightarrow{\Delta} 2CdO + 2I_2$$

$$2CdBr_2 + O_2 \xrightarrow{\Delta} 2CdO + 2Br_2$$

(g) **Alkali and alkaline earth metal bicarbonates** on heating decompose to give the respective metal carbonates and CO_2.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + CO_2 + H_2O$$

$$2KHCO_3 \xrightarrow{\Delta} K_2CO_3 + CO_2 + H_2O$$

(h) Metal sulphides on strong heating gives metal oxides and SO_2.

$$4FeS + 7O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 4SO_2$$

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

(i) Some metal sulphates on heating decompose to metal oxides.

$$\underset{\text{Blue-vitriol}}{CuSO_4 \cdot 5H_2O} \xrightarrow{100^\circ C} CuSO_4 \cdot H_2O + 4H_2O$$

$$CuSO_4 \cdot H_2O \xrightarrow{300^\circ C} CuO + SO_3 + H_2O$$

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$$

$$\underset{\text{Epsom salt}}{MgSO_4 \cdot 7H_2O} \xrightarrow{\Delta} MgSO_4 + 7H_2O$$

$$\underset{\text{Gypsum}}{2CaSO_4 \cdot 2H_2O} \xrightarrow{\Delta,\ 120^\circ C} 2CaSO_4 \cdot H_2O + 3H_2O$$

$$2CaSO_4 \cdot H_2O \xrightarrow{\Delta} 2CaSO_4 + H_2O$$

$$2NaHSO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_3$$

(j) Thiosulphates on strong heating decomposes as follows:

$$Na_2S_2O_3 \cdot 5H_2O \xrightarrow{220°C} Na_2S_2O_3 + 5H_2O$$

$$4Na_2S_2O_3 \xrightarrow{230°C} 3Na_2SO_4 + Na_2S_5$$

(k) Ammonium dichromate on heating yields N_2 and Cr_2O_3.

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

4. Characteristic flame colour and other properties of some metals:

(a) Pb imparts pale greenish colour to flame.

(b) Ag turns black in light due to the formation of Ag_2O.

(c) Cu salts impart blue or green colour to flame. Also BO_3^{3-} does so.

(d) Cu^{2+} ions in presence of NH_4OH impart blue colour to solution.

(e) ZnO turns yellow on heating and white on cooling.

(f) Zn^{2+} ions give light blue ppt. with $K_4Fe(CN)_6$.

$$2(CH_3COO)_2Zn + K_4Fe(CN)_6 \longrightarrow Zn_2[Fe(CN)_6] + 4K^+$$

(g) Ba imparts apple green colour to flame.

(h) Sr imparts crimson red colour to flame.

(i) Ca imparts brick red colour to flame.

(j) Na imparts yellow colour to flame.

(k) K imparts pink-violet (lilac) colour to flame.

(l) The white salt with colourless solution cannot have Cu, Ni, Co, Fe, Mn, Cr.

(m) The substance which swells up are alums, borates and phosphates.

(n) The substances sublime and the colour of sublimate is:

White	$HgCl_2$, Hg_2Cl_2, As_2O_3, Sb_2O_3
Yellow	$AlCl_3$ and NH_4 halides
Grey	HgO, $Hg(NO_3)_2$
Blue, black and violet	Iodides
Black	As, Sb, Hg sulphides and iodides.

• NUMERICAL PROBLEMS •

1. A compound on heating with an excess of caustic soda solution liberates a gas (*B*), which gives white fumes on exposure to HCl. Heating is continued to expel the gas completely. The resultant alkaline solution again liberates the same gas (*B*), when heated with zinc powder. However, the compound (*A*), when heated alone, does not give nitrogen. Identify (*A*) and (*B*).
2. An aqueous solution of a salt (*A*) gives a white crystalline precipitate (*B*) with NaCl solution. The filtrate gives a black precipitate (*C*) when H_2S is passed into it. Compound (*B*) dissolves in hot water and the solution gives yellow precipitate (*D*) on treatment with sodium iodide and cooling. The compound (*A*) does not give any gas with dilute HCl but liberates a reddish brown gas on heating. Identify the compounds (*A*) to (*D*) and give an equation for the liberation of the reddish brown gas.
3. An unknown solid mixture contains one or two of the following: $CaCO_3$, $BaCl_2$, $AgNO_3$, Na_2SO_4, $ZnSO_4$ and NaOH. The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to the above solution, a precipitate is formed which dissolves with further addition of the acid. What is/are present in the solid?
   Give equations to explain the appearance of the precipitate and its dissociation.
4. A mixture of two salts was treated as follows:
   (i) The mixture was heated with manganese dioxide and concentrated sulphuric acid, when yellowish green gas was liberated.
   (ii) The mixture on heating with sodium hydroxide solution gave a gas which turned red litmus blue.
   (iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocynate.
   (iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate. Identify the two salts. Give ionic equations for reactions involved in the tests (i), (ii) and (iii).
5. A compound (*A*) is greenish crystalline salt, which gave the following results:
   (i) Addition of $BaCl_2$ solution to the solution of (*A*) results in the formation of a white ppt. (*B*), which is insoluble in dil. HCl.
   (ii) On heating (*A*), water vapours and two oxides of sulphur, (*C*) and (*D*) are liberated leaving a red brown residue (*E*).
   (iii) (*E*) dissolves in warm conc. HCl to give a yellow solution (*F*).
   (iv) With H_2S, the solution (*F*) yields a pale yellow ppt. (*G*), which when filtered leaves a greenish filtrate (*H*).
   (v) Solution (*F*) on treatment with thiocyanate ions gives blood red coloured compound (*I*).
   Identify the substances from (*A*) to (*I*).
6. To a solution containing Ca^{2+}, Ag^+, Cu^{2+} and K^+, 2*M* HCl is added when a white precipitate (*A*) is obtained. After filtration H_2S is passed through the filtrate, a black ppt. (*B*) is formed. On removing (*B*) by filtration, it gave white ppt. (*C*) with conc. Na_2CO_3 solution. Identify (*A*), (*B*) and (*C*).
7. A gaseous mixture containing (*X*), (*Y*) and (*Z*) gases, when passed into acidified $K_2Cr_2O_7$ solution, gas (*X*) was absorbed and the solution was turned green. The remainder gas mixture was then passed through lime water, which turns milky by absorbing gas (*Y*). The residual gas when passed through alkaline pyrogallol solution, it turned black. Identify gas (*X*), (*Y*) and (*Z*) and explain the reaction involved.
8. When 16.8 g of a white solid (*X*) were heated, 4.4 g of a gas (*A*) that turned lime water milky was driven off together with 1.8 g of a gas (*B*), which condensed to a colourless liquid. The solid that remained (*Y*), dissolved in water to give an alkaline solution, which with excess of $BaCl_2$ solution gave a white ppt. (*Z*). The precipitate effervesced with acid giving off CO_2. Identify (*A*), (*B*) and (*Y*) and write down the equation for thermal decomposition (*X*).
9. When 20.02 g of a white solid (*X*) is heated, 4.4 g of an acid gas (*A*) and 1.8 g of a neutral gas (*B*) are evolved leaving behind a solid residue (*Y*) of mass 13.8 g. (*A*) turns lime water milky and (*B*) condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of (*Y*) is alkaline to litmus and gives 19.7 g of white precipitate (*Z*) with barium chloride solution. (*Z*) gives carbon dioxide with an acid. Identify (*A*), (*B*), (*X*), (*Y*) and (*Z*).
10. The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of K_2HgI_4. The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4, red vapours (*A*) are produced. The aqueous solution of the mixture gives a deep blue colouration (*B*) with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of (*A*) and (*B*). **(IIT 1991)**

11. Write the balanced equations for the following:
(i) Excess of ammonia added to a solution of $HgCl_2$ in water.
(ii) $AgNO_3$ solution reacts with excess of KCNS.
(iii) Reaction of potassium ferrocyanide in concentrated solution with 50% HNO_3.
(iv) Reaction of red lead with nitric acid.
(v) Reaction of sodium hydride with methyl borate in tetrahydrofuran (THF).

12. A light bluish green crystalline solid responds the following tests :
(i) Its aqueous solution gives brown precipitate or colour with alkaline K_2HgI_4 solution.
(ii) Its aqueous solution gives blue colour with $K_3Fe(CN)_6$ solution.
(iii) Its solution in HCl gives white ppt. with $BaCl_2$ solution.
Identify the ions present and suggest formula of compound. **(IIT 1992)**

13. An orange solid (*A*) on heating gives a green residue (*B*), a colourless gas (*C*) and water vapour. The dry gas (*C*) on passing over heated Mg gave a white solid (*D*). (*D*) on reaction with water gave a gas (*E*) which formed dense white fumes with HCl. Identify (*A*) to (*E*) giving reactions. **(IIT 1993)**

14. An unknown inorganic compound (*X*) gave the following reactions:
(i) The compound (*X*) on heating gave a residue, oxygen and oxide of nitrogen.
(ii) An aqueous solution of compound (*X*) on addition to tap water gave a turbidity which did not dissolve in HNO_3.
(iii) The turbidity dissolved in NH_4OH.
Identify the compound (*X*) and give equations for the reactions (i), (ii) and (iii).

15. (i) A powdered substance (*A*) on treatment with fusion mixture gives a green coloured compound (*B*).
(ii) The solution of (*B*) in boiling water on acidification with dilute H_2SO_4 gives a pink coloured compound (*C*).
(iii) The aqueous solution of (*A*) on treatment with excess of NaOH and bromine water gives a compound (*D*).
(iv) A solution of (*D*) in conc. HNO_3 on treatment with lead peroxide at boiling temperature produced a compound (*E*) which was of the same colour as that of (*C*).
(v) A solution of (*A*) in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of compound (*F*) which was insoluble in conc. HNO_3 and conc: HCl.
Identify (*A*) to (*F*) and give balanced chemical equations for the reactions at steps (i) to (v). **(Roorkee 2001)**

16. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parentheses (give reactions only):
(i) silicon (I).
(ii) linear silicon containing methyl groups only (IV).
(iii) Na_2SiO_3 (III). **(IIT 2001)**

17. A black coloured compound (*A*) on reaction with dil. H_2SO_4 gives a gas (*B*) which on passing in a solution of an acid (*C*) gives a white turbidity (*D*). Gas (*B*) when passed in an acidified solution of a compound (*E*) gives a ppt. (*F*) soluble in dil. HNO_3. After boiling this solution when an excess of NH_4OH is added, a blue coloured compound (*G*) is formed. To this solution on addition of acetic acid and aq. $K_4Fe(CN)_6$ a chocolate precipitate (*H*) is obtained. On addition of an aqueous solution of $BaCl_2$ to an aqueous solution of (*E*), a white ppt. insoluble in HNO_3 is obtained. Identify the compounds from (*A*) to (*H*).

18. On the basis of following reactions, identify (*A*), (*B*), (*C*) and (*D*) and write down their chemical formulae:

(i) $(A)\text{aq.} + Zn \xrightarrow{\text{Heat}} (B)\,\text{gas}$

(ii) $(A)\text{aq.} + (C) \xrightarrow{\text{Heat}} PH_3$

(iii) $(A)\text{aq.} + NH_4Cl \xrightarrow{\text{Heat}} (D)\,\text{gas}$

19. A soluble compound of a poisonous element *M*, when heated with Zn / H_2SO_4 gives a colourless and extremely poisonous gaseous compound *N*, which on passing through a heated tube gives a silvery mirror of element *M*. Identify *M* and *N*. **(IIT July 1997)**

20. Element (*A*) burns in nitrogen to give ionic compound (*B*). Compound (*B*) reacts with water to give (*C*) and (*D*). A solution of (*C*) becomes milky on bubbling CO_2. Identify (*A*), (*B*), (*C*) and (*D*). **(IIT July 1997)**

21. An aqueous solution of an unknown compound (*X*) gives the following reactions:
(i) It gives brown ppt. with alkaline $KMnO_4$ solution.
(ii) It forms HCl and evolves O_2 when reacted with Cl_2 gas.
(iii) It liberates I_2 from an acidified KI solution.
(iv) It gives orange yellow colour with acidified titanic sulphate solution.
Identify (*X*) and give the chemical equations for the reactions (i), (ii) and (iii).

22. An aqueous blue coloured solution of inorganic compound (*X*) gives following reactions:
(i) With an aqueous solution of barium chloride a precipitate insoluble in dil. HCl is obtained.

(ii) Addition of excess of KI gives a brown ppt. which turns white on addition of excess of hypo.

(iii) With an aqueous solution of $K_4Fe(CN)_6$ a chocolate coloured precipitate is obtained.

Identify (X) and give equations for the reactions for (i), (ii) and (iii) observations. **(IIT 2000)**

23. (i) Sodium salt of an acid (A) is formed on boiling white phosphorus with NaOH solution.

(ii) On passing chlorine through phosphorus kept fused under water, another acid (B) is formed which on strong heating gives metaphosphorus acid.

(iii) Phosphorus on treatment with conc. HNO_3 gives an acid (C) which is also formed by the action of dilute H_2SO_4 on powdered phosphorite rock.

(iv) (A) on treatment with a solution of $HgCl_2$ first gives a white precipitate of compound (D) and then a grey precipitate of (E).

Identify (A) to (E) and write balanced chemical equations for the reactions at steps (i) to (iv). **(Roorkee 2001)**

24. Two ores of same metal (M) are A_1 and A_2.

(a) $A_1 \xrightarrow{\text{Calcination}}$ Black ppt. $(C) + CO_2 + H_2O$

$$A_1 \xrightarrow[KI]{HCl} I_2 + \text{ppt. } (D)$$

(b) $A_2 \xrightarrow{\text{Roasting}}$ Gas (G) + Metal (M)

$$(G) + K_2Cr_2O_7 \xrightarrow{\text{Acidified}} \text{Green solution}$$

Identify M, (A_1), (A_2), C, D and G. **(IIT 2004)**

25. A compound (X) imparts a golden yellow flame and shows the following reactions:

(1) Zinc powder when boiled with a concentrated aqueous solution of (X), dissolves and hydrogen is evolved.

(2) When an aqueous solution of (X) is added to an aqueous solution of stannous chloride, a white precipitate is obtained first which dissolves in excess of solution of (X).

Identify (X) and write equations at steps (1) and (2). **(Roorkee 1990)**

26. A certain metal (A) is boiled in dilute nitric acid to give a salt (B) and an oxide of nitrogen (C). An aqueous solution of (B) with brine gives a precipitate (D) which is soluble in NH_4OH. On adding aqueous solution of (B) to hypo solution, a white precipitate (E) is obtained. (E) turns black on standing. Identify (A) to (E). **(Roorkee 1990)**

27. A metal chloride (X) shows the following reactions:

(i) When H_2S is passed in an acidified aqueous solution of (X), a black precipitate is obtained.

(ii) The precipitate obtained in step (i) is not soluble in yellow ammonium sulphide.

(iii) When a solution of stannous chloride is added to an aqueous solution of (X), a white precipitate is obtained which turns grey on addition of more of stannous chloride.

(iv) When an aqueous solution of KI is added to a solution of (X), a red precipitate is obtained which dissolves on addition of excess of KI.

Identify (X) and write down the equations for the reactions at steps (i), (iii) and (iv). **(Roorkee 1991)**

28. An aqueous solution of a gas (X) shows the following reactions:

(i) It turns red litmus blue.

(ii) When added in excess to a copper sulphate solution, a deep blue colour is obtained.

(iii) On addition of $FeCl_3$ solution a brown precipitate, soluble in dilute nitric acid, is obtained.

Identify (X) and give equations for the reactions at steps (ii) and (iii). **(Roorkee 1991)**

29. A mixture consists 'A' (yellow solid) 'B' (colourless solid) which gives lilac colour in flame.

(a) Mixture gives black precipitate 'C' on passing H_2S gas.

(b) 'C' is soluble in aquaregia and on evaporation of aquaregia and adding $SnCl_2$ gives greyish black precipitates 'D'.

(c) The salt solution with NH_4OH gives a brown precipitate.

(d) The sodium carbonate extract of the salt with CCl_4/ $FeCl_3$ gives a violet colour layer.

(e) The sodium carbonate extract gives yellow precipitate with $AgNO_3$ solution which is insoluble in NH_3. Identify 'A', 'B' and the precipitates 'C' and 'D'. **(IIT 2003)**

30. A certain salt (X) gives the following tests:

(i) Its aqueous solution is alkaline to litmus.

(ii) On strongly heating it swells to give glassy material.

(iii) When concentrated H_2SO_4 is added to a hot concentrated solution of (X), white crystals of a weak acid separate out. Identify (X) and write down the chemical equations for reactions at steps (i), (ii) and (iii). **(Roorkee 1991)**

31. An inorganic compound (X) gives brick red flame on performing the flame test. This (X) also shows the following reactions:

(i) Smell of chlorine when placed in moist air.

(ii) When KI is added to a aqueous suspension of (X) containing acetic acid, iodine is liberated.

(iii) When CO_2 is passed through an aqueous suspension of (X), the turbidity transforms to a ppt.

(iv) When a paste of (X) in water is heated with ethyl alcohol, a product of anaesthetic use is obtained.

Identify (X) and write down chemical equations for reactions at steps (i), (ii) and (iii). **(Roorkee 1992)**

32. An aqueous solution of an inorganic compound (X) shows the following reactions:
(i) It decolourizes an acidified $KMnO_4$ solution accompanied with evolution of oxygen.
(ii) It liberates I_2 from acidified KI solution.
(iii) It gives brown precipitate with alkaline $KMnO_4$ solution with evolution of CO_2.
(iv) It removes black stains from old oil paintings. Identify (X) and give chemical reactions for the steps (i) to (iv). **(Roorkee 1993)**

33. A solid laboratory reagents (A) give following reactions: **(Roorkee 1993)**
(i) On strongly heating, it gives two oxides of sulphur.
(ii) On adding aqueous NaOH solution to its aqueous solution, a dirty green precipitate is obtained which starts turning brown on exposure to air.

34. Identify (A) to (D) in following steps giving chemical equations:
(i) A white amorphous powder (A) on strongly heating gives a colourless non-combustible gas (B) and solid (C).
(ii) The gas (B) turns lime water milky and turbidity disappears with the passage of excess of gas.
(iii) The solution of (C) in dilute HCl gives a white precipitate with an aqueous solution of $K_4Fe(CN)_6$.
(iv) The solution of (A) in dilute HCl gives a white precipitate (D) on passing H_2S in presence of excess of NH_4OH.

35. Identify the following:

$$Na_2CO_3 \xrightarrow{SO_2} (A) \xrightarrow{Na_2CO_3} (B) \xrightarrow{\text{Elementals}} (C) \xrightarrow{I_2} (D)$$

Also mention the oxidation state of S in all the compounds. **(IIT 2003)**

36. How is boron obtained from borax? Give chemical equations with reaction conditions? Write the structure of B_2H_6 and its reaction with HCl. **(IIT 2002)**

37. A pale yellow inorganic compound (A) is insoluble in mineral acid but is soluble in aq. NH_3 forming (B). It also dissolves in $Na_2S_2O_3$ solution and forms (C). On boiling an aqueous solution of (C), a black ppt. (D) is obtained. When (D) is dissolved in HNO_3 and HCl is added, a white ppt. (E) is obtained. (A) on heating with conc. H_2SO_4 and MnO_2 yields brown fumes of (F). Identify (A) to (F).

38. (i) Write down the structure of molecule having butterfly shape.
(ii) What is the volume strength of 1 molar solution of H_2O_2?
(iii) Complete the following :

$$LiH + CO_2 \longrightarrow$$
$$LiH + SO_2 \longrightarrow$$
$$H_3PO_3 + D_2O \longrightarrow$$

(iv) Draw the structure of $CuSO_4 \cdot 5H_2O$ and point out the nature of bonds in it.
(v) What happens when As_2S_3 is mixed with yellow ammonium sulphide and then resulting mixture is acidified with HCl?
(vi) Conc. H_2SO_4 is not recommended to dry H_2 gas unless cooled in a freezing mixture. Explain.
(vii) Write the hydrogen bonded lattice structure of H_3BO_3 and polymeric metaborate $[B_3O_3(OH)_4]^-$.

39. A white substance (A) reacts with dilute H_2SO_4 to produce a colourless gas (B) and a colourless solution (C). The reaction between (B) and acidified $K_2Cr_2O_7$ solution produces a green solution and a slightly coloured precipitate (D). The substance (D) burns in air to produce a gas (E) which reacts with (B) to yield (D) and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to (C) produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify (A), (B), (C), (D) and (E). Write the equations of the reactions involved. **(IIT 2001)**

40. An inorganic compound (A), transparent like glass is a strong reducing agent. Its hydrolysis in water gives a white turbidity (B). Aqueous solution of (A) gives white ppt. (C) with NaOH(aq.) which is soluble in excess NaOH. (A) reduces auric chloride to produce purple of cassius, (A) also reduces I_2 and gives chromyl chloride test.

41. An inorganic Lewis acid (X) shows the following reactions:
(i) It fumes in moist air.
(ii) The intensity of fumes increases when a rod dipped in NH_4OH is brought near it.
(iii) An acidic solution of (X) on addition of NH_4Cl and NH_4OH gives a precipitate which dissolves in NaOH solution.
(iv) An acidic solution of (X) does not give a precipitate with H_2S. Identify (X) and give chemical equation for steps (i) to (iii). **(Roorkee 1994)**

42. A certain inorganic compound (X) shows the following reactions:
(i) On passing H_2S through an acidified solution of (X), a brown precipitate is obtained.
(ii) The precipitate obtained in first step dissolves in excess of yellow amm. sulphide.
(iii) On adding an aqueous solution of NaOH to a solution of (X), first a white precipitate is obtained which dissolves in excess of NaOH.
(iv) The aqueous solution of (X) reduces ferric chloride. Identify the cation of (X) and give chemical equations for the steps (i), (iii) and (iv).
(Roorkee 1994)

43. (i) An inorganic iodide (*A*) on heating with a solution of KOH gives a gas (*B*) and the solution of compound (*C*).
(ii) The gas (*B*) on ignition in air gives a compound (*D*) and water.
(iii) Copper sulphate is finally reduced to the metal on passing (*B*) through its solution.
(iv) A precipitate of compound (*E*) is formed on reaction of (*C*) with copper sulphate solution. Identify (*A*) to (*E*) and give chemical equations for steps (i) to (iv). **(Roorkee 1994)**

44. (i) A black mineral (*A*) on heating in presence of air gives a gas (*B*).
(ii) The mineral (*A*) on reaction with dil. H_2SO_4 gives a gas (*C*) and solution of compound (*D*).
(iii) On passing gas (*C*) into an aqueous solution of (*B*), a white turbidity is obtained.
(iv) The aqueous solution of compound (*D*) on reaction with potassium ferricyanide gives a blue compound (*E*).
Identify (*A*) to (*E*) and give chemical equations to steps (i) to (iv). **(Roorkee 1994)**

45. Write down the reactions involved in extraction of Pb. What is oxidation number of lead in litharge? **(IIT 2003)**

46. (*A*) is binary compound of a univalent metal. 1.422 g of (*A*) reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid (*B*) that formed a hydrated double salt (*C*) with $Al_2(SO_4)_3$. Identify (*A*), (*B*) and (*C*). **(IIT 1994)**

47. A scarlet compound (*A*) is treated with conc. HNO_3 to give a chocolate brown precipitate (*B*). The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate (*C*). The precipitate (*B*) on warming with conc. HNO_3 in the presence of $Mn(NO_3)_2$ produces a pink-coloured solution due to the formation of (*D*). Identify (*A*), (*B*), (*C*) and (*D*). Write the reaction sequence. **(IIT 1995)**

48. (i) A white precipitate (*B*) is formed when a mineral (*A*) is boiled with Na_2CO_3 solution.
(ii) The precipitate is filtered and the filtrate contains two compounds (*C*) and (*D*). The compound (*C*) is removed by crystallisation and when CO_2 is passed through the mother liquor left (*D*) changes to (*C*).
(iii) The compound (*C*) on strong heating gives two compounds (*D*) and (*E*).
(iv) (*E*) on heating with cobalt oxide produces blue coloured substance (*F*).
Identify (*A*) to (*F*) and give chemical equations for the reactions at steps (i) to (iv). **(Roorkee 1995)**

49. (i) A black mineral (*A*) on treatment with dilute sodium cyanide solution in presence of air gives a clear solution of (*B*) and (*C*).
(ii) The solution of (*B*) on reaction with zinc gives precipitate of a metal (*D*).
(iii) (*D*) is dissolved in dil. HNO_3 and the resulting solution gives a white precipitate (*E*) with dil. HCl.
(iv) (*E*) on fusion with sodium carbonate gives (*D*).
(v) (*E*) dissolves in aqueous solution of ammonia giving a colourless solution of (*F*).
Identify (*A*) to (*F*) and give chemical equations for reactions at steps (i) to (v). **(Roorkee 1995)**

50. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (*A*) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (*B*) on the surface. Identify the compounds (*A*) and (*B*). **(IIT 1996)**

51. Gradual addition of KI solution to $Bi(NO_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. **(IIT 1996)**

52. A colourless inorganic salt (*A*) decomposes completely at about 250°C to give only two products, (*B*) and (*C*), leaving no residue. The oxide (*C*) is a liquid at room temperature and neutral to moist litmus paper while the gas (*B*) is a neutral oxide. White phosphorus burns in excess of (*B*) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process. **(IIT 1996)**

53. (i) An inorganic compound (*A*) is formed on passing a gas (*B*) through a concentrated liquor containing sodium sulphide and sodium sulphite.
(ii) On adding (*A*) into a dilute solution of silver nitrate, a white precipitate appears which quickly changes into a black coloured compound (*C*).
(iii) On adding two or three drops of ferric chloride into the excess of solution of (*A*), a violet coloured compound (*D*) is formed. This colour disappears quickly.
(iv) On adding a solution of (*A*) into the solution of cupric chloride, a white precipitate is first formed which dissolves on adding excess of (*A*) forming a compound (*E*).
Identify (*A*) to (*E*) and give chemical equations for the reactions at steps (i) to (iv). **(Roorkee 1996)**

54. (i) A black coloured compound (*B*) is formed on passing hydrogen sulphide through the solution of a compound (*A*) in NH_4OH.
(ii) (*B*) on treatment with hydrochloric acid and potassium chlorate gives (*A*).

(iii) (A) on treatment with potassium cyanide gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (C).

(iv) The compound (C) is changed into a compound (D) when its aqueous solution is boiled.

(v) The solution of (A) was treated with excess of sodium bicarbonate and then with bromine water. On cooling and shaking for sometime, a green colour of compound (E) is formed. No change is observed on heating.

Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (v). **(Roorkee 1996)**

55. Give complete and balanced chemical equations for the following: Sodium chromite solution reacts with H_2O_2 in presence of NaOH.

56. Nickel chloride is mixed with dimethyl glyoxime. When ammonium hydroxide is slowly added, a shining red precipitate is formed.

(a) Give the structure of the complex showing hydrogen bonds.

(b) Give the charge and the state of hybridisation of the central metal ion.

(c) Predict the magnetic behaviour of complex. **(IIT 2004)**

57. (i) A blue coloured compound (A) on heating gives two products, (B) and (C).

(ii) A metal (D) is deposited on passing hydrogen through heated (B).

(iii) The solution of (B) in HCl on treatment with $K_4[Fe(CN)_6]$ gives a chocolate brown coloured precipitate of compound (E).

(iv) (C) Turns lime water milky which disappears on continuous passage of (C) forming a compound (F).

Identify (A) to (F) and give chemical equations for the reactions at steps (i) to (iv). **(Roorkee 1997)**

58. (i) An aqueous solution of a white coloured compound (A) on reaction with HCl gives a white precipitate of compound (B).

(ii) (B) becomes soluble in chlorine water with the formation of (C).

(iii) (C) reacts with KI to give a precipitate which becomes soluble in excess of it forming a compound (D). The compound (D) is used for detecting ammonium salts.

(iv) (B) and (C) both, on treatment with $SnCl_2$ give a grey precipitate of (E).

(v) When conc. H_2SO_4 is added slowly into a mixture of cold solutions of (A) and $FeSO_4$, a brown ring of compound (F) is formed. Identify (A) to (F) and give chemical equations for the reactions at steps (i) to (v). **(Roorkee 1997)**

59. Compound (X) on reduction with $LiAlH_4$ gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reaction with air. Draw the structure of (Y). **(IIT 2001)**

60. Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H_2O_2 using chemical equations. **(IIT 1998)**

61. When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also produces a silicate slag that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations. **(IIT 1998)**

62. Thionyl chloride can be synthesized by chlorinating SO_2 using PCl_5. Thionyl chloride is used to prepare anhydrous ferric chloride starting from its hexahydrated salt. Alternatively, the anhydrous ferric chloride can also be prepared from its hexahydrated salt by treating with 2,2-dimethoxypropane. Discuss all this using balanced chemical equations. **(IIT 1998)**

63. (i) An aqueous solution of a compound (A) is acidic towards litmus and (A) is sublimed at about 300°C.

(ii) (A) on treatment with an excess of NH_4SCN gives a red coloured compound (B) and on treatment with a solution of $K_4[Fe(CN)_6]$ gives a blue coloured compound (C).

(iii) (A) on heating with excess of $K_2Cr_2O_7$ in presence of concentrated H_2SO_4 evolves deep red vapours of (D).

(iv) On passing the vapours of (D) into a solution of NaOH and then adding the solutions of acetic acid and lead acetate, a yellow precipitate of compound (E) is obtained.

Identify (A) to (E) and give chemical equations for the reaction at steps (ii) to (iv). **(Roorkee 1998)**

64. (i) The yellow coloured precipitate of compound (A) is formed on passing H_2S through a neutral solution of a salt (B).

(ii) (A) is soluble in hot dilute HNO_3, but insoluble in yellow ammonium sulphide.

(iii) The solution of (B) on treatment with small quantity of NH_3 gives white precipitate which becomes soluble in excess of it forming a compound (C).

(iv) The solution of (B) gives white precipitate with small concentration of KCN which becomes soluble in excess of this reagent forming a compound (D).

(v) The solution of (B) on treatment with H_2S gives (A).

(vi) The solution of (B) in dilute HCl on treatment with a solution of $BaCl_2$ gives white precipitate of compound (E) which is insoluble in conc. HNO_3.

Identify (*A*) to (*E*) and give chemical equations for the reactions at steps (i) and (iii) to (vi). **(Roorkee 1998)**

65. A white solid is either Na_2O or Na_2O_2. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.
(i) Identify the substance and explain with balanced equation.
(ii) Explain what would happen to the red litmus if the white solid were the other compound? **(IIT 1999)**

66. (*A*), (*B*) and (*C*) are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex (*A*) does not react with concentrated H_2SO_4, whereas complexes (*B*) and (*C*) lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4. Identify (*A*), (*B*) and (*C*). **(IIT 1999)**

67. An aqueous solution containing one mole of HgI_2 and two mole of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations. **(IIT 1999)**

68. Pyrolusite on heating with KOH in the presence of air gives a dark green compound (*A*). The solution of (*A*) on treatment with H_2SO_4 gives a purple coloured compound (*B*), which gives following reactions:
(i) KI on reaction with alkaline solution of (*B*) changes into a compound (*C*).
(ii) The colour of the compound (*B*) disappears on treatment with the acidic solution of $FeSO_4$.
(iii) With conc. H_2SO_4 compound (*B*) gives (*D*) which can decompose to yield (*E*) and oxygen.
Identify (*A*) to (*E*) and write balanced chemical equations for the formation of (*A*) and (*B*) and for the steps (i) to (iii). **(Roorkee 1999)**

69. A crystalline inorganic compound (*A*), when it comes in contact with skin leaves a black stain. (*A*) is freely soluble in water and when to this solution some sodium chloride is added, a white precipitate appears which is insoluble in HNO_3 but soluble in NH_4OH. When hydrogen sulphide is passed through a solution of (*A*), a black precipitate appears. When potassium chromate is added to the solution of (*A*), a brick red precipitate results. To another portion of solution (*A*), mixed with ferrous sulphate in a test tube, concentrated sulphuric acid is added through the sides of the test tube, a brown ring results. Identify the compound and give equations for the various reactions involved.

70. An inorganic compound, dark red in anhydrous state, absorbs moisture to become yellow. On heating it sublimes to form dimeric state in vapour phase. It acts as oxidant for $SnCl_2$, liberates I_2 from KI and converts H_2S to S. Its aqueous solution is acidic. On heating aqueous solution with $K_4Fe(CN)_6$, a characteristic blue colour is obtained. What is the compound and give all the reactions involved?

71. (i) Show that XeF_4 and IF_4^- are isostructural.
(ii) Lithium does not form alum. Explain.
(iii) Write a balanced equation for the reaction of sodium thio sulphate with Cl_2 in water.
(iv) Explain with reason the chromium hydroxide is treated with H_2O_2 in presence of NaOH (aq.)
(v) Explain with reason the relative Lewis acid order for boron halides.
(vi) Why is the graphite called most stable allotrope of carbon?
(vii) Which among PbO, PbO_2 and Pb_3O_4 is the strongest oxidising agent?

72. A metallic oxide (*A*) is strongly acidic and forms violet vapours on warming and explodes violently at 55°C giving out oxygen and a weak acidic oxide. The compound (*A*) on dissolution in water gives characteristic purple colour. What is (*A*)?

73. In the contact process for industrial manufacture of sulphuric acid some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2 ? **(IIT 1999)**

74. When a white crystalline compound (*X*) is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, a reddish brown gas (*A*) is evolved. On passing (*A*) into caustic soda solution, a yellow coloured solution of (*B*) is obtained. Neutralizing the solution of (*B*) with acetic acid and on subsequent addition of lead acetate, a yellow precipitate (*C*) is obtained. When (*X*) is heated with NaOH solution, a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitate (*D*) is formed. Identify (*A*), (*B*), (*C*), (*D*) and (*X*). Write the equations of reactions involved. **(IIT 2002)**

75. Complete and balance the following equations:
(i) $H_2SO_4 + HI \longrightarrow ...+...+...$
(ii) $CaOCl_2 + NaI + HCl \longrightarrow ...+ CaCl_2 + H_2O + NaCl.$
(iii) $Ag_2S + 2CuCl_2 + 2Hg \longrightarrow ...+...+ S + 2Ag$ **(Roorkee 1998)**

76. Complete and balance the following equations:
(i) $H_2S + H_2SO_4$ (conc.) $\longrightarrow$ .....+.....+.....
(ii) NaOH (excess) $+ I_2 \longrightarrow$ .....+.....+H_2O
(iii) $NH_3 + NaOCl \longrightarrow$ .....+ NaCl + H_2O **(Roorkee 1997)**

77. Complete and balance the following equations:
(i) $I_2 + HNO_3$ (conc.) $\longrightarrow$ .....+.....+.....
(ii) $SF_6 + H_2O \longrightarrow$ .....+.....
(iii) $SF_4 + Cl_2 \longrightarrow$ .....+.....+.....

78. (a) Reaction of phosphoric acid with $Ca_5(PO_4)_3F$ yields a fertilizer "triple superphosphate".

Represent the same through a balanced chemical equation.

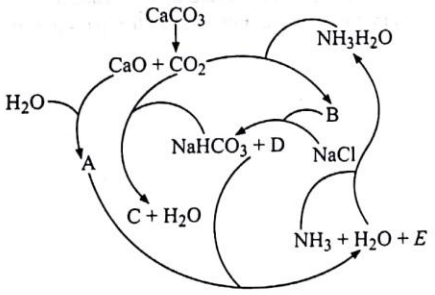
(b) Complete and balance the following chemical equations:
(i) $P_4O_{10} + PCl_5 \longrightarrow$
(ii) $SnCl_4 + C_2H_5Cl + Na \longrightarrow$

(c) Work out the following using chemical equations:
(i) In moist air copper corrodes to produce a green layer on the surface.
(ii) Chlorination of calcium hydroxide produces bleaching powder. **(IIT 1998)**

79. Complete and balance the following chemical equations:
(i) $Au + HCl + HNO_3 \longrightarrow ... + ... + H_2O$
(ii) $C + HNO_3$ (conc.) $\longrightarrow CO_2 + ... + H_2O$
(iii) $Sn + KOH$ (hot) $+ H_2O \longrightarrow ... + ...$
(iv) $Cu(OH)_2 + NH_4NO_3 + NH_4OH(aq.) \longrightarrow ... + H_2O$
(Roorkee 1999)

80. In the following equation,
$$A + 2B + H_2O \longrightarrow C + 2D$$
($A = HNO_2$, $B = H_2SO_3$, $C = NH_2OH$). Identify D. Draw the structures of A, B, C and D. **(IIT 1999)**

81. The Haber process can be represented by the following scheme:



Identify A, B, C, D and E. **(IIT 1999)**

82. Match the following choosing one item from Column X and the appropriate item from Column Y: **(Roorkee 2000)**

X	Y
A. SO_2Cl_2	(i) Paramagnetic
B. Ice	(ii) Refrigeration
C. $CuSO_4$ (anhydrous)	(iii) Testing NH_3
D. $K_2HgI_4 + NaOH$	(iv) Testing H_2O
E. Fluorocarbons	(v) Hydrogen bonding
F. NO	(vi) Tetrahedral

83. Complete the following by identifying (A) to (H):
(i) $CuSO_4 \cdot 5H_2O \xrightarrow{100°C} (A) \xrightarrow{230°C} (B) \xrightarrow{800°C} (C) + (D)$
(ii) $AgNO_3 \xrightarrow{\text{Red heat}} (E) + (F) + O_2$
(iii) $Na_2B_4O_7 \xrightarrow{740°C} (G) + (H)$ **(Roorkee 2000)**

84. During the qualitative analysis of a mixture containing Cu^{2+} and Zn^{2+} ions, H_2S gas is passed through an acidified solution containing these ions in order to test Cu^{2+} alone. Explain briefly. **(IIT 1998)**

85. Give reasons for the following:
(i) The solubility of calcium acetate decreases while that of lead nitrate increases with increase in temperature.
(ii) Magnesium is not precipitated from a solution of its salt by NH_4OH in the presence of NH_4Cl.
(iii) Yellow phosphorus is kept under water but not the red phosphorus.
(iv) Bleaching of flowers with SO_2 gas is temporary while that with Cl_2 gas is permanent.
(Roorkee 2000)

86. (a) Write down the IUPAC nomenclature of the given complex along with its hybridisation and structure
$K_2[Cr(NO)(NH_3)(CN)_4]$; $\mu = 1.73$ BM.
(IIT 2003)

(b) Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case.
(IIT 2000)

87. (a) AlF_3 is not soluble in anhydrous HF but soluble in KF; Also when BF_3 is added to the above solution, AlF_3 is precipitated. Write the balanced chemical equation. **(IIT 2004)**

(b) Predict whether Me_3N and $(SiMe_3)_3N$ are isostructural or not. Also justify your answer.
(IIT 2005)

88. Write the order of Bronsted basic nature for the following oxides: CO_2, BaO, Cl_2O_7, SO_3, B_2O_3
(IIT 2004)

89. (a) Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction.

(b) Write the M.O., electron distribution of O_2. Specify its bond order and magnetic property. **(IIT 2000)**

90. Write balanced equations for the reactions of the following compounds with water:
(i) Al_4C_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_4
(IIT 2002)

91. (a) (i) Write the chemical reactions involved in the extraction of metallic silver from argentite.
(IIT 2000)

(ii) Write the balanced chemical equation for developing of black and white photographic films.

When sodium thiosulphate solution is treated with acidic solution, it turns milky. Explain.

(IIT 2000, 05)

(b) Write the chemical reactions associated with the 'borax bead test' of cobalt(II) oxide. **(IIT 2000)**

(c) Draw the shape of PCl_5 and BrF_5 using VSEPR theory. **(IIT 2003)**

(d) Write structure of P_4O_{10}. **(IIT 2005)**

92. (B) (White fumes having pungent smell) $\xleftarrow{\text{Moist air}}$ MCl_4 (M = transition element colourless) $\longrightarrow$ (A) (Purple colour)

Identify the metal M and hence, MCl_4. Explain the difference in colours of MCl_4 and A. **(IIT 2005)**

93. Identify (A) and (B) in the given sequence of reaction. Also write their IUPAC names and calculate only spin magnetic moment for B.

$$Fe^{3+}_{(aq.)} \xrightarrow{SCN^- \text{ excess}} \text{Blood - red } (A) \xrightarrow{F^- \text{ excess}} \text{Colourless } (B)$$

(IIT 2005)

94. Explain the following:

(i) Ammonium salts are much more soluble than the corresponding sodium salts.

(ii) $Ag(CN)_2^-$ is stable while $AgCl_2^-$ is unstable.

(iii) Why do bond angles of NH_3, PH_3, AsH_3 and SbH_3 are 106.5°, 93.3°, 91.8° and 91.3°, although each show sp^3 hybridisation?

(iv) Write an example of tridentate ligand.

(v) Arrange in their increasing acidic nature : Mn_2O_3, MnO, MnO_2, MnO_3, Mn_2O_7. Also point out strongly basic and strongly acidic oxides of Mn.

95. (a) Interhalogen compounds AX are more reactive than halogens (except F_2).

(b) What product is formed when SO_2 react with ethyl magnesium bromide and the product is hydrolysed?

(c) How many sulphur atoms in polythionic acid $H_2S_nO_6$ have only S—S bonds?

(d) Complete the reaction: $CS_2 + NaOH \rightarrow ...+...+...$

(e) What happens when cyanogen gas is passed through NaOH?

(f) How you will convert Na_2SO_4 to NaCl?

96. Explain why?

(i) Concentrated HNO_3 acquires yellow colour on standing.

(ii) Hard water consumes more soap.

(iii) BeO reacts with acids and alkali both.

(iv) Lead pollution is caused by car exhaust.

(v) Tin vessels are not useful for packing in cold countries.

SOLUTIONS (Numerical Problems)

1. (i) (A) on heating with excess of NaOH gives gas (B) which forms white fumes with HCl and thus, (B) is NH_3 and (A) is ammonium salt.

(ii) The product formed in reaction between (A) and NaOH, on treating with Zn + NaOH gives NH_3 and thus, it should be nitrate or nitrite. Thus (A), should be ammonium nitrate or nitrite, however (A) does not give N_2 on heating and thus, it is nitrate.

Reactions:

(i) $\underset{(A)}{NH_4NO_3} + NaOH \longrightarrow NaNO_3 + H_2O + \underset{(B)}{NH_3}\uparrow$

$NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl}$

(ii) $NaNO_3 + 8H \xrightarrow{Zn/NaOH} NaOH + 2H_2O + NH_3$

2. (1) Since (A) gives white ppt. (B) with NaCl solution, soluble in hot water as well as filtrate of this with H_2S gives black ppt. and thus, (A) has Pb^{2+} ion in it.

(2) (A) liberates reddish brown gas on heating and thus it should have NO_3^- ion in it, *i.e.*, (A) is $Pb(NO_3)_2$.

Reactions:

$\underset{(A)}{Pb(NO_3)_2} + 2NaCl \longrightarrow \underset{(B)}{PbCl_2} + 2NaNO_3$

$PbCl_2 + H_2S \longrightarrow \underset{(C)}{PbS} + 2HCl$

$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + \frac{1}{2}O_2$

$PbCl_2 + 2KI \longrightarrow \underset{(D)\text{ Yellow ppt.}}{PbI_2} + 2KCl$

3. (1) The mixture is soluble in water to give strong alkali, it must contain NaOH as one of the constituent.

(2) The aqueous solution of mixture gives white ppt. with dil. HCl which dissolves in excess of dil. HCl and thus, it must have Zn salt, *i.e.*, $ZnSO_4$.

(3) Thus, mixture is NaOH + $ZnSO_4$.

Reactions:

(i) $ZnSO_4 + 4NaOH \longrightarrow \underset{\text{Soluble}}{Na_2ZnO_2} + Na_2SO_4 + 2H_2O$

(ii) $Na_2ZnO_2 + 2HCl \longrightarrow 2NaCl + Zn(OH)_2\downarrow$

$Zn(OH)_2 + 2HCl \longrightarrow \underset{\text{Soluble}}{ZnCl_2} + 2H_2O$

4. (1) Step (i) of the problem indicates the presence of Cl^- in mixture. (A test for Cl^-).

(2) Step (ii) of the problem indicates the presence of NH_4^+ in mixture (A test for NH_4^+).

(3) Step (iii) of the problem indicates the presence of Fe^{2+} ion in mixture.

(4) Thus, mixture has Fe^{2+}, Cl^- and NH_4^+ ions, *i.e.*, it is a mixture of $FeCl_2$ and NH_4Cl.

Reactions:

(1) $2NH_4Cl + MnO_2 + 2H_2SO_4 \xrightarrow{\Delta} MnSO_4 + Cl_2\uparrow + 2H_2O + (NH_4)_2SO_4$

$NH_4Cl + NaOH \xrightarrow{\Delta} \underset{\text{Turns red litmus to blue}}{NH_3\uparrow} + H_2O + NaCl$

(2) $3FeCl_2 + 2K_3Fe(CN)_6 \longrightarrow \underset{\text{Blue colour}}{Fe_3[Fe(CN)_6]_2} + 6KCl$

$Fe^{2+} \xrightarrow[\text{aqueous sol.}]{\text{Oxidation in}} Fe^{3+}$

$Fe^{3+} + 3CNS^- \longrightarrow \underset{\text{Blood-red colour}}{Fe(CNS)_3}$

Note : If mixture already contains Fe^{3+} ion, it should give brown ppt. with $K_3Fe(CN)_6$. Thus, Fe^{3+} ions are believed to be formed by the oxidation of Fe^{2+} ions in solution.

(3) $KOH + NH_4Cl \longrightarrow NH_3 + KCl + H_2O$

$NH_3 + 3NaOH + 2K_2HgI_4 \longrightarrow \underset{\text{Brown}}{O(Hg)(Hg)NH_2I} + 4KI + 2H_2O + 3NaI$

5. (1) Compound (A) forms white insoluble ppt. with $BaCl_2$. So it is a sulphate.

(2) (A) produces red colouration with thiocyanate, so it may be iron sulphate.

(3) Since it is greenish in colour, so it is crystalline $FeSO_4 \cdot 7H_2O$.

Reactions:

(i) $\underset{(A)}{FeSO_4} + BaCl_2 \longrightarrow FeCl_2 + \underset{\text{White ppt. } (B)}{BaSO_4}$

(ii) $FeSO_4 \cdot 7H_2O \xrightarrow{\text{Heat}} FeSO_4 + 7H_2O$

$2FeSO_4 \xrightarrow{\text{Heat}} \underset{\text{Brown residue}}{\underset{(E)}{Fe_2O_3}} + \underset{(C)}{SO_2} + \underset{(D)}{SO_3}$

(iii) $\underset{(E)}{Fe_2O_3} + 6HCl \longrightarrow \underset{\text{Yellow solution}}{\underset{(F)}{2FeCl_3}} + 3H_2O$

(iv) $\underset{(F)}{2FeCl_3} + H_2S \longrightarrow \underset{(H)}{2FeCl_2} + 2HCl + \underset{\text{Pale yellow}}{\underset{(G)}{S}}$

(v) $\underset{(F)}{FeCl_3} + 3NH_4CNS \longrightarrow \underset{\text{Blood-red colour}}{\underset{(H)}{Fe(CNS)_3}} + 3NH_4Cl$

Hence, (A) is $FeSO_4 \cdot 7H_2O$.

6. (i) Ag^+ ions with HCl will form a white ppt. of AgCl, *i.e.*,

$Ag^+ + Cl^- \longrightarrow \underset{\text{White ppt. } (A)}{AgCl}$

(ii) After filtration AgCl is filtered out and filtrate contains Cu^{2+}, Ca^{2+} and K^+ ions. With H_2S, Cu^{2+} ions form a black ppt. of CuS, *i.e.*,

$Cu^{2+} + S^{2-} \longrightarrow \underset{\text{Black ppt. } (B)}{CuS}$

(iii) On filtration the filtrate has Ca^{2+} and K^+ ions. With conc. Na_2CO_3, Ca^{2+} ions will form white ppt. of $CaCO_3$, *i.e.*,

$$Ca^{2+} + CO_3^{2-} \longrightarrow \underset{\text{White ppt. } (C)}{CaCO_3}$$

So, $(A) = AgCl$, $(B) = CuS$, $(C) = CaCO_3$.

7. (1) Gas (X) is absorbed in acidified $K_2Cr_2O_7$ and the solution turns green. So, (X) is SO_2.

(2) Gas (Y) is absorbed in lime water turning it white so (Y) is CO_2.

(3) Gas (Z) is absorbed in pyrogallol so (Z) is O_2.

Reactions:

(1) $\underset{(X)}{3SO_2} + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$

(2) $Ca(OH)_2 + \underset{(Y)}{CO_2} \longrightarrow \underset{\text{White}}{CaCO_3\downarrow} + H_2O$

(3) $\underset{(Z)}{O_2} + \text{Pyrogallol} \longrightarrow \text{Absorbed}$

8. (1) (A) turns lime water milky, so (A) is CO_2 or SO_2 gas.

(2) (Y) gives alkaline solution and its solution forms white ppt. (Z) with $BaCl_2$ and (Z) on heating with acid gives effervescences of CO_2, so (Z) is $BaCO_3$ and (Y) is metal carbonate.

(3) Since, (Y) and (A) are formed from (X) and thus, (X) is metal bicarbonate and (A) is CO_2.

(4) $\underset{16.8\text{ g}}{X} \xrightarrow{\Delta} \underset{4.4\text{ g}}{A} + \underset{1.8\text{ g}}{B} + Y$

(5) The above data reveal that,

$2MHCO_3 \longrightarrow CO_2 + H_2O + M_2CO_3$

4.4 g CO_2 is obtained by 16.8 g $MHCO_3$

44 g CO_2 is obtained by 168 g $MHCO_3$

Molar mass of $MHCO_3 = \frac{168}{2} = 84\text{ g mol}^{-1}$

$\therefore$ Atomic mass of metal = 23

Hence, metal is Na.

Reactions: $\underset{(X)}{2NaHCO_3} \longrightarrow \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{Na_2CO_3}$

9. (1) (A) turns lime water milky so (A) is CO_2 or SO_2.

(2) (B) condenses into liquid turning anhydrous $CuSO_4$ to blue, so (B) is H_2O.

(3) (Y) gives alkaline solution and its solution forms white ppt. (Z) with $BaCl_2$ and (Z) on heating with acid gives CO_2 so (Z) is $BaCO_3$ and (Y) is metal carbonate.

(4) Since, (Y) and (A) are formed from (X) and thus, (X) is metal bicarbonate.

(5) $\underset{20.02\text{ g}}{X} \xrightarrow{\Delta} \underset{4.4\text{ g}}{A} + \underset{1.8\text{ g}}{B} + \underset{13.8\text{ g}}{Y}$

(6) The above data reveal that,

$\underset{(X)}{2MHCO_3} \longrightarrow \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{M_2CO_3}$

4.4 g CO_2 is obtained by 20.02 g $MHCO_3$

44 g CO_2 is obtained by 200.2 g $MHCO_3$

Molar mass of $MHCO_3 = \frac{200.2}{2} = 100.1\text{ g mol}^{-1}$

$\therefore$ Atomic mass of $M = 39.1$

Thus, metal is potassium.

Reactions: $\underset{(X)}{2KHCO_3} \longrightarrow \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{K_2CO_3}$

10. (1) The gas liberated on heating the mixture with NaOH gives red ppt. with K_2HgI_4, so gas is NH_3 and mixture contains NH_4^+ ions.

(2) The aqueous solution gives white ppt. with $BaCl_2$, so mixture contains SO_4^{2-} ions.

(3) Mixture on heating with $K_2Cr_2O_7$ and H_2SO_4 gives red vapours (of CrO_2Cl_2), so mixture contains Cl^- ions.

(4) Aqueous solution of mixture gives blue colour with $K_3Fe(CN)_6$ and thus, it contains Fe^{2+} ions.

(5) Thus, mixture has NH_4^+, Fe^{2+}, SO_4^{2-} and Cl^-.

Reactions:

(I) $NH_4^+ + NaOH \longrightarrow NH_3 + Na^+ + H_2O$

$2K_2HgI_4 + 3NaOH + NH_3 \longrightarrow \underset{\text{Brown}}{O(Hg)_2NH_2I} + 4KI + 2H_2O + 3NaI$

(II) $SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 + 2Cl^-$

(III) $4Cl^- + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow \underset{(A)\text{ Red}}{2CrO_2Cl_2} + K_2SO_4 + 3H_2O + 2SO_4^{2-}$

(IV) $3Fe^{2+} + 2K_3Fe(CN)_6 \longrightarrow \underset{(B)\text{ Blue}}{Fe_3[Fe(CN)_6]_2} + 6K^+$

11. (i) $HgCl_2 + 2NH_3 \longrightarrow Hg(NH_2)Cl + NH_4Cl$

(ii) $AgNO_3 + 2KCNS \longrightarrow KNO_3 + K[Ag(SCN)_2]$

(iii) $3K_4[Fe(CN)_6] + 4HNO_3 \longrightarrow 3K[Fe(CN)_6] + NO + 3KNO_3 + 2H_2O$

(iv) $Pb_3O_4 + 4HNO_3 \longrightarrow PbO_2 + 2Pb(NO_3)_2 + 2H_2O$

(v) $4NaH + 4B(OCH_3)_3 \xrightarrow{THF} NaBH_4 + 3NaB(OCH_3)_4$

12. (i) Compound gives brown ppt. with alkaline K_2HgI_4 and so contains NH_4^+ ions.

(ii) Compound gives blue colour with $K_3Fe(CN)_6$ and so contains Fe^{2+} ions.

(iii) Solution of compound in HCl gives white ppt. with $BaCl_2$ and so it contains SO_4^{2-} ions.

(iv) Bluish green compound with NH_4^+, Fe^{2+} and SO_4^{2-} is Mohr's salt, *i.e.*,

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \longrightarrow Fe^{2+} + SO_4^{2-} + 2NH_4^+ + SO_4^{2-} + 6H_2O$

Reactions:

$3NaOH + NH_3 + 2K_2HgI_4 \longrightarrow \underset{\text{Brown ppt.}}{O(Hg)_2NH_2I} + 4KI + 3NaI + 2H_2O$

$$3Fe^{2+} + 2K_3Fe(CN)_6 \longrightarrow \underset{\text{Blue ppt.}}{Fe_3[Fe(CN)_6]_2} + 6K^+$$

$$SO_4^{2-} + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{BaSO_4} + 2Cl^-$$

13. (1) Assume compound (A) $(NH_4)_2Cr_2O_7$.

Reactions: $\underset{(A)}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{(C)}{N_2} + \underset{\text{Green } (B)}{Cr_2O_3} + 4H_2O$

$$N_2 + 3Mg \xrightarrow{\Delta} \underset{(D)}{Mg_3N_2}$$

$$\underset{(D)}{Mg_3N_2} + 6H_2O \longrightarrow 3Mg(OH)_2 + \underset{(E)}{2NH_3}$$

$$\underset{(E)}{NH_3} + HCl \longrightarrow \underset{\text{(White fumes)}}{NH_4Cl}$$

14. (1) Step (ii) suggests, (X) to be a compound of Ag as it gives turbidity with tap water which contains Cl^- and the turbidity is soluble in NH_4OH.

(2) (X) may be $AgNO_3$ since, it gives oxide of nitrogen.

Reactions: $\underset{(X)}{2AgNO_3} \longrightarrow \underset{\text{Residue}}{2Ag} + O_2 + 2NO_2$

$$\underset{(X)}{AgNO_3} + \underset{\text{Tap water}}{Cl^-} \longrightarrow \underset{\text{Turbidity}}{AgCl} + NO_3^-$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{(Soluble)}}{Ag(NH_3)_2Cl} + 2H_2O$$

15. (i) $\underset{(A)}{MnSO_4} + 2Na_2CO_3 + 2KNO_3 \longrightarrow \underset{(B)}{Na_2MnO_4} + 2KNO_2 + Na_2SO_4 + 2CO_2$

(ii) $3Na_2MnO_4 + 2H_2SO_4 \longrightarrow \underset{(C)}{2NaMnO_4} + MnO_2 + 2Na_2SO_4 + 2H_2O$

(iii) $MnSO_4 + 4NaOH + Br_2 \longrightarrow \underset{(D)}{MnO_2} + Na_2SO_4 + 2NaBr + 2H_2O$

(iv) $2MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$

$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow \underset{(E)}{2HMnO_4} + 5Pb(NO_3)_2 + 2H_2O$

(v) $MnSO_4 + BaCl_2 \longrightarrow \underset{(F)}{BaSO_4}\downarrow + MnCl_2$

16. (i) $3SiCl_4(v) + 4Al(\text{molten}) \longrightarrow 4AlCl_3 + 3Si$

(ii) (a) $3SiCl_4 + 4Al \longrightarrow 4AlCl_3 + 3Si$

(b) $Si + CH_3Cl \xrightarrow[570\ K]{\text{Cu powder}} (CH_3)_2SiCl_2$

(c) $(CH_3)_2SiCl_2 \xrightarrow{HOH} HO{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}{-}OH$

(d) $n\,HO{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}{-}OH \xrightarrow{\text{Polymerisation}}$

$$HO\left[-Si(CH_3)_2-O-\right]_n-Si(CH_3)_2-O-$$

Linear silicone
(Thermoplastic polymer)

(iii) (a) $SiCl_4 + 4H_2O \longrightarrow \underset{\text{ortho-silicic acid}}{H_4SiO_4} + 4HCl$

(b) $H_4SiO_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$

(c) $SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + H_2O$

17. (1) The black coloured compound may be FeS, CuS or PbS CoS, NiS because it reacts with dil. H_2SO_4 to produce H_2S.

$$\underset{(A)}{MS} + H_2SO_4 \longrightarrow MSO_4 + \underset{(B)}{H_2S}$$

(2) Gas H_2S on passing through HNO_3 (an oxidant) gives turbidity of S.

$$\underset{(B)}{H_2S} + \underset{(C)}{2HNO_3} \longrightarrow 2NO_2 + 2H_2O + \underset{(D)}{S}$$

(3) (E) is $CuSO_4$ because it gives white ppt. of $BaSO_4$ with $BaCl_2$ and blue colour with NH_4OH (A test for SO_4^{2-} and Cu^{2+} respectively).

$$\underset{(E)}{CuSO_4} + BaCl_2 \longrightarrow CuCl_2 + \underset{\text{White}}{BaSO_4}$$

(4) Gas (B) *i.e.*, H_2S gives black ppt. with $CuSO_4$.

$$\underset{(E)}{CuSO_4} + H_2S \longrightarrow \underset{\substack{(F)\\ \text{Black}}}{CuS} + H_2SO_4$$

(5) Compound (F) (CuS) gives $Cu(NO_3)_2$ with HNO_3 which on treating with NH_4OH gives blue colour.

$$\underset{(F)}{CuS} + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2S$$

$$Cu(NO_3)_2 + 4NH_4OH \longrightarrow \underset{(G)\ \text{Blue}}{Cu(NH_3)_4(NO_3)_2} + 4H_2O$$

(6) (G) on acidifying with CH_3COOH and then treating with $K_4Fe(CN)_6$ gives chocolate coloured ppt. of $Cu_2Fe(CN)_6$.

$$Cu(NH_3)_4(NO_3)_2 + 4CH_3COOH \longrightarrow Cu(NO_3)_2 + 4CH_3COONH_4$$

$$2Cu(NO_3)_2 + K_4Fe(CN)_6 \longrightarrow \underset{\text{Chocolate ppt.}}{Cu_2[Fe(CN)_6]} + 4KNO_3$$

Thus, (A) FeS, CuS, PbS, HgS, CoS, NiS, (B) H_2S, (C) HNO_3, (D) S, (E) $CuSO_4$, (F) CuS, (G) $Cu(NH_3)_4(NO_3)_2$, (H) $Cu_2Fe(CN)_6$.

18. (i) (A) is an alkali and the equation is,

$$\underset{(A)}{2NaOH} + Zn \xrightarrow{\text{Heat}} Na_2ZnO_2 + \underset{(B)}{H_2}$$

(ii) (A) is NaOH and (C) is phosphorus. The equation will be,

$$\underset{(A)}{3NaOH} + 3H_2O + \underset{(C)}{P_4} \xrightarrow{\text{Heat}} PH_3 + 3NaH_2PO_2$$

(iii) (D) is NH_3 gas and (A) is NaOH. The equation will be,

$$\underset{(A)}{NaOH} + NH_4Cl \xrightarrow{Heat} \underset{(D)}{NH_3} + NaCl + H_2O$$

19. M is As; $AsCl_3 + 6H \xrightarrow[(N)]{Zn/H_2SO_4} AsH_3 + 3HCl$

$$2AsH_3 \xrightarrow{\Delta} \underset{\text{Silvery mirror } (M)}{2As} + 3H_2$$

20. $\underset{\text{or Ba}\ (A)}{3Ca + N_2} \longrightarrow \underset{\text{or } Ba_3N_2\ (B)}{Ca_3N_2} \xrightarrow{6H_2O} \underset{\text{or } 3Ba(OH)_2\ (C)}{3Ca(OH)_2} + 2NH_3$

$$\xrightarrow{CO_2} \underset{\text{or } BaCO_3\ (D)}{CaCO_3} + H_2O$$

21. From the (iv) point it is clear that the compound (X) is H_2O_2.

$$Ti(SO_4)_2 + 2H_2O + \underset{(X)}{H_2O_2} \longrightarrow \underset{\substack{\text{Pertitanic acid}\\ \text{(Yellow solution)}}}{H_2TiO_4} + 2H_2SO_4$$

(i) $2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O$

$$\underset{(X)}{H_2O_2} + O \longrightarrow H_2O + O_2$$

or $2KMnO_4 + 2KOH + \underset{(X)}{H_2O_2} \longrightarrow 2K_2MnO_4 + 2H_2O + O_2$

$$2K_2MnO_4 + 2H_2O \longrightarrow \underset{\text{Brown ppt.}}{2MnO_2} + O_2 + 4KOH$$

(ii) $\underset{(X)}{H_2O_2} + Cl_2 \longrightarrow 2HCl + O_2$

(iii) $\underset{(X)}{H_2O_2} + 2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O + I_2\uparrow$

Hence, (X) is H_2O_2.

22. (i) Step (i) suggests that compound (X) contains SO_4^{2-} radical.

(ii) Step (iii) suggests that the compound (X) contains Cu^{2+} radical.

(iii) Hence, the salt is $CuSO_4$.

Reactions:

(i) $\underset{(X)}{CuSO_4} + BaCl_2 \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{(Insoluble in HCl)}}}{BaSO_4} + CuCl_2$

(ii) $\underset{(X)}{2CuSO_4} + 4KI \longrightarrow 2CuI_2 + 2K_2SO_4$

$$\underset{\text{Unstable}}{2CuI_2} \longrightarrow Cu_2I_2 + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow \underset{\text{Colourless}}{Na_2S_4O_6} + 2NaI$$

(iii) $\underset{(X)}{2CuSO_4} + K_4Fe(CN)_6 \longrightarrow \underset{\substack{\text{Chocolate coloured}\\ \text{ppt.}}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$

23. (i) $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{(Sodium hypophosphite)}}{3NaH_2PO_2} + PH_3$

Thus, acid (A) is H_3PO_2, *i.e.*, hypophosphorus acid.

(ii) $2P + 3Cl_2 + 6H_2O \longrightarrow \underset{\text{(Phosphorus acid)}}{2H_3PO_3} + 6HCl$

Thus, acid (B) is H_3PO_3.

$$H_3PO_3 \longrightarrow HPO_2 + H_2O$$

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

$$P_4 + 10H_2SO_4 \longrightarrow \underset{\substack{\text{Phosphoric acid}\\ (C)}}{4H_3PO_4} + 10SO_2 + 4H_2O$$

Thus, acid (C) is H_3PO_4.

(iv) $H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$

$$HgCl_2 + 2H \longrightarrow \underset{\text{(White) } (D)}{Hg_2Cl_2} + 2HCl$$

$$Hg_2Cl_2 + 2H \longrightarrow \underset{\text{(Grey) } (E)}{2Hg} + 2HCl$$

24. (a) $CuCO_3 \cdot Cu(OH)_2 \longrightarrow \underset{\text{Black ppt.}}{2CuO} + CO_2\uparrow + H_2O$

A_1 is malachite, an ore of Cu.

$$CuCO_3 \cdot Cu(OH)_2 + 4HCl \longrightarrow 2CuCl_2 + CO_2 + 3H_2O$$

$$2CuCl_2 + 4KI \longrightarrow \underset{\text{ppt.}}{2CuI} + 4KCl + I_2$$

(b) $2Cu_2S + 3O_2 \xrightarrow{\text{Roasting}} \underset{(G)}{2Cu_2O} + 2SO_2\uparrow$

A_2 is copper glance an ore of Cu.

$$2Cu_2O + Cu_2S \xrightarrow[\text{During roasting}]{\text{Auto reduction}} 6Cu + SO_2\uparrow$$

$$\underset{(G)}{3SO_2} + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O$$

25. (i) (X) imparts golden yellow flame and so contains Na^+.

(ii) Step 1 suggests that (X) is NaOH because it reacts with Zn to give H_2.

$$Zn + \underset{(X)}{2NaOH} \longrightarrow Na_2ZnO_2 + H_2$$

(iii) (X) is also justified by step 2 reactions.

$$\underset{(X)}{2NaOH} + SnCl_2 \longrightarrow \underset{\text{White ppt.}}{Sn(OH)_2} + 2NaCl$$

$$Sn(OH)_2 + \underset{\substack{(X)\\ \text{(Excess)}}}{2NaOH} \longrightarrow \underset{\text{Soluble}}{Na_2SnO_2} + 2H_2O$$

26. (i) The compound (B) reacts with NaCl solution (brine) to give white precipitate (D) soluble in NH_4OH so (D) is AgCl.

(ii) Thus, (B) must contain Ag^+ ion.

(iii) (B) is obtained from (A) and dilute HNO_3, so (B) is $AgNO_3$ and (A) is Ag.

Reactions: $\underset{(A)}{3Ag} + 4HNO_3 \longrightarrow \underset{(B)}{3AgNO_3} + \underset{(C)}{NO} + 2H_2O$

$$\underset{(B)}{AgNO_3} + NaCl \longrightarrow \underset{(D)}{AgCl} + NaNO_3$$

$$\underset{(D)}{AgCl} + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$\underset{(B)}{2AgNO_3} + Na_2S_2O_3 \longrightarrow \underset{(E)\ \text{White}}{Ag_2S_2O_3} + 2NaNO_3$$

$$\underset{(E)}{Ag_2S_2O_3} \longrightarrow \underset{\text{Black}}{Ag_2S} + SO_3$$

27. (1) (X) gives black ppt. in acid medium with H_2S and thus, it may be $HgCl_2$, $PbCl_2$, $CuCl_2$ or $SnCl_2$.

(2) Black ppt. is insoluble in yellow ammonium sulphide and thus, it is not $SnCl_2$.

(3) Steps (iii) and (iv) suggest that (X) is $HgCl_2$.

Reactions:

(i) $\underset{(X)}{HgCl_2} + H_2S \longrightarrow \underset{\text{Black ppt.}}{HgS} + 2HCl$

(ii) $\underset{(X)}{2HgCl_2} + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{White ppt.}}{Hg_2Cl_2}$

$Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{Grey ppt.}}{2Hg}$

(iii) $\underset{(X)}{HgCl_2} + 2KI \longrightarrow \underset{\text{Red ppt.}}{HgI_2} + 2KCl$

$HgI_2 + 2KI \longrightarrow \underset{\text{Nessler's reagent (solution) (Red)}}{K_2HgI_4}$

28. (i) Aqueous solution of gas (X) turns red litmus blue, the solution is alkaline in nature. So the gas may be NH_3.

(ii) With $CuSO_4$, NH_4OH gives deep blue coloured $Cu(NH_3)_4SO_4$.

i.e.,

$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{(Deep blue complex)}}{Cu(NH_3)_4SO_4} + H_2O$

(iii) $FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{(Brown ppt.)}}{Fe(OH)_3} + 3NH_4Cl$

The brown precipitate of $Fe(OH)_3$ form soluble $Fe(NO_3)_3$ with dil. HNO_3.

$Fe(OH)_3 + 3HNO_3 \longrightarrow \underset{\text{(Soluble)}}{Fe(NO_3)_3} + 3H_2O$

Hence, (X) is NH_3.

29. 'A' is KI and 'B' is HgI_2

(a) $HgI_2 + H_2S \longrightarrow \underset{\text{Black '}C\text{'}}{HgS} + 2HI$

(b) $HgS \xrightarrow{\text{Aquaregia}} HgCl_2$

$HgCl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{Grey black '}D\text{'}}{Hg}$

(c) $2KI(aq.) + HgI_2(aq.) \longrightarrow K_2HgI_4$

$K_2HgI_4 + NH_4OH + 3KOH \longrightarrow O\begin{matrix}Hg\\ \diagup\ \diagdown\\ Hg\end{matrix}NH_2I + 7KI + 2H_2O$

Sodium carbonate extract contains NaI.

(d) $2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$

(e) $I^- + AgNO_3 \longrightarrow NO_3^- + AgI$

(Yellow ppt. insoluble in NH_4OH)

30. (i) Aqueous solution of (X) is alkaline, so (X) may be an alkali metal salt.

(ii) On strong heating, (X) swells upto give a glassy mass, it may be borax.

(iii) This is further supported by the fact that its concentrated solution on treatment with concentrated solution of H_2SO_4 yields crystals of boric acid (a weak monobasic acid).

(iv) Hence, (X) is borax $(Na_2B_4O_7 \cdot 10H_2O)$.

Reactions:

(i) $\underset{(X)}{Na_2B_4O_7} + 7H_2O \longrightarrow \underset{\text{Alkali}}{2NaOH} + 4H_3BO_3$

(ii) $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 + 10H_2O$

$Na_2B_4O_7 \xrightarrow{\text{Heat}} 2NaBO_2 + \underset{\text{Glassy mass}}{B_2O_3}$

(iii) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + \underset{\text{Weak acid}}{4H_3BO_3}$

31. (X) gives brick red flame so, it contains Ca^{2+}. Reactions (i), (ii) and (iii) suggest that the probable compound is bleaching powder $(CaOCl_2)$.

Reactions:

(i) $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Smell}}{Cl_2}\uparrow$

(ii) $\underset{(X)}{CaOCl_2} + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + Cl_2 + H_2O$

$2KI + Cl_2 \longrightarrow 2KCl + I_2$

(iii) $\underset{\text{Turbid}}{CaOCl_2(aq.)} + CO_2 \longrightarrow \underset{\text{White ppt.}}{CaCO_3} + Cl_2$

(iv) $\underset{(X)}{CaOCl_2} + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

$C_2H_5OH + Cl_2 \longrightarrow CH_3CHO + 2HCl$

$CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl$

$2Ca(OH)_2 + 2CCl_3CHO \longrightarrow \underset{\text{Anaesthetic}}{2CHCl_3} + (HCOO)_2Ca$

32. (i) (X) removes black stains from old oil painting, so (X) is H_2O_2.

Reactions:

(i) $\underset{(X)}{5H_2O_2} + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

(ii) $\underset{(X)}{H_2O_2} + 2KI + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2H_2O$

(iii) $\underset{(X)}{3H_2O_2} + 2KMnO_4 \longrightarrow 2MnO_2 + 2KOH + 3O_2 + 2H_2O$

(iv) $\underset{(X)}{4H_2O_2} + \underset{\text{Black}}{PbS} \longrightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$

33. **Compound (A):** (i) (A) gives on heating two oxides of sulphur and so (A) is $FeSO_4 \cdot 7H_2O$.

(ii) $\underset{(A)}{FeSO_4 \cdot 7H_2O} \xrightarrow{\Delta} FeSO_4 + 7H_2O$

$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

(iii) $FeSO_4 + 2NaOH \longrightarrow \underset{\text{green}}{Fe(OH)_2} + Na_2SO_4$

$Fe^{2+} \xrightarrow[\text{Alkaline medium}]{\text{Oxidation/air}} \underset{\text{brown}}{Fe^{3+}} + e$

34. (1) Gas (B) is formed on heating (A) and it turns lime water milky so (B) is CO_2 and (A) has CO_3^{2-} ions.

(2) Solution of (A) in alkaline medium gives white ppt. with H_2S and so (A) may have Zn^{2+} ions.

(3) The compound (A), if taken $ZnCO_3$, is also justified by the other reactions.

Reactions:

(i) $\underset{(A)}{ZnCO_3} \longrightarrow \underset{(C)}{ZnO} + \underset{(B)}{CO_2}$

(ii) $\underset{(B)}{CO_2} + Ca(OH)_2 \longrightarrow \underset{\text{White}}{CaCO_3} + H_2O$

$CaCO_3 + H_2O + \underset{\text{Excess}}{CO_2} \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$

(iii) $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

$2ZnCl_2 + K_4Fe(CN)_6 \longrightarrow \underset{\text{White ppt.}}{Zn_2[Fe(CN)_6]} + 4KCl$

(iv) $ZnCl_2 + H_2S \longrightarrow \underset{(D)}{ZnS} + 2HCl$

White ppt.

35. $Na_2CO_3 + SO_2 \xrightarrow{H_2O} \underset{(A)}{2NaHSO_3} + CO_2$

$NaHSO_3 + Na_2CO_3 \longrightarrow \underset{(B)}{2Na_2SO_3} + H_2O + CO_2$

$\underset{(B)}{Na_2SO_3} + S \longrightarrow \underset{(C)}{Na_2S_2O_3}$

$\underset{(C)}{2Na_2S_2O_3} + I_2 \longrightarrow \underset{(D)}{Na_2S_4O_6} + 2NaI$

Oxidation states of S are +4 in $NaHSO_3$ and Na_2SO_3 and Na_2SO_3 +6 and −2 (an average +2) in $Na_2S_2O_3$ and +5 and 0 (an average +5/2) in $Na_2S_4O_6$.

36. $\underset{\text{(Borax)}}{Na_2B_4O_7 \cdot 10H_2O} \xrightarrow{\Delta} Na_2B_4O_7$

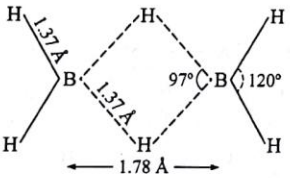
$Na_2B_4O_7 + 2HCl \longrightarrow 2NaCl + \underset{\text{Tetraboric acid}}{H_2B_4O_7}$

$H_2B_4O_7 + 5H_2O \longrightarrow \underset{\text{Boric acid}}{4H_3BO_3}$

$2H_3BO_3 \xrightarrow{\text{Red hot}} \underset{\text{Boric anhydride}}{B_2O_3} + 3H_2O$

$B_2O_3 + 3Mg \xrightarrow{\text{Fusion}} \underset{\text{Boron}}{2B} + 3MgO$

Structure of B_2H_6:



(H---B---H is hydrogen bridge bond, *i.e.*, 3 centre-two electron bond)

Reaction with HCl:

$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$

37. (1) (*A*) on heating with conc. H_2SO_4 and MnO_2 yields brown fumes and so it contains Br^- ions.

(2) (*A*) is pale yellow solid insoluble in mineral acid but soluble in NH_3 and thus, it is AgBr.

Reactions:

(1) $\underset{(A)}{AgBr} + 2NH_3 \longrightarrow \underset{(B)}{Ag(NH_3)_2}Br$ (Partially soluble)

(2) $2AgBr + Na_2S_2O_3 \longrightarrow \underset{(C)}{Ag_2S_2O_3} + 2NaBr$

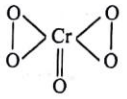
$Ag_2S_2O_3 \xrightarrow{\text{Boil}} \underset{\text{Black ppt.}}{Ag_2S} + SO_3$

(D)

(3) $Ag_2S + 2HCl \longrightarrow \underset{\text{White ppt.}}{2AgCl} + H_2S$

(E)

38. (i) CrO_5 :



(ii) 1 *M* H_2O_2 means 34 g/litre H_2O_2,

$\because$ 34 g H_2O_2 or 1 litre H_2O_2 gives 11200 mL O_2

$\therefore$ Volume strength = 11.2

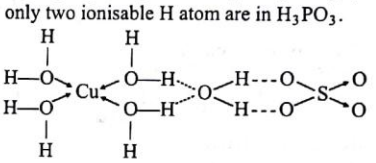
(iii) $LiH + CO_2 \longrightarrow HCOOLi$

$LiH + 2SO_2 \longrightarrow \underset{\text{Lithium sulphosulphite}}{Li_2S_2O_4} + H_2\uparrow$

$H_3PO_3 + D_2O \longrightarrow D_2HPO_3 + H_2O$;

only two ionisable H atom are in H_3PO_3.

(iv)



Co-ordinate bond $4H_2O$ with Cu^{2+} fifth H_2O molecule bond with SO_4^{2-} and H bond between 2 of the co-ordinated H_2O.

The pentahydrate has a hydrogen bonded water molecule between the square planar $Cu(H_2O)_4^{2+}$ and tetrahedral SO_4^{2-} ion. In this anion is also hydrated and has anion water.

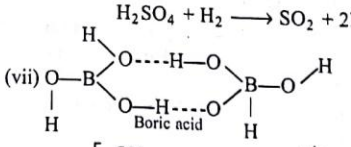
(v) $As_2S_3 + 3(NH_4)_2S + 2S \longrightarrow \underset{\text{Soluble}}{2(NH_4)_3 \cdot AsS_4}$

$2(NH_4)_3AsS_4 + 6HCl \longrightarrow 6NH_4Cl + 3H_2S + \underset{\text{ppt.}}{As_2S_5}$

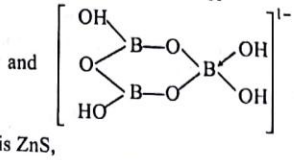
(vi) At ordinary temperature it reacts with H_2 to form some SO_2 due to its reduction

$H_2SO_4 + H_2 \longrightarrow SO_2 + 2H_2O$

(vii)



and



39. (*A*) is ZnS,

$\underset{(A)}{ZnS} + H_2SO_4 \longrightarrow \underset{(C)}{ZnSO_4} + \underset{(B)}{H_2S}$

$$\underset{(B)}{3H_2S} + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + \underset{\text{White-grey}\ (D)}{3S}$$

$$\underset{(D)}{S} + \underset{(Air)}{O_2} \longrightarrow \underset{(E)}{SO_2}$$

$$\underset{(E)}{SO_2} + \underset{(B)}{2H_2S} \longrightarrow \underset{\text{Colourless liquid}\ (C)}{2H_2O} + \underset{(D)}{3S}$$

$$5H_2O + \underset{\text{White}}{CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4 \cdot 5H_2O}$$

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$$

$$Zn(OH)_2 + NaOH \longrightarrow Na_2ZnO_2\ (\text{Soluble})$$

Also in excess of NH_4OH it forms soluble complex $[Zn(NH_3)_4](OH)_2$.

40. (1) Since, (A) gives chromyl chloride test and thus, it has Cl^- ions.

(2) Since, (A) is strong reducing agent so (A) is $SnCl_2$.

Reactions:

(1) $\underset{\substack{\text{White transparent}\\ \text{Solid}\ (A)}}{SnCl_2} + H_2O \longrightarrow \underset{\substack{(B)\\ \text{White turbidity}}}{Sn(OH)Cl} + HCl$

(2) $\underset{(A)}{SnCl_2} + 2NaOH \longrightarrow \underset{(C)\ \text{White ppt.}}{Sn(OH)_2} + 2NaCl$

$$\underset{(C)}{Sn(OH)_2} + 2NaOH \longrightarrow \underset{\text{Soluble}}{Na_2SnO_2} + 2H_2O$$

(3) $3SnCl_2 + 2AuCl_3 \longrightarrow 3SnCl_4 + \underset{\substack{\text{Purple of cassius}\\ \text{(Colloidal gold)}}}{2Au}$

(4) $SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$

41. (X) is $AlCl_3$, a Lewis acid which exist as dimer (Al_2Cl_6), sublimes at 180° C and forms monomer $AlCl_3$ at 400° C.

(i) $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + \underset{\text{Fumes}}{3HCl\uparrow}$

(ii) $HCl + NH_4OH \longrightarrow \underset{\text{White fumes}}{NH_4Cl\uparrow} + H_2O$

(iii) $AlCl_3 + 3NH_4OH \longrightarrow \underset{\text{White ppt.}}{Al(OH)_3} + 3NH_4Cl$

$$Al(OH)_3 + NaOH \longrightarrow \underset{\text{Soluble}}{NaAlO_2} + 2H_2O$$

(iv) Dissociation of H_2S is suppressed in acidic medium and thus does not provide sufficient $[S^{-2}]$ to cross over the K_{sp} of Al_2S_3.

42. The cation of (X) is Sn^{2+}.

(i) $Sn^{2+} + H_2S \xrightarrow{H^+} SnS$

(Brown ppt. soluble in yellow ammonium sulphide step ii)

(iii) $Sn^{2+} + 2NaOH \longrightarrow 2Na^+ + \underset{\text{White ppt.}}{Sn(OH)_2}$

$$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Soluble}}{Na_2SnO_2} + 2H_2O$$

(iv) $Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$

43. (A) is PH_4I.

(i) $\underset{(A)}{PH_4I} + KOH \longrightarrow \underset{(C)}{KI} + \underset{(B)}{PH_3} + H_2O$

(ii) $\underset{(B)}{2PH_3} + 4O_2 \longrightarrow \underset{(D)}{P_2O_5} + 3H_2O$

(iii) $3CuSO_4 + 2PH_3 \longrightarrow 3H_2SO_4 + Cu_3P_2 \longrightarrow Cu$

(iv) $2CuSO_4 + 4KI \longrightarrow \underset{\substack{(E)\\ \text{Precipitate}}}{Cu_2I_2} + 2K_2SO_4 + I_2$

44. (A) is FeS.

(i) $\underset{(A)}{4FeS} + 7O_2 \longrightarrow 2Fe_2O_3 + \underset{(B)}{4SO_2}$

(ii) $FeS + H_2SO_4 \longrightarrow \underset{(D)}{FeSO_4} + \underset{(C)}{H_2S}$

(iii) $\underset{(C)}{2H_2S} + \underset{(B)}{SO_2} \longrightarrow 2H_2O + \underset{\text{Turbidity}}{3S}$

or $2H_2S + H_2SO_3 \longrightarrow S + 3H_2O$

(iv) $\underset{(D)}{3FeSO_4} + 2K_3[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Ferro ferricyanide}\\ \text{(Blue)}}}{Fe_3[Fe(CN)_6]_2} + 3K_2SO_4$

45. $\underset{\text{Galena}}{2PbS} + O_2 \longrightarrow 2PbO + 2SO_2$ (Roasting)

$PbS + 2O_2 \longrightarrow PbSO_4$ (Roasting)

$PbS + 2PbO \longrightarrow 3Pb + SO_2$ (Auto reduction)

$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$ (Auto reduction)

Oxidation number of Pb in litharge (PbO) = +2.

46. (i) (B) forms double salt with $Al_2(SO_4)_3$ and thus, may be K_2SO_4.

(ii) $(A) + S \longrightarrow (B)\ K_2SO_4$

$\because$ 1.743 g K_2SO_4 is obtained by 1.422 g (A)

$\therefore$ 174 g K_2SO_4 is obtained by

$$\frac{1.422 \times 174}{1.743} = 142\text{ g}\ (A)$$

$\because$ 174 g K_2SO_4 requires 32 g S

$\therefore$ 1.743 g K_2SO_4 requires $\frac{32 \times 1.743}{174} = 0.321$ g S

Thus, given data confirms that (B) is K_2SO_4.

Now $\underset{\text{(A potassium salt)}}{2(A)} + S \longrightarrow K_2SO_4$

Molar mass of $(A) \times 2 = 142$

$\therefore$ Molar mass of $(A) = 71$

Since, (A) is pot. salt

$\therefore$ Molar mass of left component = 71 − 39 = 32

Thus, salt is KO_2.

$$\underset{(A)}{2KO_2} + S \longrightarrow \underset{(B)}{K_2SO_4} \xrightarrow[Aq.]{Al_2(SO_4)_3} \underset{(C)}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O}$$

47. The scarlet red compound (A) is Pb_3O_4.

The reactions are,

$$Pb_3O_4 + \underset{\text{Conc.}}{4HNO_3} \longrightarrow \underset{\text{Solution}}{2Pb(NO_3)_2} + \underset{\text{(Brown ppt.)}\ (B)}{PbO_2\downarrow} + H_2O$$

$$Pb(NO_3)_2 + 2KI \longrightarrow \underset{\text{Yellow ppt.}\ (C)}{PbI_2\downarrow} + 2KNO_3$$

$$5PbO_2 + 2Mn(NO_3)_2 + 4HNO_3 \longrightarrow 4Pb(NO_3)_2 + \underset{\text{Purple colour}\ (D)}{Pb(MnO_4)_2} + 2H_2O$$

48. The mineral (A) and other compounds are:

(A) $Ca_2B_6O_{11}\cdot 5H_2O$ (Colemanite)
(B) $CaCO_3$ (Calcium carbonate)
(C) $Na_2B_4O_7$ (Borax)
(D) $NaBO_2$ (Sodium metaborate)
(E) B_2O_3 (Boric anhydride)
(F) $Co(BO_2)_2$ (Cobalt metaborate)

The reactions are,

$$Ca_2B_6O_{11} + 2Na_2CO_3\,(aq.) \longrightarrow \underset{(B)}{2CaCO_3}\downarrow + \underbrace{\underset{(C)}{Na_2B_4O_7} + \underset{(D)}{NaBO_2}}_{\text{Soluble}}$$

$$\underset{(D)}{4NaBO_2} + CO_2 \longrightarrow \underset{(C)}{Na_2B_4O_7} + Na_2CO_3$$

$$\underset{(C)}{Na_2B_4O_7} \xrightarrow{\Delta} \underset{(D)}{2NaBO_2} + \underset{(E)}{B_2O_3}$$

$$\underset{(E)}{B_2O_3} + CoO \longrightarrow \underset{\text{(Blue)}}{Co(BO_2)_2}$$

49. (A) Ag_2S (a black mineral)
(B) $NaAg(CN)_2$
(C) Na_2S
(D) Ag
(E) AgCl
(F) $Ag(NH_3)_2Cl$

The reactions are,

(1) $\underset{(A)}{Ag_2S} + 4NaCN \longrightarrow \underset{(B)}{2NaAg(CN)_2} + \underset{(C)}{Na_2S}$

(2) $2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + \underset{(D)}{2Ag}$

(3) $3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$

(4) $AgNO_3 \xrightarrow{HCl} \underset{(E)}{AgCl} + HNO_3$

(5) $\underset{(E)}{AgCl} + 2NH_3 \longrightarrow \underset{(F)}{Ag(NH_3)_2Cl}$

(6) $4AgCl + 2Na_2CO_3 \longrightarrow 4Ag + 4NaCl + 2CO_2 + O_2$

50. $3Ca + N_2 \longrightarrow Ca_3N_2 \xrightarrow{6H_2O} \underset{\text{Alkali}}{3Ca(OH)_2} + \underset{(A)}{2NH_3}$

$$Ca(OH)_2 \xrightarrow{CO_2} \underset{\text{Solid}}{CaCO_3} + H_2O$$

51. $Bi(NO_3)_2 + H_2O \longrightarrow Bi[(OH)(NO_3)_2] + HNO_3$

$$NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O$$

$$2I^- \longrightarrow I_2 + 2e$$

$$I_2 + KI \longrightarrow KI_3 \quad \text{(Yellow solution)}$$

52. $NH_4NO_3 \longrightarrow \underset{(B)}{N_2O} + \underset{(C)}{2H_2O}$

$$10N_2O + P_4 \longrightarrow \underset{\text{(Dehydrating agent)}}{P_4O_{10}} + 10N_2$$

53. (i) $Na_2S + Na_2SO_3 + \underset{(B)}{I_2} \longrightarrow \underset{(A)}{Na_2S_2O_3} + 2NaI$

(ii) $Na_2S_2O_3 + 2AgNO_3 \longrightarrow \underset{\text{(White)}}{Ag_2S_2O_3} + 2NaNO_3$

$$Ag_2S_2O_3 + H_2O \longrightarrow \underset{(C)\text{ Black}}{Ag_2S} + H_2SO_4$$

(iii) $3Na_2S_2O_3 + 2FeCl_3 \longrightarrow \underset{\text{Violet }(D)}{Fe_2(S_2O_3)_3} + 6NaCl$

$$Fe_2(S_2O_3)_3 \xrightarrow[\text{disappears}]{\text{Colour}} 2Fe^{2+} + S_4O_6^{2-}$$

(iv) $Na_2S_2O_3 + CuCl_2 \longrightarrow CuS_2O_3 + 2NaCl$

$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow \underset{\text{White}}{Cu_2S_2O_3} + Na_2S_4O_6$$

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow \underset{(E)\text{ (Soluble)}}{Na_4[Cu_6(S_2O_3)_5]}$$

54. (i) $\underset{(A)}{CoCl_2} + H_2S \xrightarrow{NH_4OH} \underset{(B)\text{ Black}}{CoS} + 2HCl$

(ii) $CoS + 2HCl \xrightarrow{KClO_3} CoCl_2 + H_2S$

(iii) $CoCl_2 + 2KCN \longrightarrow \underset{\text{Buff ppt.}}{Co(CN)_2} + 2KCl$

$$Co(CN)_2 + 4KCN \longrightarrow \underset{(C)\text{ Soluble}}{K_4Co(CN)_6}$$

(iv) $\underset{(C)}{2K_4Co(CN)_6} \xrightarrow[[O]]{H_2O,\,\Delta} \underset{(D)}{2K_3Co(CN)_6} + 2KOH$

(v) $CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$

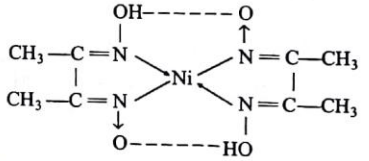
$$Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4[Co(CO_3)_3] + 3H_2O + 3CO_2$$

$$2Na_4Co(CO_3)_3 + H_2O + O \longrightarrow 2Na_3[Co(CO_3)_3] + 2NaOH$$

55. $Na_2CrO_3 + H_2O_2 \longrightarrow Na_2CrO_4 + H_2O$

56. (a) Ni^{2+} ions react with dimethyl glyoxime in slightly alkaline medium as:

$$Ni^{2+} + \begin{matrix} CH_3-C=NOH \\ | \\ CH_3-C=NOH \end{matrix} + 2NH_4OH \longrightarrow$$



(b) The charge on Ni in the complex is +2 and the hybridisation of Ni^{2+} in the given complex is dsp^2 having square planar nature.

(c) The complex is diamagnetic as it has no unpaired electron.

57. (i) $\underset{(A)}{CuCO_3} \longrightarrow \underset{(B)}{CuO} + \underset{(C)}{CO_2}$

(ii) $CuO + H_2 \longrightarrow \underset{(D)}{Cu} + H_2O$

(iii) $CuO + 2HCl \longrightarrow CuCl_2 + H_2O$

$$2CuCl_2 + K_4Fe(CN)_6 \longrightarrow \underset{\text{Chocolate }(E)}{Cu_2Fe(CN)_6} + 4KCl$$

(iv) $Ca(OH)_2 + \underset{(C)}{CO_2} \longrightarrow \underset{\text{White}}{CaCO_3} + H_2O$

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{(F)\text{ Soluble}}{Ca(HCO_3)_2}$$

58. (i) $\underset{(A)}{Hg_2(NO_3)_2} + HCl \longrightarrow \underset{(B)}{Hg_2Cl_2} + 2HNO_3$

(ii) $Hg_2Cl_2 + Cl_2 \longrightarrow \underset{(C)}{2HgCl_2}$ (Soluble)

(iii) $HgCl_2 + 2KI \longrightarrow 2KCl + HgI_2$ (ppt.)

$HgI_2 + 2KI \longrightarrow \underset{(D)}{K_2HgI_4}$ (used for test of NH_3; Nessler's reagent)

(iv) $\underset{(B)}{Hg_2Cl_2} + SnCl_2 \longrightarrow SnCl_4 + \underset{(E)\text{ Grey}}{Hg_2}$

$2HgCl_2 + 2SnCl_2 \longrightarrow 2SnCl_4 + \underset{(E)}{Hg_2}$

(v) $Hg_2(NO_3)_2 + 2H_2SO_4 \longrightarrow 2HgHSO_4 + 2HNO_3$

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$

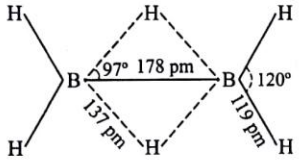
$FeSO_4 + NO \longrightarrow \underset{(F)\text{ Brown ring}}{FeSO_4 \cdot NO}$

59. $\underset{(X)}{4BCl_3} + 3Li[AlH_4] \longrightarrow \underset{(Y)}{2B_2H_6} + 3AlCl_3 + 3LiCl$

$$\%\text{ of H in } B_2H_6 = \frac{6}{27.62} \times 100 = 21.72\%$$

$B_2H_6 + 3O_2 \xrightarrow[\text{in air}]{\text{Explosion}} 2B_2O_3 + 3H_2O;\ \Delta H = -2008\text{ kJ}$

Structure of B_2H_6:



Dotted line represents three centre-2-electron pair bond or banana bond.

60. Oxidising nature of H_2O_2:

$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$

Reducing nature of H_2O_2 :

$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$

61. Haematite (Fe_2O_3) on burning with coke and lime at 2000° C results in the following:

$C + O_2 \longrightarrow CO_2$

$CO_2 + C \longrightarrow 2CO$

$3CO + Fe_2O_3 \longrightarrow \underset{(\text{Steel})}{2Fe} + 3CO_2$

[Reduction of Fe_2O_3 to form steel]

$SiO_2 + \underset{(\text{Lime})}{CaO} \longrightarrow \underset{(\text{Slag})}{CaSiO_3}$

[Slag, ($CaSiO_3$) is used as building material]

62. $SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3$

$FeCl_3 \cdot 6H_2O + 6SOCl_2 \longrightarrow FeCl_3 + 6SO_2 + 12HCl$

$FeCl_3 \cdot 6H_2O + 6CH_3C(OCH_3)_2 \cdot CH_3 \longrightarrow FeCl_3 + 12CH_3OH + 6CH_3COCH_3$

63. An observation of the experimental data reveals that A is $FeCl_3$; Red colour of $Fe(CNS)_3$ with NH_4SCN from (ii) and chromyl chloride test for Cl from (iii). The reactions are:

(i) $\underset{(A)}{FeCl_3} + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$

(acidic solution due to hydrolysis of Fe^{3+})

or $Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$

$FeCl_3$ sublimes at 300° C.

(ii) $FeCl_3 + 3NH_4SCN \longrightarrow \underset{(B)\text{ Red}}{Fe(CNS)_3} + 3NH_4Cl$

$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{(C)\text{ Blue}}{Fe_4[Fe(CN_6)]_3} + 12KCl$

(iii) $4FeCl_3 + 9H_2SO_4 + 3K_2Cr_2O_7 \longrightarrow \underset{(D)\text{ (Red yellow vapours)}}{6CrO_2Cl_2} + 2Fe_2(SO_4)_3 + 3K_2SO_4 + 9H_2O$

(iv) $CrO_2Cl_2 + 4NaOH \longrightarrow 2NaCl + Na_2CrO_4 + 2H_2O$

$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{(E)\text{ (Yellow ppt.)}}{PbCrO_4\downarrow} + 2CH_3COONa$

64. An observation of the experimental data reveals that (A) is $CdSO_4$; yellow ppt. of CdS from observation (i) and sulphate from observation (vi). The reactions are:

(i) $\underset{(B)}{CdSO_4} + H_2S \longrightarrow \underset{(A)}{CdS} + H_2SO_4$

(ii) $CdS + 2HNO_3 \longrightarrow \underset{\text{Soluble}}{Cd(NO_3)_2} + H_2S$

$CdS + \underset{\text{Yellow amm. sulphide}}{(NH_4)_2S_x} \longrightarrow \text{Insoluble}$

$CdSO_4 + 2NH_4OH \longrightarrow Cd(OH)_2 + (NH_4)_2SO_4$

(iii) $Cd(OH)_2 + 4NH_4OH \longrightarrow \underset{(C)\text{ Soluble}}{[Cd(NH_3)_4](OH)_2} + 4H_2O$

(iv) $CdSO_4 + 2KCN \longrightarrow \underset{\text{White ppt.}}{Cd(CN)_2} + K_2SO_4$

$Cd(CN)_2 + KCN \longrightarrow \underset{(D)\text{ Soluble}}{K_2[Cd(CN)_4]}$

(v) $K_2[Cd(CN)_4] + H_2S \longrightarrow CdS + 2KCN + 2HCN$

(vi) $CdSO_4 + BaCl_2 \longrightarrow \underset{\substack{(E)\\ \text{Insoluble in } HNO_3}}{BaSO_4} + CdCl_2$

65. (i) Na_2O_2 is a powerful oxidant and bleaching agent and bleaches red litmus paper to white in aqueous solution state.

$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

H_2O_2 + litmus red $\longrightarrow$ White (Bleaching)

(ii) The other compound Na_2O will give NaOH on dissolution in water. The red litmus will turn to blue.

66. (A) $[Cr(H_2O)_6]Cl_3$ (Violet)

(B) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (Green)

(molar mass = 266.5 g mol^{-1})

(C) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (Dark green)

Compound (A) contains six water molecules as coordinated water and thus, does not lose H_2O on treatment with H_2SO_4. Compound (B) contains five water molecules as coordinated water and one molecule as lattice water which is lost to H_2SO_4 showing a loss of 18 g out of 266.5 g, *i.e.*, 6.75% loss. Similarly, compound (C) contains four coordinated water molecules and two molecules of lattice water which are taken out by H_2SO_4 to show a loss of 13.5%.

67. A solution containing one mole of HgI_2 and two mole of NaI is orange in colour due to the partial solubility of HgI_2. On addition of excess of NaI, the colourless complex Na_2HgI_4 is formed.

$$\underset{\text{Excess}}{2NaI} + HgI_2 \longrightarrow Na_2HgI_4$$

The Na_2HgI_4 on addition of NaOCl, oxidises as:

$$3Na_2HgI_4 + 2NaOCl + 2H_2O \longrightarrow 3HgI_2 + 2NaCl + 4NaOH + 2NaI_3$$

Thus, colour of partially soluble HgI_2 is restored.

68.
$$\underset{\text{Pyrolusite}}{MnO_2} + KOH \xrightarrow{[O]} \underset{\substack{\text{Dark green}\\(A)}}{K_2MnO_4} + H_2O$$

$$3K_2MnO_4 + 2H_2O \xrightarrow{\text{Dil. } H_2SO_4} \underset{\text{Purple } (B)}{2KMnO_4} + MnO_2 + 4KOH$$

(i) $2KMnO_4 + KI + H_2O \longrightarrow \underset{(C)}{KIO_3} + 2MnO_2 + 2KOH$

(ii) $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

(iii) $2KMnO_4 + 2H_2SO_4\ (\text{conc.}) \longrightarrow 2K_2SO_4 + \underset{(D)}{Mn_2O_7} + H_2O$

$$\underset{(D)}{2Mn_2O_7} \longrightarrow \underset{(E)}{4MnO_2} + 3O_2$$

69. The compound can be **$AgNO_3$.**

Solution of $A + NaCl \rightarrow$ a white precipitate insoluble in HNO_3 but dissolves in NH_4OH, indicating the presence of Ag^+ ions in solution.

Solution of $A + H_2S \rightarrow Ag_2S$—a black precipitate soluble in HNO_3.

Solution of $A + K_2CrO_4 \rightarrow Ag_2CrO_4$—a brick red precipitate. Presence of Ag^+ is confirmed.

Solution of $A + FeSO_4 + \text{conc. } H_2SO_4 \rightarrow$ a brown ring indicates the presence of nitrate. The compound is therefore identified as $AgNO_3$.

$$2AgNO_3 + H_2SO_4 \longrightarrow Ag_2SO_4 + 2HNO_3$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$FeSO_4 + NO \longrightarrow \underset{\text{A brown ring}}{[FeSO_4 \cdot NO]}$$

70. The given statements suggest that given compound is **$FeCl_3$.**

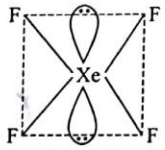
$$2FeCl_3 + SnCl_2 \longrightarrow SnCl_4 + 2FeCl_2$$

$$2FeCl_3 + 2KI \longrightarrow 2FeCl_2 + 2KCl + I_2$$

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

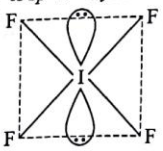
$$4FeCl_3 + 3K_4Fe(CN)_6 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$

71. (i) **XeF_4 :** Xe in XeF_4^- is sp^3d^2 hybridised.



Lone pair

IF_4^- : I in IF_4^- is sp^3d^2 hybridised.



(ii) Lithium is too smaller in size to have a co-ordination number six.

(iii) $Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + S + 2HCl$

(iv) $2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$

(v) Boron halides being electron deficient compounds are Lewis acid. The order of basic nature is

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

The order is just reverse to the normal expected order on the basis of electronegativity of halogens. This anomalous nature has been explained on the relatively decreasing tendency of halogens from F_2 to I_2 to back donate the unutilised electrons to the vacant *p*-orbitals of boron atom.

(vi) In graphite the sp^2 hybridisation takes place giving rise to 3σ and 1π bond. The sigma bonds formed possess more *s*-character and thus, show more extent of overlapping in comparison to diamond which possesses sp^3 hybridised state. Thus graphite possesses lower energy level.

(vii) Pb in Pb^{4+} state is a strong oxidising agent and thus PbO_2 is the strongest among given oxidants and oxidises even HCl to Cl_2.

72.
$$Mn_2O_7 \longrightarrow 2MnO_2 + \frac{3}{2}O_2;$$

$$Mn_2O_7 + H_2O \longrightarrow \underset{\text{Purple}}{2HMnO_4}$$

73. The SO_2 is obtained by burning sulphur in air as,

$$S + O_2 \longrightarrow SO_2$$

The SO_2 so obtained is impure. Dust present in sulphur is removed by allowing the gas to expand, when some dust settles down by passage through electrostatic precipitators and finally washing with water. The moistened gas is now treated with conc. H_2SO_4 to dry it which is kept in use until its concentration falls to 94%.

The SO_2 so obtained is then catalytically converted to SO_3.

$$2SO_2 + O_2 \xrightarrow[\substack{\text{Finely divided Pt. deposited on } MgSO_4\\ \text{or } Fe_2O_3 \text{ and CuO}\\ \text{or Pt.-silica gel}}]{\text{Pt. asbestos or}} 2SO_3$$

74.
$$\underset{(X)}{4NH_4Cl} + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow \underset{\substack{\text{Reddish brown gas}\\(A)}}{2CrO_2Cl_2} + 4NH_4HSO_4 + 2KHSO_4 + 3H_2O$$

[This is chromyl chloride test]

$$CrO_2Cl_2 + 2NaOH \longrightarrow \underset{\substack{\text{Yellow}\\(B)}}{Na_2CrO_4} + 2HCl$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\text{Yellow ppt. } (C)}{PbCrO_4} + 2CH_3COONa$$

$$\underset{(X)}{NH_4Cl} + NaOH \longrightarrow \underset{\text{Colourless gas}}{NH_3} + NaCl + H_2O$$

$$K_2HgI_4 + NH_3 + 3KOH \longrightarrow \underset{\text{Reddish brown ppt. } (D)}{NH_2HgO\cdot HgI} + 7KI + 3H_2O$$

75. (i) $H_2SO_4 + 2HI \longrightarrow I_2 + SO_2 + 2H_2O$

(ii) $CaOCl_2 + 2NaI + 2HCl \longrightarrow I_2 + CaCl_2 + H_2O + 2NaCl$

(iii) $Ag_2S + 2CuCl_2 + 2Hg \longrightarrow Cu_2Cl_2 + Hg_2Cl_2 + 2Ag + S$

76. (i) $H_2S + H_2SO_4\ (conc.) \longrightarrow 2H_2O + SO_2 + S$

(ii) $6NaOH\ (excess) + 3I_2 \longrightarrow 5NaI + NaIO_3 + 3H_2O$

(iii) $2NH_3 + 3NaOCl \longrightarrow N_2 + 3NaCl + 3H_2O$

77. (i) $I_2 + 10HNO_3\ (conc.) \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(ii) $SF_6 + 3H_2O \longrightarrow SO_3 + 6HF$

(iii) $3SF_4 + 8Cl_2 \longrightarrow 4BF_3 + 3SCl_2 + 3Cl_2$

78. (a) $Ca_5(PO_4)_3F + 7H_3PO_4 + 5H_2O \longrightarrow 5Ca(H_2PO_4)_2\cdot H_2O + HF$

(b) (i) $P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3$

(ii) $SnCl_4 + 4C_2H_5Cl + 8Na \longrightarrow (C_2H_5)_4Sn + 8NaCl$

(c) (i) $2Cu + CO_2 + H_2O + O_2 \longrightarrow CuCO_3\cdot Cu(OH)_2$

(ii) $3Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2\cdot Ca(OH)_2\cdot H_2O + H_2O$

79. (i) $Au + 4HCl + 3HNO_3 \longrightarrow HAuCl_4 + 3NO_2 + 3H_2O$

(ii) $C + 4HNO_3\ (conc.) \longrightarrow CO_2 + 4NO_2 + 2H_2O$

(iii) $Sn + 2KOH(hot) + H_2O \longrightarrow K_2SnO_3 + 2H_2$

(iv) $Cu(OH)_2 + 2NH_4NO_3 + 2NH_4OH(aq.) \longrightarrow Cu(NH_3)_4(NO_3)_2 + 4H_2O$

80. $\underset{(A)}{HNO_2} + \underset{(B)}{2H_2SO_3} + H_2O \longrightarrow \underset{(C)}{NH_2OH} + \underset{(D)}{2H_2SO_4}$

(*A*) HNO_2 : HO—N=O

(*B*) H_2SO_3 : HO—S(=O)—OH

(*C*) NH_2OH: H—N(—OH)—H

(*D*) H_2SO_4 : HO—S(=O)(↑O)—OH

81.

A	:	$Ca(OH)_2$
B	:	NH_4HCO_3
C	:	Na_2CO_3
D	:	NH_4Cl
E	:	$CaCl_2$

82.

A.	SO_2Cl_2	(vi) Tetrahedral
B.	Ice	(v) H-bonding
C.	$CuSO_4$ (anhy.)	(iv) Testing H_2O
D.	K_2HgI_4 + NaOH	(iii) Testing NH_3
E.	Fluorocarbons	(ii) Refrigeration
F.	NO	(i) Paramagnetic

83. (i) $CuSO_4\cdot 5H_2O \xrightarrow{100°C} \underset{(A)}{CuSO_4\cdot H_2O} \xrightarrow{230°C} \underset{(B)}{CuSO_4} \xrightarrow{800°C} \underset{(C)}{CuO} + \underset{(D)}{SO_3}$

(ii) $2AgNO_3 \xrightarrow{\text{Red heat}} \underset{(E)}{2Ag} + \underset{(F)}{2NO_2} + O_2$

(iii) $Na_2B_4O_7 \xrightarrow{740°C} \underset{(G)}{NaBO_2} + \underset{(H)}{B_2O_3}$

84. K_{sp} of CuS is less than K_{sp} of ZnS. On passing H_2S in acidic medium, the dissociation of H_2S is suppressed due to common ion effect and it provides $[S^{2-}]$ which is just sufficient to cross over K_{sp} of CuS and not K_{sp} of ZnS. Thus, only CuS gets precipitated.

85. (i) $(CH_3COO)_2Ca$ shows exothermic dissolution whereas $Pb(NO_3)_2$ shows endothermic dissolution. According to Le-Chatelier principle the solubility of $(CH_3COO)_2Ca$ decreases and solubility of $Pb(NO_3)_2$ increases with temperature.

(ii) The dissociation of NH_4OH (a weak electrolyte) is suppressed in presence of NH_4Cl due to common ion effect. Thus, $[OH^-]$ in solution becomes low. The ionic product of concentrations of Mg^{2+} and OH^- ions does not exceed the solubility product of $Mg(OH)_2$ and thus $Mg(OH)_2$ is not precipitated.

(iii) Yellow phosphorus is very reactive (ignition temperature 30° C) towards air whereas red phosphorus is quite unreactive (ignition temperature 260° C). Thus, to avoid contact of yellow phosphorus from air, it is kept under water.

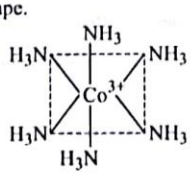
(iv) Bleaching of flower by SO_2 follows reduction. The colour of bleached material is regained due to oxidation by air and is thus, temporary. The bleaching of flower by Cl_2 follows oxidation and is thus permanent.

86. (a) Potassium ammine tetra cyano nitrosonium chromium (I).

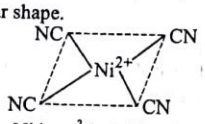
Cr is in +1 oxidation state and possesses d^2sp^3 hybridisation with one unpaired electron.

$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = \mathbf{1.73\ BM}$

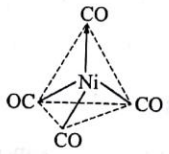
(b) $[Co(NH_3)_6]^{3+}$: Co^{3+} is d^2sp^3 hybridised to show octahedral shape.



$[Ni(CN)_4]^{2-}$: Ni^{2+} is dsp^2 hybridised to show square planar shape.



$[Ni(CO)_4]$: Ni is sp^3 hybridised to show tetrahedral shape.



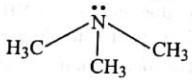
87. (a) AlF_3 dissolves in ionic KF due to the formation of K_3AlF_6. On the other hand anhydrous

$$AlF_3 + 3KF \longrightarrow \underset{\text{Soluble}}{K_3[AlF_6]}$$

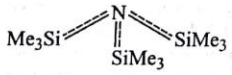
HF being weak acid does not dissociate to appreciable extent and AlF_3 does not form $[AlF_4]$ or $H[AlF_4]$. Addition of BF_3 in $K_3[AlF_6]$ forms AlF_3 as insoluble mass because BF_3 is more acidic than AlF_3.

$$K_3[AlF_6] + BF_3 \longrightarrow AlF_3 + 3K[BF_4]$$

(b) Me_3N or $(CH_3)_3N$ has three σ-bonds between sp^3 hybridised nitrogen and carbon atom of CH_3 gp. The lone pair on N atom give rise to pyramidal shape.



In $(SiMe_3)_3N$, three Si—N bonds are present and lone pair on N atom is involved in back bonding with vacant $3d$-orbitals of Si giving rise to trigonal planar geometry.



88. $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$

89. (a) $2KI(aq.) + Cl_2 \longrightarrow 2KCl(aq.) + I_2$

In the reaction Cl_2 oxidises iodide ion (−1 oxidation state) to I_2 (0 oxidation state). Cl_2 has higher reduction potential than I_2 and thus oxidises iodide to iodine getting itself reduced to chloride ion. Similarly,

$$2KI + X_2\ (X = Cl, Br, F) \longrightarrow 2KX + I_2$$

(b) M.O. configuration of O_2 :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^1, \pi^* 2p_y^1$$

Bond order $= \frac{1}{2}$ [No. of bonding electrons − No. of antibonding electrons]

$$= \frac{1}{2}[10 - 6] = 2$$

Also, O_2 molecule is paramagnetic as it possesses two unpaired electrons.

90. (i) $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

(ii) $CaNCN + 3H_2O \longrightarrow CaCO_3 + 2NH_3$

(iii) $BF_3 + 2H_2O \longrightarrow [BF_3OH]^- H_3O^+$

(iv) $NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$

(v) $3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + \left(\frac{1}{2}\right)O_2 + 12HF$

91. (a) (i) Argentite ore is Ag_2S

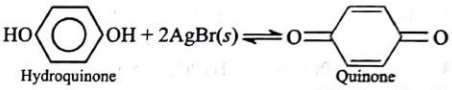
$$Ag_2S + 4NaCN \overset{\text{Leaching}}{\rightleftharpoons} 2Na[Ag(CN)_2] + Na_2S$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

(ii) A developer is usually a weak reducing agent such as potassium ferrous oxalate or an alkaline solution of pyragallol or an alkaline solution of quinol.

$$\underset{\text{II}}{K_2Fe(C_2O_4)_2} + AgBr(s) \rightleftharpoons \underset{\text{III}}{KFe(C_2O_4)_2} + Ag(s) + KBr$$

or



$+ 2HBr + 2Ag(s)$

Therefore, silver bromide is fixed with $Na_2S_2O_3$ or developed image is made stable by fixing with $Na_2S_2O_3$.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

On acidification of hypo, insoluble turbidity of colloidal sulphur (milky-white is formed).

$$Na_2S_2O_3 + 2H^+ \longrightarrow 2Na^+ + H_2O + SO_2\uparrow + \underset{\text{(Milky white sol.)}}{S}$$

(b) Borax is heated on loop of platinum wire to give **borax bead.**

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{740°C} \underset{\text{Bead}}{NaBO_2} + B_2O_3 + 10H_2O$$

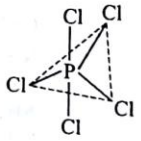
Cobalt (II) salts are placed on this bead and heated strongly on bunsen flame to produce blue flame.

$$Co\ (salt) \xrightarrow{\Delta} CoO + gas\uparrow$$

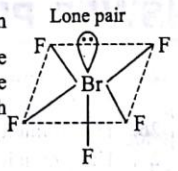
$$CoO + B_2O_3 \xrightarrow{\Delta} \underset{\text{(Blue)}}{Co(BO_2)_2};$$

Cobalt metaborate is blue in oxidising as well as in reducing flame.

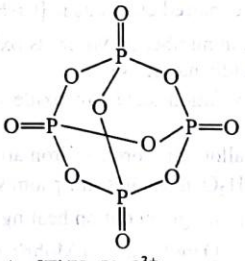
(c) PCl_5 : sp^3d hybridisation having trigonal bipyramidal shape with five $3sp^3d - 3p$ bonds.



BrF_5 : sp^3d^2 hybridisation having distorted octahedral shape with arc position occupied by lone pair (*i.e.*, square pyramidal) with five $4sp^3d^2 - 2p$ bonds.



(d) P_4O_{10} :



92. M = Ti, $A = [Ti(H_2O)_6]^{3+}$, $B = TiO_2$

Ti(+IV) ion contains no d-electrons, while d—d transition of single electron of Ti(+III) will cause colour change.

93. $Fe^{3+}_{(aq.)} \xrightarrow{\text{Excess of } SCN^-} \underset{\substack{\text{Blood-red}\\ \text{colour } (A)}}{Fe(SCN)_3} \xrightarrow{\text{Excess } F^-} \underset{\text{Colourless } (B)}{[FeF_6]^{3-}}$

(A) : Trithiocyanato ferrum (III)

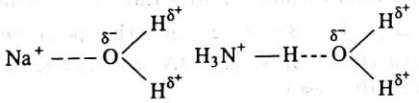
(B) : Hexafluoro ferrate (III) ion

Spin magnetic moment of

$$B = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35}\ BM$$

$[FeF_6]^{3-}$ has five unpaired electrons.

94. (i) NH_4^+ is solvated by H—bonding and ion-dipole forces whereas Na^+ is solvated merely by an ion-dipole interaction.



(ii) Ag^+ is soft acid, CN^- is soft base whereas Cl^- is hard base. A complex of soft acid and soft base is more stable.

(iii) Electronegativity also plays a part in the distortion of molecules from the ideal shape. With decreasing electronegativity of the central atom as in the series NH_3, PH_3, AsH_3, SbH_3 (N > P > As > Sb), the bonding electron pairs are drawn closer to H atom and further away from central atom. Thus, repulsion between bonding pairs of electrons decreases and so the bond angle decreases progressively.

(iv) $CH_2(NH_2)—CH_2—\ddot{N}H—CH_2—CH_2(NH_2)$ (Diethylene triamine)

(v) $\underset{\text{Strong basic}}{MnO} < \underset{\text{Weak basic}}{Mn_2O_3} < \underset{\text{Amphoteric}}{MnO_2} < \underset{\text{Acidic}}{MnO_3} < \underset{\text{Strong acidic}}{Mn_2O_7}$

95. (a) A—X bond is polar; X—X bond is non-polar.

(b) $O=S=O + C_2H_5MgBr \xrightarrow{\text{Ether}} O=S(OMgBr)—C_2H_5 \xrightarrow{HOH} O=S(OH)—C_2H_5$ Sulphinic acid

(c) $n-2$; $HO—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—\underset{(n-2)}{\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}}—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—OH$

(d) $3CS_2 + 6NaOH \longrightarrow Na_2CO_3 + 2Na_2CS_3 + 3H_2O$

(e) $(CN)_2 + 2NaOH \longrightarrow NaCN + NaCNO + H_2O$; Disproportionation like halogens

(f) $Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$

$Na_2S + 2HCl \longrightarrow 2NaCl + H_2S$

96. (i) NO_2 formed get dissolved in HNO_3 to give brown or yellow colour.

(ii) Soaps get precipitated in presence of hard water to give Ca or Mg salts.

(iii) BeO is amphoteric in nature.

(iv) TEL used as antinock compound in petrol comes out from exhaust as $PbBr_4$.

(v) Tin becomes brittle at low temperature.

● SINGLE INTEGER ANSWER PROBLEMS ●

1. Red lead Pb_3O_4 contains lead oxide and lead dioxide in the ratio .....
2. 'n' factor of O_3 in the reaction
$I_2 + 5O_3 + H_2O \longrightarrow 2HIO_3 + 5O_2$.
3. Total number of lone pair of electrons in valence shells of oxygen atoms in ozonide O_3^- ion are .....
4. Atomicity of arsenic is .....
5. Total number of H-bonding sites available in H_2O are .....
6. Number of nearest neighbour NH_3 molecules in solid NH_3 are .....
7. Number of iron atoms involved in one molecule of ferri-ferrocyanide.
8. Number of P = O in cyclotetraphosphate ion ($P_4O_{12}^{-4}$) are .....
9. Number of oxygen atoms in molybdate ion is .....
10. Oxidation number of P in peroxydiphosphoric acid ($H_4P_2O_8$) is .....
11. One mole of As_2O_5 on treatment with fuming hydrochloric acid gives how much mole of Cl_2 ?
12. Liquid HF shows an equilibrium at 15-19°C
$HF_{(l)} \rightleftharpoons (HF)_{n(V)}$. The value of n is .....
13. Iodine iodate an ionic compound on heating decomposes to give how much mole of gases?
14. Total number of gases obtained on heating ammonium iodate.
15. Number of S = O bonds in cyclic trimer S_3O_9 are .....
16. Number of canonical forms of CO_2 are .....
17. Number of H-bond formed in trimer form of H_2O, *i.e.*, $(H_2O)_3$.
18. In medicine and first aid of shock, gas poisoning and asphyxiation a mixture of O_2 and CO_2 is administered in gas mask to stimulate natural respiration. The percentage of CO_2 in mixture is:
19. Number of CO molecules in bridged carbonyl of iron having two iron atoms is .....
20. Number of B—O—B bonds in sodium metaborate, *i.e.*, $Na_3B_3O_6$ is .....
21. Number of H_2O molecule per molecule of bauxite in bauxite ore of Al is .....
22. The co-ordination number of Al in Al_2Cl_6 is .....
23. Oxidation number of Cu in potassium tetracyanocuprate is .....
24. The mole ratio of the two gases NO_2 and O_2 obtained on heating copper nitrate is .....
25. The co-ordination number of Be in aqueous solution of $BeCl_2$ is .....
26. The atomicity of Hg vapours is .....
27. The atomicity of mercurous ion is .....
28. Number of unpaired electrons in $[Cr(NH_3)_6]^{3+}$ is:
29. The oxidation number of Mn in its oxide which posses strongest acidic nature is .....
30. In which oxidation state Mn oxide show amphoteric nature?
31. Number of allotropic forms of iron are .....
32. Number of H_2O molecules in Epsom salt is .....
33. Number of gases given out on heating $FeSO_4$ strongly.
34. Number of H_2O molecules in Mohr's salt.
35. Number of mole of gas given out on heating one mole of ferric sulphate.
36. Number of mole of SO_2 formed on heating one mole of iron pyrite in air.
37. The number of Fe^{3+} ions in one molecule of prussian blue is .....
38. Oxidation number of Fe in sodium nitroprusside is .....
39. Number of canonical forms in Resonating structure of N_3^- is .....
40. Bond order of NO^+ is .....
41. A species has magnetic moment 1.73 B M. The number of unpaired electron in it is .....
42. The bond length of H—I is 1.61×10^{-8} cm and partial charge is 3.8×10^{-7} esu cm. The percentage ionic character of HI is ..... (Assume charge on electron 4.8×10^{-10} esu)
43. At 300 K and 1.0 atm pressure, the density of $HF_{(v)}$ is 3.1 g / litre. If $R = 0.08$, the no. of HF molecules associated in vapour phase are .....
44. No. of unpaired electrons in complex ion $[CoF_6]^{3-}$.
45. Effective atomic no. of $_{42}Mo$ is 54. The formula of its carbonyl is $Mo(CO)_x$. The value of x is .....
46. No. of unpaired electrons in $[Mn(CN)_6]^{3-}$ is .....
47. Number of geometrical isomers of $Co(en)Cl_3\ Br^-$ are .....
48. Number of isomers of $Co(en)\ Cl_2\ Br_2^-$ are .....
49. No. of ions furnished by an electrolyte (2 +, 3 –) on dissolution in water is .....
50. A sample of alloy contains a% copper (as $CuAl_2$) by mass. If % of $CuAl_2$ in alloy is 7.40 then what is a?

51. The number of water molecules directly bonded to metal centre in $CuSO_4 \cdot 5H_2O$: **[IIT 2009]**

52. The coordination number of Al in the crystalline state of $AlCl_3$ is: **[IIT 2009]**

53. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$: **[IIT 2010]**

54. Among the following, the number of compounds that can react with PCl_3 to give $POCl_3$ is: **[IIT 2011]**

$O_2, CO_2, SO_2, H_2O, H_2SO_4, P_4O_{10}$

55. The numerical value of the factor effective atomic number of Mn in $[Mn_2(CO)_{10}] \times \frac{1}{5}$ is:

ANSWERS

1. Two	**2.** Two	**3.** Six	**4.** Four	**5.** Four	**6.** Six	**7.** Seven	**8.** Four	**9.** Four	**10.** Five	**11.** Two	**12.** Six
13. Five	**14.** Three	**15.** Six	**16.** Three	**17.** Two	**18.** Five	**19.** Nine	**20.** Three	**21.** Two	**22.** Four	**23.** One	**24.** Four
25. Four	**26.** One	**27.** Two	**28.** Three	**29.** Seven	**30.** Four	**31.** Three	**32.** Seven	**33.** Two	**34.** Six	**35.** Three	**36.** Two
37. Four	**38.** Two	**39.** Three	**40.** Three	**41.** One	**42.** Five	**43.** Four	**44.** Four	**45.** Six	**46.** Two	**47.** Two	**48.** Four
49. Five	**50.** Four	**51.** Four	**52.** Four	**53.** Three	**54.** Four	**55.** Seven					

OBJECTIVE PROBLEMS (One Answer Correct)

1. Which statement about zirconium hydride is not correct?
   (a) It is non stoichiometric mixture
   (b) It is non stoichiometric compound
   (c) It has distinct properties from those of its element
   (d) It has definite composition
2. For the reaction $PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI$: the correct statement is:
   (a) It is intramolecular redox
   (b) It is disproportional reaction
   (c) It is salt hydrolysis
   (d) It is double decomposition
3. Normally highest oxidation states are seen with fluorine and oxygen but OsO_4 exist and OsF_8 not. This is because:
   (a) the size of fluorine atom is large than oxygen atom
   (b) electronegativity of F is more than oxygen atom
   (c) Os cannot accomodate 8 fluorine atoms due to crowding of atoms
   (d) the size of fluorine atom is smaller than oxygen atom
4. Which is a characteristic of silicones?
   (a) Water repellant (b) Weak Si—C bond
   (c) Si—Si bond (d) Less stable to heat
5. Which is not correct for hydroxyl amine?
   (a) It disproportionates slowly in acid medium
   (b) It is strong oxidant
   (c) It disproportionate readily in alkaline medium
   (d) It is very poisonous
6. pK_a of which halogen acid is positive :
   (a) HF (b) HCl
   (c) HBr (d) HI
7. During hydration of alkali metal cations:
   (a) ΔG, ΔH, ΔS are –ve
   (b) ΔG, ΔH, are –ve, ΔS is +ve
   (c) ΔG, ΔH, ΔS are +ve
   (d) ΔG, ΔS, are –ve, ΔH is +ve
8. Which carbonate of alkaline earth metals decomposes on heating 373 K?
   (a) $BeCO_3$ (b) $MgCO_3$
   (c) $CaCO_3$ (d) $SrCO_3$
9. Which one is not an application of boron carbide?
   (a) As an abrasive for polishing
   (b) Possesses enormous tensile strength and used in making bullet proof cloth
   (c) In brake lining of cars
   (d) In paints
10. Which one is not a characteristic of R_3Al?
   (a) It shows sp^2-hybridisation
   (b) It exist as dimer
   (c) It shows sp^3-hybridisation
   (d) Used as catalyst in the dimerisation of propene to give finally isoprene
11. Which are correct for boric oxide?
   (a) It is anhydride of boric acid as well as also called sesquioxide
   (b) It reacts with metal oxides forming metaborates
   (c) It acts as basic oxide and reacts with strong acidic oxides to form boron salts
   (d) All of the above
12. Bi^{3+} and Sb^{3+} ions:
   (a) are stable in acid medium
   (b) are stable in neutral medium
   (c) are stable in water
   (d) slows the equilibrium $Bi^{3+} \overset{HCl}{\rightleftharpoons} [BiO]^+$
13. Which one is not correct about calgon?
   (a) It is a high molar mass polymer $[NaPO_3]_n$
   (b) It is a water softener
   (c) It is called Graham's salt
   (d) It is used as catalyst
14. About Lapis lazuli, which one is not correct?
   (a) It is $Na_8[(AlSiO_4)_6]S_2$ and named as ultramarine
   (b) It was a precious pigment for oil paintings in middle age
   (c) Presence of polysulphide ion imparts blue colour to it
   (d) It possesses chain silicate structure
15. Which of the following is not correct?
   (a) P_4S_6 exists like P_4O_6
   (b) In P_4S_3, there exists 3P—S—P bond whereas in P_4S_5, there exists four P—S—P bonds
   (c) Both P_4S_{10} and P_4O_{10} have same structure
   (d) P_4S_3 is most stable sulphide of phosphorus
16. Which of the following chromium oxide is acidic?
   (a) CrO (b) Cr_2O_3
   (c) CrO_3 (d) None of these
17. Which of the following statements is wrong about CO ?
   (a) It acts as Lewis base in the formation of metal carbonyls
   (b) It is a neutral oxide
   (c) It acts as acid with NaOH under high P, T to give sodium formate
   (d) It acts as π acceptor by accepting electrons from the central metal during complex formation
18. Cyclic trimer structure of SO_3 contains :
   (a) 6S = O bonds at three S—O—S bonds

(b) 3S = O bonds and six S—O—S bonds
(c) 6S = O bonds and six S—O—S bonds
(d) none of the above

19. Which of the following sulphuryl halides is not known?
(a) SO_2F_2 (b) SO_2Cl_2
(c) SO_2FBr (d) SO_2Br_2

20. Tellurium hydride on dissolution in water gives :
(a) $H_2Te + H_2O \rightleftharpoons H_3O^+ + HTe^-$
(b) $H_2Te + H_2O \rightleftharpoons H_3Te^+ + OH^-$
(c) $H_2Te + H_2O \rightleftharpoons TeO + 2H_2$
(d) none of the above

21. H_2O_2 cannot be formed by the following reaction:
(a) electrolysis of 50% $H_2S_2O_8$ (*aq.*)
(b) hydrolysis of H_2SO_5
(c) action of H_2O on BaO_2
(d) action of H_2O on MnO_2

22. Which characteristic is not shown by S_4N_4?
(a) It has cage structure
(b) It has two S—S strong bonds
(c) Thermochromic
(d) Stable in air but detonates on shock, grinding or sudden heating

23. Which does not show thermochromic property?
(a) ZnO (b) S_4N_4
(c) $CuSO_4 \cdot 5H_2O$ (d) $KMnO_4$

24. Among the following gps., the last element of which group is not radioactive :
(a) gp 1 (b) gps 17
(c) gps 18 (d) gps 14

25. Which of the following does not give oxygen on heating?
(a) $KClO_3$ (b) $Zn(ClO_3)_2$
(c) $K_2Cr_2O_7$ (d) $(NH_4)_2Cr_2O_7$

26. Which compounds of Xe contain lone pair of electron?
(a) $[XeO_6]^{4-}$ (b) XeO_3F_2
(c) XeO_4 (d) XeO_2F_2

27. Which of the following does not contain $p\pi - d\pi$ bonding?
(a) PF_3
(b) Oxoacid of sulphur
(c) Oxoacid of phosphorus
(d) PF_5

28. The oxidation number and hybridisation of xenon in barium perxenate is:
(a) +6, sp^3 (b) +8, sp^3d^2
(c) +6, sp^3d (d) +8, sp^3

29. Which among the following the transition elements have their density more than 5 g / cm^3?
(a) Sc (b) Y
(c) Ti (d) Ir

30. Which of the transition metal element has highest density?
(a) Os (b) Ir
(c) Pt (d) Au

31. Highest m. pt. of transition element exists for:
(a) Ta (b) W
(c) Re (d) Zn

32. The colours of AgCl (white), AgBr (pale yellow) and AgI (yellow) is due to the fact that:
(a) Cl_2, Br_2 and I_2 are green, brown and violet respectively
(b) Ag^+ polarises the anions in the order: $I^- > Br^- > Cl^-$
(c) Ag^+ have $4d^{10}$, configuration
(d) the anions Cl^-, Br^- and I^- have np^6 configuration

33. VO_4^-, CrO_4^{2-} and MnO_4^- are pale yellow, strong yellow and intense purple respectively in aqueous solution. The darkening of colour is due to:
(a) charge transfer
(b) d—d transition
(c) half-filled d-sub-shells
(d) increasing number of unpaired electron

34. The complex $[Fe(H_2O)_5NO]^{2+}$ formed during brown ring test for NO_3^-; select the wrong statement:
(a) Is coloured due to charge transfer
(b) has no unpaired electrons
(c) Has magnetic moment 3.9 BM
(d) Has Fe in +1 oxidation state and NO in +1 oxidation state

35. For the given values, the correct statement is:
$[Fe(H_2O)_6]^{3+} + e \longrightarrow [Fe(H_2O)_6]^{2+}$ $E° = +0.77$ V
$[Fe(CN)_6]^{3-} + e \longrightarrow [Fe(CN)_6]^{4-}$ $E° = +0.36$ V
(a) It is easier to oxidise $[Fe(H_2O)_6]^{2+}$ than $[Fe(CN)_6]^{4-}$
(b) It is easier to oxidise $[Fe(CN)_6]^{4-}$ than $Fe[(H_2O)_6]^{2+}$
(c) $[Fe(CN)_6]^{3-}$ is more stable than $Fe[(H_2O)]_6^{3+}$
(d) $[Fe(CN)_6]^{3-}$ is less stable than $Fe[(H_2O)_6]^{3+}$

36. Select the incorrect statement for $FeCl_3$:
(a) It is yellow-brown in colour in solid state
(b) It is used as mordant in dyeing and as an oxidant
(c) It is used as catalyst in manufacture of CCl_4
(d) It does not sublimes on heating

37. Select the correct statements :
(a) Vitamin B-12 has Co
(b) Co^{2+} ions are very stable and difficult to oxidise
(c) $[Co(NH_3)_6]^{2+}$ are readily oxidised to $[Co(NH_3)_6]^{3+}$
(d) All of the above

38. The stable oxidation state of Cu, Ag and Au are respectively:
(a) Cu^+, Ag^+, Au^+ (b) Cu^{2+}, Ag^+, Au^{2+}
(c) Cu^+, Ag^+, Au^{3+} (d) Cu^{2+}, Ag^+, Au^{3+}

39. Select the incorrect statement :
(a) H_2O_2 can be detected by Ti^{4+} ion where a yellow-orange solution of $[TiO_2 \cdot OH(H_2O)_n]^+$ is formed
(b) BrF_3 is potential non-aqueous ionising solvent
(c) ICl can be used for iodination as well chlorination of organic compounds
(d) NaBr on reaction with ICl gives NaCl

40. The reaction which do not occur is:
(a) $Ni(CO)_4 + 4PF_3 \longrightarrow Ni(PF_3)_4 + 4CO$
(b) $PCl_3 + 6NH_3 \longrightarrow P(NH_2)_3 + 3NH_4Cl$
(c) $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$
(d) $SbCl_3 + 3H_2O \longrightarrow H_3SbO_3 + 3HCl$

41. The reaction which do not occur is:
(a) $COCl_2 + 2NH_3 \longrightarrow NH_2CONH_2 + 2HCl$
(b) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
(c) $5CO + I_2O_5 \longrightarrow 5CO_2 + I_2$
(d) $NaNH_2 + C \xrightarrow{750°C} NaH + HCN$

42. Select the correct statement:
(a) Lithopone is $BaS + ZnSO_4$
(b) Ammoniacal CuCl absorbs CO and CO_2
(c) H_2 can be dried by conc. H_2SO_4
(d) Wood metal melts at b.pt. of water

43. The decreasing order of molar conductances of the given compounds in their aqueous solution is:
(I) : $K[Co(NH_2)_2(NO_2)_4]$;
(II) : $[Cr(NH_3)_3(NO_2)_3]$;
(III) : $[Cr(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$;
(IV) : $Mg[Cr(NH_3)(NO_2)_5]$
(a) III > IV > I > II (b) I < II < IV < III
(c) II > I > IV > III (d) III < II < IV < I

44. Which complex of Co^{2+} will show the weakest crystal field splitting?
(a) $Co(CN)_6]^{4-}$ (b) $[Co(NH_3)_6]^{2+}$
(c) $[Co(en)_3]^{2+}$ (d) $[CoCl_6]^4$

45. The effective atomic number rule (EAN) is obeyed by :
(a) $[PtCl_6]^{2-}$ (b) $[Ni(NH_3)_6]^{2+}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Pt(NH_3)_4]^{2+}$

46. The EAN rule is not obeyed by :
(a) $Fe(CO)_5$ (b) $CO_2(CO)_8$
(c) $H_2[Cr(CO)_5]$ (d) $[Cr(NH_3)_6]Cl_3$

47. Select the wrong statement about $[CoI_4]^{2-}$ ion:
(a) It is high spin complex
(b) It is a low spin complex
(c) It is sp^3-hybridised with three unpaired electron
(d) Its magnetic moment is 3.5 BM

48. Which of the following forms square planar complex and diamagnetic in nature?
(a) Cr^{2+} in weak field ligand
(b) Ag^{2+} in weak or strong field ligand
(c) Ni^{2+} in strong field
(d) Co^{2+} in strong field

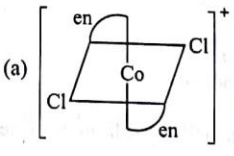
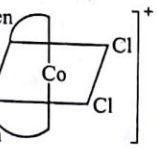
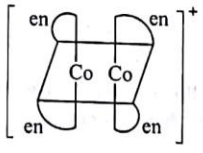
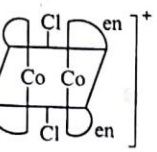
49. Which one is not correct?
(a) Purification of Ti using I_2 is called zone refining
(b) Extraction of Ti from $TiCl_4$ by Mg is called Kroll process
(c) Extraction of Ti from $TiCl_4$ by Na is called IMI process
(d) Purification of Ni using CO is called Mond's process

50. Select the incorrect statement:
(a) Salt like hydrides on reaction with water give H_2
(b) H_2 is obtained in excess in chlor-alkali industries
(c) CO is oxidised by NaH
(d) CO acts as acid on reaction with NaOH at high P and T

51. Select the incorrect statement:
(a) Melting point order : $(CH_4 > SiH_4) < GeH_4 < SnH_4$
(b) Boiling point order : $CH_4 < SiH_4 < GeH_4 < SnH_4$
(c) Hydrides of carbon family are mostly covalent and sp^3-hybridised
(d) PbH_4 is ionic hydride

52. Carbonatoaquotetraammine cobalt (III) chloride does not show ..... isomerism:
(a) geometric (b) hydrate
(c) coordination (d) optical

53. The possible number of isomers of the complex $[Cr(NH_3)(OH)_2Cl_3]^{2-}$ are:
(a) 1 (b) 2
(c) 3 (d) 4

54. Which of the following is optically active?
(a) 
(b) 
(c) 
(d) 

55. The IUPAC name for $[Pt(py)_4][PtCl_4]$ is:
(a) tetrapyridinium platinum (II) tetrachloroplatinate (II)
(b) tetrapyridinium platinum (II) tetrachloroplatinum (II)
(c) tetrachloroplatinum (II) tetrapyridine platinum (II)
(d) tetrachloroplatinate (II) tetrapyridine platinum (II)

56. Coordination number for which ion cannot exceed than two:
(a) Cu^+ (b) Cu^{2+}
(c) Al^{3+} (d) Zn^{2+}

57. EDTA in form of its dihydrogen calcium salt is used as antidote for ..... poisoning in body:
(a) Pb (b) Sn
(c) Ca (d) Ba

58. Which of the following change shows an increase in bond order and a change in magnetic behaviour?
(a) $N_2 \rightarrow N_2^+$ (b) $C_2 \rightarrow C_2^+$
(c) $NO \rightarrow NO^+$ (d) $O_2 \rightarrow O_2^+$

59. The species having bond order different from that in CO is:
(a) NO^- (b) NO^+
(c) CN^- (d) N_2

60. Which of the following pairs have isostructural nature:
(a) SO_3^{2-} and NO_3^- (b) BF_3 and NF_3
(c) BrO_3^- and XeO_3 (d) SF_4 and XeF_4

61. Which of the following oxide is neutral?
(a) MnO_2 (b) N_2O_3
(c) CO_2 (d) Mn_2O_7

62. Which of the following statements about pH of salt solution is incorrect?
(a) pH of NaF < pH of NaCN
(b) pH of Na_2SO_3 < pH of Na_2TeO_3
(c) pH of NaOBr < pH of NaOCl
(d) pH of CH_3COONa < pH of NaCN

63. Select the incorrect statement about terminology of meta, pyro, hypo, ortho and peroxyacids:
(a) The meta acid has one water molecule fewer than an ortho acid of the same element is same oxidation state per atom of central element, *e.g.*, HPO_3 is meta phosphoric acid
(b) The pyro acid has one half water molecule fewer than an ortho acid per atom of central element, *e.g.*, $H_4P_2O_7$ pyrophosphoric acid
(c) The hypo acid has an oxidation state lower than the ic acid, *e.g.*, H_3PO_2 is hypo phosphorus acid
(d) The per acid has same oxidation state as in, ic acid, *e.g.*, $HClO_4$

64. Select the incorrect statement:
(a) Pure $HClO_4$ does not conduct electricity
(b) Solid hydrate $HClO_4 \cdot H_2O$ on melting conducts electricity
(c) H-bonding is extensive in pure $HClO_4$
(d) H-bonding is more powerful in $HClO_4 \cdot H_2O$ than $HClO_4$

65. Which of the following does not favour to call CN^- as pseudohalide ion?
(a) Cyanogen undergoes disproportionation like disproportionation of halogens
(b) It forms a wide variety of complexes like halide ions
(c) CN^- acts as oxidising agent like halogens
(d) CN^- acts as reducing agent like halide ions

66. Alkali metals conduct current in liquid NH_3 at $-33°C$. Which is wrong about this fact?
(a) The conductance increases on lowering the temperature
(b) The solution conduct like metallic conductor
(c) The current is carried out by electrons and not by ions
(d) The solution conduct like electrolytic conductor

67. Which represents incorrect reaction?
(a) $Cu_2O + 2HCl(dil.) \longrightarrow CuCl_2 + Cu + H_2O$
(b) $Cu_2O + 2HCl(conc.) \longrightarrow 2HCuCl_2 + 2H_2O$
(c) $Cu_2O + 2HI \longrightarrow CuI_2 + Cu + H_2O$
(d) $2Cu^+ \xrightarrow{H_2O} Cu^{2+} + Cu^+$

68. Which of the following statements is incorrect?
(a) To remove impurities of SO_2 and P_4O_{10}, a SiO_2 lining in furnace is preferred
(b) To remove impurities of MgO and CaO, a SiO_2 lining in furnace is preferred
(c) To remove impurities of metal oxide, a lining of SiO_2 is preferred
(d) To remove impurities of SiO_2, a lining of MgO or CaO is preferred

69. $Pd(NH_3)_2Cl_2$ does not conduct electricity in aqueous solution. Therefore:
(a) it is weak electrolyte
(b) Cl-atoms are covalently bonded in the coordination sphere
(c) the structure involves covalent bonding only
(d) all of the above

70. In which hybridization is not d^2sp^3 ?
(a) $[V(H_2O)_6]^{3+}$ (b) $[Cr(CN)_6]^{3-}$
(c) $Cr(CO)_6$ (d) $[MnBr_4]^{2-}$

71. Which of the following does not involve innershell hybridisation?
(a) $[CoF_6]^{3-}$ (b) $[Co(CN)_6]^{3-}$
(c) $[Fe(CN)_6]^{4-}$ (d) $[Ni(NH_3)_6]^{2+}$

72. Which of the following d^n ions will have the smallest crystal field stabilization energy, if Δ is greater than P, the pairing energy ?
(a) d^6 (b) d^8
(c) d^9 (d) d^{10}

73. One of the constituent of German silver is:
(a) Ag (b) Cu
(c) Mg (d) Al

74. The value of X in $Mo(CO)_X$ is:
(a) 2 (b) 4
(c) 5 (d) 6

75. Which of the following is incorrect?
(a) NO^+ is more stable than NO
(b) CO^+ is more stable than CO
(c) OF is less stable than F_2
(d) CN is more stable than CN^+

76. Which of the following is incorrect about O_2 and O_2^{2-}?
(a) Bond order of O_2^{2-} and O_2 are 1 and 2 respectively
(b) O_2^{2-} have longer bond than O_2
(c) O_2^{2-} has weaker bond than O_2
(d) Both have same number of antibonding electrons

77. Pick up the incorrect statement:
(a) Bond length of N_2^+ > bond length of N_2
(b) Bond length of NO^+ < bond length of NO
(c) Bond length of CN^- < bond length of CN
(d) Bond length of CO < bond length of CO^+

78. In which of the following, fact is incorrectly reported about N_2, NO^+, CN^- and CO?
(a) Bond order for all these is three
(b) M.O. diagram for all these is same
(c) No. of bonding electrons and antibonding electrons in each is same
(d) $\sigma^* 2s$-orbital in CO has higher energy the $\sigma 2p_x$ as well as $\pi 2p_y$ and $\pi 2p_z$ orbitals whereas in rest all it has lower energy

79. Which of the following salts containing either of the ion reported below are water soluble?
(a) NH_4^+ (b) ClO_4^-
(c) NO_3^- (d) All of these

80. Which metal chloride is water soluble?
(a) $NiCl_2$ (b) AgCl
(c) $PbCl_2$ (d) $HgCl_2$

81. Which of the following chloride will not fume in air?
(a) $BiCl_3$ (b) $SbCl_3$
(c) PCl_5 (d) CCl_4

82. In diborane the two H—B—H angles are nearly:
(a) 60°, 120° (b) 95°, 120°
(c) 95°, 150° (d) 120°, 180°

83. Tear gas is:
(a) $COCl_2$ (b) CCl_3NO_2
(c) N_2O (d) NO

84. Phosphorus glass in dark, the cold light emission is the phenomenon of:
(a) chemiluminescence (b) phosphorescence
(c) fluorescence (d) all of these

85. S—S bond is present in:
(a) $S_2O_7^{2-}$ (b) S_3O_9
(c) $S_2O_4^{2-}$ (d) $S_2O_3^{2-}$

86. Which of the following species possess $p\pi - d\pi$ bonding?
(a) NO_3^- (b) SO_3^{2-}
(c) BO_3^{3-} (d) CO_3^{2-}

87. Among NO_3^-, AsO_3^{3-}, CO_3^{2-}, ClO_3^-, SO_3^{2-} and BO_3^{3-}, the non-planar species are:
(a) CO_3^{2-}, SO_3^{2-}, BO_3^{3-} (b) AsO_3^{3-}, ClO_3^-, SO_3^{2-}
(c) NO_3^-, CO_3^{2-}, BO_3^{3-} (d) SO_3^{2-}, NO_3^-, BO_3^{3-}

88. Which one is not correct about the reaction of K_2MnF_6 with SbF_5?
(a) It gives F_2
(b) It involves acid-base reaction
(c) It gives acidialysis of MnF_4
(d) It involves redox change

89. Maximum number of lone pair of electrons on central atom exists in:
(a) Br_3^- (b) XeF_6
(c) XeF_4 (d) ClO_4^-

90. The same number of lone pair of electrons but different hybridisation state exist in:
(a) XeO_3, $XeOF_4$, XeF_6
(b) XeO_3, XeO_2F_2, XeF_4
(c) $XeOF_2$, XeO_2F_2, XeF_4
(d) XeF_2, XeF_4 and XeF_6

91. Radon is not formed as intermediate in one of the radioactive series called:
(a) Thorium series (b) Naptunium series
(c) Uranium series (d) Actinium series

92. Which one is incorrect?
(a) SF_4, CF_4 and XeF_4 show sp^3d, sp^3 and sp^3d^2-hybridisation respectively
(b) SF_4 = 1 lone pair; CF_4 = 0 lone pair; XeF_4 = 2 lone pairs
(c) SF_4 is T-shaped; CF_4 is tetrahedral; XeF_4 square planar
(d) Only in SF_4 S—F bonds energy in different and is rest all it is same

93. Which one is not correct about $Cr_2O_7^{2-}$?
(a) It has 6Cr—O bonds of equal bond energy
(b) The 6Cr—O bond lengths are 161 pm and Cr—O bonds are 180 pm
(c) The Cr—O—Cr angle is 131°
(d) Its structure contains 6π bonds and 6σ bonds

94. The reaction of KI and $KMnO_4$ in alkaline medium results in the formation of:
(a) KIO_3 and MnO_2 (b) I_2 and MnO_2
(c) KIO and MnO_2 (d) KIO_4^- and K_2MnO_4

95. Among the following pairs of ions, the lower oxidation state in aqueous solution is more stable than the other in:
(a) Tl^+ and Tl^{3+} (b) Cu^+ and Cu^{2+}
(c) Cr^{2+} and Cr^{3+} (d) V^{2+} and VO^{2+}

96. The highest paramagnetic character is noticed in:
(a) $MnSO_4 \cdot 4H_2O$ (b) $CuSO_4 \cdot 5H_2O$
(c) $FeSO_4 \cdot 6H_2O$ (d) $NiSO_4 \cdot 6H_2O$

97. Which is correct about the reaction of KCN with $CuSO_4$?
(a) It involves a redox reaction
(b) The reaction yields $K_3[Cu(CN)_4]$ and pseudo halogen
(c) The reaction involves complex formation
(d) All of the above

98. Which does not dissolve in hot dilute HNO_3?
(a) CuS (b) PbS
(c) HgS (d) CdS

99. The phenomenon in which white transparent crystal changes to white powder is called:
(a) Deliquescence (b) Efflorescence
(c) Allotropy (d) Sublimation

100. Which gives red colour with KCNS?
(a) Cu^{2+} (b) Fe^{3+}
(c) Al^{3+} (d) Zn^{2+}

101. Solder is an alloy of:
(a) 70% lead + 30% tin (b) 33% lead + 67% tin
(c) 80% lead + 20% tin (d) 90% Cu + 10% tin

102. Laughing gas is:
(a) $COCl_2$ (b) CCl_3NO_2
(c) N_2O (d) NO_2

103. Supercritical CO_2 is used as:
(a) dry ice
(b) solvent for extraction of organic compound from natural sources
(c) fire fighting
(d) to provide inert medium for carrying out various reactions

104. The basic character of transition metal monoxide follows the order:
(a) VO > CrO > TiO > FeO
(b) CrO > VO > FeO > TiO
(c) TiO > VO > CrO > FeO
(d) TiO > FeO > VO > CrO

105. Litharge is chemically:
(a) PbO (b) PbO_2
(c) Pb_3O_4 (d) $Pb(CH_3COO)_2$

106. An aqueous solution of $CoCl_2$ on addition of excess of conc. HCl turns blue due to the formation of:
(a) $[Co(H_2O)_4Cl_2]$ (b) $[Co(H_2O)_2Cl_4]^{2-}$
(c) $[CoCl_4]^{2-}$ (d) $[Co(H_2O)_2Cl_2]$

107. Number of P — O — P bonds in P_4O_{10} and P_4O_6 are respectively:
(a) 6, 6 (b) 5, 5
(c) 5, 6 (d) 6, 5

108. Which of the following oxides of nitrogen is coloured?
(a) N_2O (b) NO
(c) N_2O_4 (d) NO_2

109. The correct order for the wavelength of absorption in visible region is:
(a) $[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$
(b) $[Ni(NO_2)_6]^{4-} < [Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+}$
(c) $[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$
(d) $[Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+} < [Ni(NO_2)_6]^{4-}$

110. Which of the following will give more H_2 if equal masses of each of the following react with H_2O?
(a) LiH (b) NaH
(c) CaH_2 (d) BaH_2

111. Zeolite, *i.e.*, hydrated sodium aluminium silicate on treatment with hard water shows exchange of Na^+ ion with:
(a) H^+ (b) Ca^{2+}
(c) SO_4^{2-} (d) OH^-

112. Which of the halide is least stable and has a doubtful existence?
(a) CI_4 (b) GeI_4
(c) SnI_4 (d) PbI_4

113. On heating ammonium dichromate, the gas evolved is:
(a) O_2 (b) NH_3
(c) N_2 (d) N_2O

114. One mole of calcium phosphide on reaction with excess water gives:
(a) one mole of phosphine
(b) two mole of phosphoric acid
(c) two mole of phosphine
(d) one mole of P_2O_5

115. There is no S—S bond in:
(a) $S_2O_4^{2-}$ (b) $S_2O_6^{2-}$
(c) $S_2O_3^{2-}$ (d) $S_2O_7^{2-}$

116. Which of the following is not pseudo halide?
(a) CNO^- (b) $RCOO^-$
(c) OCN^- (d) NNN^-

117. The correct decreasing acidic strength is:
(a) ClOH > BrOH > IOH (b) BrOH > ClOH > IOH
(c) IOH > BrOH > ClOH (d) ClOH > IOH > BrOH

118. Chlorine acts as bleaching agent only in presence of:
(a) dry air (b) moisture
(c) sunlight (d) pure O_2

119. In the dichromate dianion:
(a) 4 Cr—O bonds are equivalent
(b) 6 Cr—O bonds are equivalent
(c) all Cr—O bonds are equivalent
(d) all Cr — O bonds are non-equivalent

120. An aqueous solution of $FeSO_4 \cdot Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are:
(a) a colourless filtrate and a green residue
(b) a yellow filtrate and a brown residue
(c) a green filtrate and a brown residue
(d) none of the above

121. An aqueous solution contains Hg^{2+}, Hg_2^{2+}, Pb^{2+} and Cd^{2+}. The addition of 6 *N* HCl will precipitate:
(a) Hg_2Cl_2 only (b) $PbCl_2$ only
(c) $PbCl_2$ and Hg_2Cl_2 (d) $PbCl_2$ and $HgCl_2$

122. The geometries of $Ni(CO)_4$ and $Ni(PPH_3)_2Cl_2$ are:
(a) both square planar
(b) tetrahedral and square planar respectively
(c) both tetrahedral
(d) square planar and tetrahedral respectively

123. Refining of Pb is made by :
(a) Bett's process (b) Polling process
(c) Serpeck's process (d) Cyanide process

124. Which of the following is known as spring reaction :
(a) $Na_2SO_3 + Na_2S + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$
(b) $2CaOCl_2 \xrightarrow{COCl_2} 2CaCl_2 + O_2$
(c) $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$
(d) $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$

125. Which of the following is not a component of German silver :
(a) Ag (b) Cu
(c) Zn (d) Ni

126. Which one does not contain Al :
(a) Feldspar (b) Mica
(c) Fluorspar (d) Cryolite

127. Total no. of donor atoms in EDTA is :
(a) 2 (b) 4
(c) 6 (d) 8

128. Number of H-bonds present in complex formed by Ni^{2+} with DMG legand is :
(a) 2 (b) 3
(c) 4 (d) 5

129. The number of unpaired electrons in $[Co(NH_3)_6]^{3+}$ an inner orbital complex and in $[CoCl_6]^{3-}$, an outer orbital complex are respectively :
(a) 0, 4 (b) 4, 2
(c) 2, 4 (d) 4, 4

130. The formula of Xenon hexafluoro platinate (V) is :
(a) $Xe[PtF_4]$ (b) $Xe[PtF_5]$
(c) $Xe[PtF_6]$ (d) $Xe[PtF_3]$

131. The *d*-orbitals which is used by central metal during formation of MnO_4^- :
(a) $d_{x^2-y^2}, d_{xy}, d_{zx}$ (b) $d_{x^2-y^2}, d_{yz}, d_{xz}$
(c) d_{xy}, d_{xz}, d_{yz} (d) d_{z^2}, d_{xy}, d_{zy}

132. AgCl on fusion with Na_2CO_3 gives :
(a) Ag_2O (b) Ag_2CO_3
(c) Ag (d) silver carbide

133. CO although being neutral but acts as acid on reaction with solid caustic soda heated to 200°C to give :
(a) Na_2CO_3 (b) HCOONa
(c) $NaHCO_3$ (d) Na_2O

134. Products (*A*) and (*B*) in the reaction :

$$KO_2 + CO_2 + H_2O \xrightarrow[\text{of } CO_2]{\text{Excess}} [A] + [B]$$

(a) $KHCO_3, CO$ (b) $KHCO_3, O_2$
(c) K_2CO_3, CO (d) K_2CO_3, KOH

135. Dissolution of sulphur in hot and concentrated H_2SO_4 gives:
(a) SO_2 (b) SO_3
(c) $H_2S_2O_6$ (d) $H_2S_2O_3$

136. A gas which exists in three allotropic forms (*i.e.*, α, β and γ) is :
(a) SO_2 (b) SO_3
(c) CO_2 (d) NH_3

137. Which one is called mixed anhydride of nitrogen :
(a) N_2O (b) NO_2
(c) N_2O_3 (d) N_2O_5

138. Which one is not a constituent of tincture of iodine :
(a) I_2 (b) KI
(c) Rectified sprit (d) CCl_4

139. Pure boron can be obtained by :
(a) Heating B_2O_3 with H_2
(b) Heating KBF_4 with Na or K
(c) Heating BBr_3 with Na or K
(d) Heating B_2O_3 with Na or K

140. Which of the following is not known :
(a) IPO_4 (b) $(CH_3COO)_3I$
(c) IF_7 (d) ICl_7

141. Which of the following reaction represents plumbosolvency :
(a) $2Pb + O_2 + 2H_2O \longrightarrow 2Pb(OH)_2$
(b) $2Pb + O_2 \longrightarrow 2PbO$
(c) $Pb + 2HCl \longrightarrow PbCl_2 + H_2$
(d) none of the above

142. Both P_2O_5 and PCl_5 on passing through excess of water gives :
(a) H_3PO_3 (b) H_3PO_2
(c) H_3PO_4 (d) $H_4P_2O_7$

143. NH_3 can be dried by :
(a) CaO (b) H_2SO_4
(c) P_4O_{10} (d) $CaCl_2$

144. Which of the following is correct for N_2O_5 :
(a) N_2O_5 in solid state has nitronium ion (NO_2^+)
(b) N_2O_5 in gaseous state N — O — N bond is linear
(c) N_2O_5 in solid state has nitrate ion NO_3^-
(d) all of the above

145. Select the incorrect statement :
(a) Li can be obtained by the electrolysis of LiCl solution in pyridine
(b) Oxides of metals placed below H in electrochemical series are thermally unstable
(c) Cucumber contains vanadium metal
(d) Thomas slag is $CaSO_4$

146. Which of the following is incorrect?
(a) Metals of 7, 8 and 9 groups do not form hydride
(b) Water gas shift reaction is :

$$CO + H_2O \xrightarrow[FeO/CoO]{673\ K} CO_2 + H_2$$

(c) Glauber salt is deliquescent
(d) Epsom salt is efflorescent

147. Free flow salt contains small amount of ..... with NaCl.
(a) $Ca_3(PO_4)_2$ (b) Na_3PO_4
(c) Mg_3PO_4 (d) Li_3PO_4

148. In fire crackers, which of the following is used to develop green fire :
(a) KNO_3 (b) $Ba(NO_3)_2$
(c) $Ni(NO_3)_2$ (d) $Al(NO_3)_3$

149. Which is not correct for SF_4 :
(a) It is a gas
(b) It acts as Lewis acid
(c) It acts as Lewis base
(d) It neither acts as Lewis acid or Lewis base

150. Pure chlorine can be obtained by :
(a) $KClO_3 + MnO_2$
(b) $PtCl_4$ or $AuCl_4$
(c) $HCl + O_2$
(d) $KClO_3 + KX$ in alk. medium

151. Select the incorrect statement :
(a) Liquid He is cryogenic liquid
(b) Fluorine is only halogen which reacts with noble gases
(c) Xe has + 6 Ox. no. in perxenates
(d) $He + O_2$ mixture is used for as ethane pahent

152. Copper can be extracted from :
(a) Kupfernickel (b) Dolomite
(c) Cinnabar (d) Malachite

153. In the manufacture of iron from haematite, the function of lime stone is as :
(a) a reducing agent (b) slag
(c) flux (d) gangue

154. In the metallurgy of iron, when limestone is added to the blast furnace, the calcium ion ends up in :
(a) slag (b) gangue
(c) metallic calcium (d) calcium carbonate

155. In the aluminothermite process, aluminium acts as :
(a) an oxidizing agent (b) a flux
(c) a reducing agent (d) a solder

156. Hydrogen gas will not reduce :
(a) heated cupric oxide (b) heated ferric oxide
(c) heated stannic oxide (d) heated aluminium oxide

157. The major role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is :
(a) as a catalyst
(b) to make the fused mixture very conducting
(c) to lower the temperature of the melt
(d) to decrease the rate of oxidation of carbon at the anode

158. Among the following statements, the incorrect one is :
(a) Calamine and siderite are carbonates
(b) Argenite and cuprite are oxides
(c) Zinc blende and pyrites are sulphides
(d) malachite and azurite are ores of copper

159. In the commercial electrochemical process for aluminium extraction, the electrolyte used is :
(a) $Al(OH)_3$ in NaOH solution
(b) an aqueous solution of $Al_2(SO_4)_3$
(c) a molten mixture of Al_2O_3 and Na_3AlF_6
(d) a molten mixture of Al_2O_3 and $Al(OH)_3$

160. The element with the highest first ionization potential is:
(a) Boron (b) Carbon
(c) Nitrogen (d) Oxygen

161. Which one of the following is the smallest in size?
(a) N^{3-} (b) O^{2-}
(c) F^- (d) Na^+

162. Which of the following is the strongest base :
(a) AsH_3 (b) NH_3
(c) PH_3 (d) SbH_3

163. The statement that is not correct for the periodic classification of elements is :
(a) The properties of elements are the periodic functions of their atomic numbers
(b) Non-metallic elements are lesser in number than metallic elements

(c) The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number
(d) For transition elements the *d*-sub shells are filled with electrons monotonically with increase in atomic number

164. Which has most stable + 2 oxidation state :
(a) Sn (b) Pb
(c) Fe (d) Ag

165. The correct order of ionic radii of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is :
(a) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$
(b) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$
(c) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$
(d) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$

166. Complete combustion of H_2S in air results in the production of :
(a) S and H_2O (b) SO_2, H_2
(c) H_2SO_4 (d) H_2O, SO_2

167. N_2O is an :
(a) acidic (b) basic
(c) amphoteric (d) neutral oxide

168. The gas least soluble in water is :
(a) HCl (b) N_2
(c) NH_3 (d) CO_2

169. The formula of indian salt petre is :
(a) KNO_3 (b) $NaNO_3$
(c) NaCl (d) NH_4NO_3

170. The substance having the lowest boiling point is :
(a) NH_3 (b) H_2S
(c) H_2O (d) none of these

171. Gypsum is :
(a) $MgSO_4 \cdot 7H_2O$ (b) $CuSO_4 \cdot 5H_2O$
(c) $CaSO_4 \cdot \frac{1}{2} H_2O$ (d) $CaSO_4 \cdot 2H_2O$

172. Among the following the coloured compound is :
(a) CuCl (b) $K_3[Cu(CN)_4]$
(c) CuF_2 (d) $[Cu(CH_3CN)_4]BF_4$

173. Hydrogen is evolved by the action of cold dil. HNO_3 on :
(a) Fe (b) Cu
(c) Mn (d) Al

174. The temporary hardness of water due to calcium bicarbonate can be removed by adding :
(a) $CaCO_3$ (b) $Ca(OH)_2$
(c) $CaCl_2$ (d) HCl

175. The reddish-brown coloured gas formed when nitric oxide is oxidised by air is :
(a) N_2O_5 (b) N_2O_4
(c) NO_2 (d) N_2O_3

176. Which of the following is most stable to heat :
(a) HCl (b) HOCl
(c) HBr (d) HI

177. A gas '*X*' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas '*Y*'. Identify '*X*' and '*Y*' :
(a) $X = CO_2, Y = Cl_2$ (b) $X = Cl_2, Y = CO_2$
(c) $X = Cl_2, Y = H_2$ (d) $X = H_2, Y = Cl_2$

178. Calcium is obtained by :
(a) electrolysis of molten $CaCl_2$
(b) electrolysis of a solution of $CaCl_2$ in water
(c) reduction of $CaCl_2$ with carbon
(d) roasting of limestone

179. Which of the following dissolve in hot concentrated NaOH solution.
(a) Fe (b) Zn
(c) Cu (d) Ag

180. "Lead pencil" contains :
(a) Pb (b) FeS
(c) Graphite (d) PbS

181. Which of the following are coloured?
(a) NO (b) N_2O
(c) CO (d) None of these

182. HCl is added to the following oxides which one would give H_2O_2 ?
(a) MnO_2 (b) PbO_2
(c) BaO (d) None of these

183. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is formed. The substance in a :
(a) Hg_2^{+} salt (b) Cr^{2+} salt
(c) Ag^{+} salt (d) Pb^{2+} salt

184. White phosphorus reacts with caustic soda. The products are PH_3 and NaH_2PO_2. This reaction is an example of :
(a) Oxidation
(b) Reduction
(c) Oxidation and reduction
(d) Neutralization

185. In nitroprusside ion the iron and NO exist. As Fe^{II} and NO^{+} rather than Fe^{III} and NO. These forms can be differentiated by :
(a) estimating the concentration of iron
(b) measuring the concentration of CN
(c) measuring the solid state magnetic moment
(d) thermally decomposing the compound

186. A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of :

(a) Sodium atoms (b) Sodium hydride
(c) Sodium amide (d) Solvated electrons

187. HBr and HI reduce sulphuric acid, HCl can reduce $KMnO_4$ and HF can reduce :
(a) H_2SO_4 (b) $KMnO_4$
(c) $K_2Cr_2O_7$ (d) None of these

188. Which of the following statements about anhydrous aluminium chloride is correct?
(a) It exists as $AlCl_3$ molecules
(b) It is not easily hydrolysed
(c) It sublimes at 100°C under vacuum
(d) It is a strong Lewis base

189. Sodium thiosulphate is used in photography because of its :
(a) Reducing behaviour
(b) Oxidising behaviour
(c) Complex forming behaviour
(d) Reaction with light

190. Moderate electrical conductivity is shown by :
(a) Silica (b) Graphite
(c) Diamond (d) Carborundum

191. The ion that can not be precipitated by both HCl and H_2S :
(a) Pb^{2+} (b) Cu^{+}
(c) Ag^{+} (d) Sn^{2+}

192. Heavy water is :
(a) H_2O^{18}
(b) Water obtained by repeated distillation
(c) D_2O
(d) Water at 4°C

193. Chlorine is used as a bleaching agent only in presence of :
(a) Dry air (b) Moisture
(c) Sunlight (d) Pure oxygen

194. Nitrogen dioxide cannot be obtained by heating :
(a) KNO_3 (b) $Pb(NO_3)_2$
(c) $Cu(NO_3)_2$ (d) $AgNO_3$

195. A gas that cannot be collected over water is :
(a) N_2 (b) O_2
(c) SO_2 (d) PH_3

196. Molecular formula of Glauber's salt is :
(a) $MgSO_4 \cdot 7H_2O$ (b) $CuSO_4 \cdot 5H_2O$
(c) $FeSO_4 \cdot 7H_2O$ (d) $Na_2SO_4 \cdot 10H_2O$

197. The oxide that gives H_2O_2 on treatment with a dilute acid is :
(a) PbO_2 (b) Na_2O_2
(c) MnO_2 (d) TiO_2

198. The compound which gives off oxygen on moderate heating is :
(a) Cupric oxide (b) Mercuric oxide
(c) Zinc oxide (d) Aluminium oxide

199. The bonds present in N_2O_5 are :
(a) Only ionic (b) Covalent and coordinate
(c) Only covalent (d) Covalent and ionic

200. The compound whose 0.1 *M* solution is basic is :
(a) Ammonium acetate (b) Ammonium chloride
(c) Na_2CO_3 (d) NaCl

201. Which of the following oxides of nitrogen is a coloured gas?
(a) N_2O (b) NO
(c) N_2O_5 (d) NO_2

202. The aqueous solution of $FeSO_4 \cdot Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The material obtained are :
(a) A colourless filtrate and green residue
(b) A yellow filtrate and green residue
(c) A yellow filtrate and brown residue
(d) A green filtrate and brown residue

203. Amongst the trihalides of nitrogen which one is least basic?
(a) NF_3 (b) NCl_3
(c) NBr_3 (d) NI_3

204. Bromine can be liberated from potassium bromide solution by the action of :
(a) Iodine solution (b) Chlorine water
(c) Sodium chloride (d) Potassium iodide

205. The only cations present in a slightly acidic solution are $Fe^{3+}, Zn^{2+}, Cu^{2+}$. The reagent when added in excess to this solution would identify to seperate Fe^{3+} in one step.
(a) 2*M* HCl (b) 6*M* NH_3
(c) 6*M* NaOH (d) H_2S

206. An aqueous solution contains Hg^{2+}, Hg_2^{2+}, Pb^{2+} and Cd^{2+}. The addition of HCl (6*N*) will precipitate :
(a) Hg_2Cl_2 only (b) $PbCl_2$ only
(c) $PbCl_2$ and Hg_2Cl_2 (d) $PbCl_2$ and $HgCl_2$

207. There is no S—S bond in :
(a) $S_2O_4^{2-}$ (b) $S_2O_5^{2-}$
(c) $S_2O_3^{2-}$ (d) $S_2O_7^{2-}$

208. The species that do not contain peroxide ions are :
(a) PbO_2 (b) H_2O_2
(c) SrO_2 (d) BaO_2

209. H_2SO_4 cannot be used to prepare HBr from NaBr as it :
(a) reacts slowly with NaBr
(b) oxidises HBr
(c) reduces HBr
(d) disproportionates HBr

210. Arrange

List A	List B
I. Explosive	A. NaN_3
II. Artificial gem	B. Fe_3O_4
III. Self reduction	C. Cr

IV. Magnetic material
D. Al_2O_3
E. $Pb(N_3)_2$
F. Fe_2O_3
G. Cu
H. SiC

(a) I-A, II-D, III-G, IV-B (b) I-E, II-D, III-G, IV-F
(c) I-A, II-D, III-G, IV-F (d) I-E, II-H, III-C, IV-B

211. Hydrolysis of one mole of peroxodisulphuric acid produces:
(a) two mole of sulphuric acid
(b) two mole of peroxomonosulphuric acid
(c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
(d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide

212. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order :
K_2CO_3 (I), $MgCO_3$ (II), $CaCO_3$ (III), $BeCO_3$ (IV)
(a) I < II < III < IV (b) IV < II < III < I
(c) IV < II < I < III (d) II < IV < III < I

213. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order :
ClOH (I), BrOH (II), IOH (III)
(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

214. Sodium thiosulphate is prepared by :
(a) reducing Na_2SO_4 solution with H_2S
(b) boiling Na_2SO_3 solution with S in alkaline medium
(c) neutralising $H_2S_2O_3$ solution with NaOH
(d) boiling Na_2SO_3 solution with S in acidic medium

215. Which of the following halides is least stable and has doubtful existence?
(a) Cl_4 (b) GeI_4
(c) SnI_4 (d) PbI_4

216. Which one of the following oxides is neutral?
(a) CO (b) SnO_2
(c) ZnO (d) SiO_2

217. Which one of the following species is not pseudohalide?
(a) CNO^- (b) $RCOO^-$
(c) OCN^- (d) NNN^{-1}

218. On heating ammonium dichromate, the gas evolved is :
(a) Oxygen (b) Ammonia
(c) Nitrous oxide (d) Nitrogen

219. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (at 25°C) is :
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

220. Which one amongst the following pairs of ions cannot be separated by H_2S in dilute HCl?
(a) Bi^{3+}, Sn^{4+} (b) Al^{3+}, Hg^{2+}
(c) Zn^{2+}, Cu^{2+} (d) Ni^{2+}, Cu^{2+}

221. Polyphosphates are used as water softening agents because they :
(a) From soluble complexes with anionic species
(b) Precipitate anionic species
(c) Form soluble complexes with cationic species
(d) Precipitate cationic species

222. Identify the correct order of acidic strength of CO_2, CuO, CaO, H_2O :
(a) $CaO < CuO < H_2O < CO_2$
(b) $H_2O < CuO < CaO < CO_2$
(c) $CaO < H_2O < CuO < CO_2$
(d) $H_2O < CO_2 < CaO < CuO$

223. For H_3PO_3 and H_3PO_4 the correct choice is :
(a) H_3PO_3 is dibasic and reducing
(b) H_3PO_3 is dibasic and non-reducing
(c) H_3PO_4 is tribasic and reducing
(d) H_3PO_3 is tribasic and non-reducing

224. The pair of compounds which cannot exist together in solution is :
(a) $NaHCO_3$ and NaOH
(b) Na_2CO_3 and $NaHCO_3$
(c) Na_2CO_3 and NaOH
(d) $NaHCO_3$ and NaCl

225. $(Me)_2SiCl_2$ on hydrolysis will produce :
(a) $(Me)_2Si(OH)_2$
(b) $(Me)_2Si=O$
(c) $-[-O(Me)_2Si-O-]_n-$
(d) $Me_2SiCl(OH)$

226. When same mass of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volume of H_2 evolved is :
(a) 1 : 1 (b) 1 : 2
(c) 2 : 1 (d) 9 : 4

227. Which of the following is the weakest base?
(a) NaOH (b) $Ca(OH)_2$
(c) KOH (d) $Zn(OH)_2$

228. The compound insoluble in acetic acid is :
(a) calcium oxide (b) calcium carbonate
(c) calcium oxalate (d) calcium hydroxide

229. Iron is rendered passive by treatment with concentrated:
(a) H_2SO_4 (b) H_3PO_4
(c) HCl (d) HNO_3

230. The types of bonds present in $CuSO_4 \cdot 5H_2O$ are only :
(a) electrovalent and covalent
(b) electrovalent and coordinate covalent
(c) electrovalent, covalent and coordinate covalent
(d) covalent and coordinate covalent

231. Zinc-copper couple that can be used as a reducing agent is obtained by :
(a) mixing zinc dust and copper gauze

(b) zinc coated with copper
(c) copper coated with zinc
(d) zinc and copper wires welded together

232. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by :
(a) $MnSO_4 \cdot 4H_2O$ (b) $CuSO_4 \cdot 5H_2O$
(c) $FeSO_4 \cdot 6H_2O$ (d) $NiSO_4 \cdot 6H_2O$

233. Ferric sulphate on heating gives :
(a) SO_2 and SO_3 (b) SO_2 only
(c) SO_3 only (d) none of these

234. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$:
(a) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic
(b) $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic
(c) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $NiCl_4^{2-}$ is paramagnetic
(d) $Ni(CO)_4$ is diamagnetic and $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic

235. Among the following ions which one has the highest paramagnetism?
(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{2+}$
(c) $[Cu(H_2O)_6]^{2+}$ (d) $[Zn(H_2O)_6]^{2+}$

236. Which one is solder?
(a) Cu + Pb (b) Zn + Cu
(c) Pb + Sn (d) Fe + Zn

237. Which pair gives Cl_2 at room temperature?
(a) Conc. HCl + $KMnO_4$
(b) NaCl + Conc. H_2SO_4
(c) NaCl + MnO_2
(d) NaCl + Conc. HNO_3

238. Which of the following is formed when excess of KCN is added to aqueous solution of copper sulphate?
(a) $Cu(CN)_2$ (b) $K_2[Cu(CN)_4]$
(c) $K[Cu(CN)_2]$ (d) $K_3[Cu(CN)_4]$

239. Which compound does not dissolve in hot, dilute HNO_3?
(a) HgS (b) PbS
(c) CuS (d) CdS

240. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is :
(a) CrO_3 (b) Cr_2O_3
(c) Cr (d) $CrO(O_2)$

241. Which of the following compounds is expected to be coloured?
(a) Ag_2SO_4 (b) CuF_2
(c) MgF_2 (d) CuCl

242. Which of the following is an organometallic compound?
(a) Lithium methoxide
(b) Lithium acetate
(c) Lithium dimethylamide
(d) Methyl lithium

243. Among the following, the compound that is both paramagnetic and coloured is :
(a) $K_2Cr_2O_7$ (b) $(NH_4)_2(TiCl_6)$
(c) $CoSO_4$ (d) $K_3[Cu(CN)_4]$

244. A black sulphide is formed by the action of H_2S on :
(a) Sodium chloride (b) Cadmium chloride
(c) Zinc chloride (d) Cupric chloride

245. In the dichromate anion :
(a) 4 Cr — O bonds are equivalent
(b) 6 Cr — O bonds are equivalent
(c) All Cr — O bonds are equivalent
(d) All Cr — O bonds are non-equivalent

246. The geometry in $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are :
(a) both square planar
(b) tetrahedral and square planar, respectively
(c) both tetrahedral
(d) square planar and tetrahedral, respectively

247. Animal charcoal used is decolorising agent contains carbon and .....
(a) $Ca_3(PO_4)_2$ (b) $MgCl_2$
(c) $KMnO_4$ (d) $K_2Cr_2O_7$

248. Which of the following is called super acid.
(a) HI (b) SbF_5
(c) H_3SbO_4 (d) H_3AsO_4

249. A complex $[CoL_6]^{n+}$, where L is neutral ligand has a magnetic moment $\mu = 4.5$ B.M. Hence :
(a) Co must be in +2 oxidation state
(b) Co must be in +3 oxidation state
(c) The complex is diamagnetic
(d) L must be a strong ligand

250. CrO_4^{2-} is yellow in colour because :
(a) Cr is a transition metal
(b) Cr and O are π-bonded and the allowed $\pi \rightarrow \pi^*$ transition occurs in visible region
(c) of charge transfer from $Cr \rightarrow O$
(d) of its strong tendency of absorption ~ 640 nm wavelength

251. Number of unpaired electrons in $[Cr(en)_2]^{2+}$ are :
(a) 4 (b) 2
(c) 3 (d) 1

252. MnO_4^{2-} ion shows ..... colour in aqueous solution :
(a) Green (b) Purple
(c) Organge (d) Blue

SOLUTIONS (One Answer Correct)

1. (a) Zirconium hydride is $ZrH_{1.9}$.
2. (d) The reaction is neither redox nor PI_3 is a salt.
3. (c) Steric hinderance prevents 8 fluorine atoms to form OsF_8.
4. (a) Silicones have strong Si—C bonds as well as Si—O—Si bond. These are stable to heat, insulators and water repellent.
5. (b) NH_2OH is strong reductant and poisonous.

$$4NH_2OH \xrightarrow[\text{Slow}]{2H^+} N_2O + 2NH_4^+ + 3H_2O$$

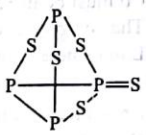
$$3NH_2OH \xrightarrow[\text{Fast}]{OH^-} N_2 + NH_3 + 3H_2O$$

6. (a) pK_a for HF, HCl, HBr and HI are 3, −7, −9, −10 respectively.
7. (a) Hydration is exothermic and spontaneous. Also randomness decreases.
8. (a) The decomposition temperature for Be, Mg, Ca, Sr and Ba carbonates are 373, 813, 1173, 1563 and 1633 K.
9. (d) Rest all are applications of B_4C.
10. (c) Rest all are facts.
11. (d) $CoO + B_2O_3 \longrightarrow Co(BO_2)_2$; B_2O_3 is anhydride of H_3BO_3

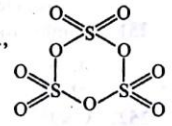
$$P_2O_5 + B_2O_3 \longrightarrow 2BPO_4$$

12. (a) $Bi^{3+} \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} [BiO]^+$
13. (d) Rest all are characteristics of calgon.
14. (d) Ultramarine possesses three dimensional silicate structure like Zeolites and Feldspar.
15. (a) The existence of P_4S_6 is not reported although P_4O_6 is known.

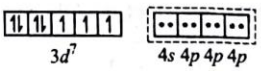
P_4S_3



16. (c) It forms H_2CrO_4; $CrO_3 + H_2O \longrightarrow H_2CrO_4$
17. (a) CO is not electron donor. See point (d).
18. (a) Cyclic trimer of SO_3 is $(SO_3)_3$, *i.e.*,



19. (d) It is a fact.
20. (a) H_2Te belongs to hydride of sulphur family (H_2S, H_2Se).
21. (d) MnO_2 is dioxide and does not contain O—O bond.
22. (b) S_4N_4 has two weak S—S bonds in cage structure. It is thermochronic, *i.e.*, its colour changes with temperature, *i.e.*, colourless at liq. N_2 temperature, orange-yellow at room temperature, red at 100° C.
23. (d) Rest all show colour change on heating.
24. (d) Pb is not radioactive.
25. (d) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$
26. (d) Follow their geometry.
27. (d) PF_5 has no p—d π bonding.
28. (b) Perxenate ion is $[XeO_6]^{4-}$ having no peroxide bond.
29. (d) Transition elements Sc = 3, Y and Ti = 4.5 g / cm^3 have density less than 5 g / cm^3
30. (b) Os (22.57 g / cm^3) and Ir (22.61 g / cm^3) have highest densities.
31. (b) Only the three transition elements have m.pt. > 3000° C. These are Ta = 3000° C, W = 3410° C and Re = 3180° C. Zn has 420° C.
32. (b) The colour arises due to different degree of polarisation by Ag^+ ion.
33. (a) In MnO_4^- an electron is momentarily transferred from O to the metal and the momentarily changing O^{2-} to O^- and reducing the oxidation state of metal.
34. (b) Rest all are correct.
35. (b) More is $E°_{OP}$ (−0.36 > −0.77 V) and thus easier is oxidation. Stability of complex can be evaluated if stability constants are given.
36. (d) $FeCl_3$ sublimes at 300° C.
37. (d) All are correct.
38. (d) This is experimental fact.
39. (d) $NaBr + ICl \longrightarrow Na^+ [BrICl]^-$
40. (d) $SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$
41. (d) $NaNH_2 + C \longrightarrow NaCN + H_2$
42. (d) Wood metal an alloy of Bi, Pb, Sn and Cd has m. pt. 71° C.
43. (a) II has non-ionisable nature and thus minimum conductance.
44. (d) Cl^- ligand is listed at bottom in spectrochemical series of ligand.
45. (a) EAN of Pt = 78 − 4 + 12 = 86 (*i.e.*, Rn)
46. (d) EAN of Cr = 24 − 3 + 12 = 33 (nearest noble gas 36, *i.e.*, Kr)
47. (b) Co^{2+} in $[CoI_4]^{2-}$ is



$3d^7$ $\quad$ $4s\ 4p\ 4p\ 4p$

sp^3

48. (c) Cr^{2+}, Ag^{2+}, Ni^{2+} and Co^{2+} have 4, 1, 2, 1 unpaired electrons and thus Ni^{2+} can show pairing of electron in

strong field to give diamagnetic nature. Cr^{2+} is in weak field.

49. (a) It is called van Arkel process.

50. (c) $2CO + NaH \longrightarrow HCOONa + C$; CO is reduced.

51. (d) PbH_4 too is covalent hydride.

52. (d) $\underset{I}{[Co(NH_3)_4CO_3Cl]\cdot 2H_2O}$;

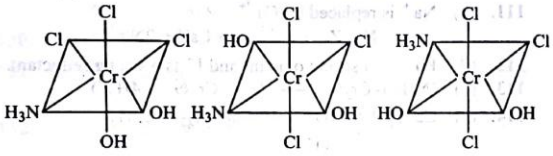
$\underset{II}{[Co(NH_3)_4(H_2O)_2]CO_3\cdot Cl}$;

$\underset{III}{[Co(NH_3)_4H_2OCl]CO_3\cdot H_2O}$;

$\underset{IV}{[Co(NH_3)_4CO_3\cdot H_2O]Cl\cdot H_2O}$

see all shows geometrical isomerism; each having *cis*-and *trans*- form. Also notice hydrate isomerism and coordination isomerism.

53. (c)



54. (b) Rest all possess symmetry.

55. (a) Follow IUPAC rules.

56. (a) Coordination numbers of Cu^+, Cu^{2+}, Al^{3+} and Zn^{2+} are 2, 4, 6, 4 respectively.

57. (a) It is a fact.

58. (c) Bond order for NO is $+\frac{1}{2}$ (15 electrons paramagnetic)

Bond order for NO^+ is zero (14 electrons diamagnetic)

59. (a) Bond order for NO^- is 2. Rest all has bond order 3.

60. (c) Both have sp^3-hybridisation and pyramidal in shape.

61. (a) MnO_2 is neutral oxide.

62. (c) HOCl is stronger acid than HOBr

$\therefore$ OCl^- is weak base than OBr^-

63. (d) The per acids has an oxidation state higher than, ic acid.

64. (d) In $HClO_4\cdot H_2O$, the ions are localised because of the lattice forces and thus, H-bonding is not extensive as in $HClO_4$.

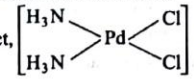
65. (c) $C_2N_2 + 2OH^- \longrightarrow CN^- + CNO^- + H_2O|CN^-$ acts as reducing agent like X^-.

$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$

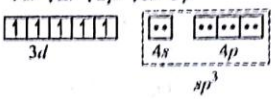
66. (d) $Na + (X+Y)NH_3 \longrightarrow [Na(NH_3)_X]^+ + [e(NH_3)_Y]^-$ conductor of current.

67. (c) $Cu_2O + 2HI \longrightarrow 2CuI + H_2O$

68. (a) To remove impurities of acidic oxide, basic lining in furnace is preferred and *vice-versa*.

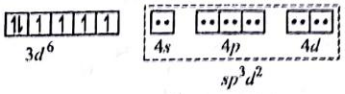
69. (d) All are correct, 

70. (d) $_{25}Mn^{2+}: 1s^2, 2s^2, 2p^6, 3s^2 3p^6$



sp^3

71. (a) $Co^{3+}: 1s^2, 2s^2, 2p^6, 3s^2 3p^6$



sp^3d^2

72. (d) According to crystal field theory, the total energy separation $\Delta = Y - X$ where XY is energy of destabilization and X is energy of stabilisation if d^{10}, *i.e.*, completely filled orbitals have zero stabilisation energy (CFSE) whatever be the value of Δ.

73. (b) German silver is an alloy of Cu.

74. (d) EAN = Atomic number of metal – electrons lost in forming cation + '*e*' gained during complex formation

$54 = 42 - 0 + 2 \times$ No. of ligand

$\therefore$ No. of ligand = 6 (one CO donate 2 electrons)

75. (c) OF is more stable as it has less antibonding electrons.

76. (d) Bonding and antibonding electrons are different in both.

77. (d) Bond order for N_2, N_2^+, NO^+, NO, CN^- and CN are 3, 2.5, 3, 2.5, 3, 2.5 respectively. Higher is bond order smaller is bond length bond order of CO and CO^+ are 3 and 3.5.

78. (b) MO diagram for CO is : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2 \sigma^* 2s^2$. This is due to the fact that 2*s*-orbital of O (lower energy) than 2*s*-orbital of C (higher energy) on mixing give rise $\sigma^* 2s$ with higher energy than $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$.

79. (d) Nitrates, per chlorates of all metals are water soluble. Ammonium salts are water soluble.

80. (a) Chlorides of Ag, Pb and Hg are water insoluble.

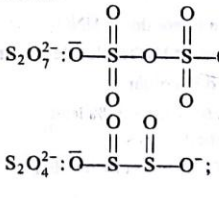
81. (d) Rest all reacts with moisture to give fumes of HCl.

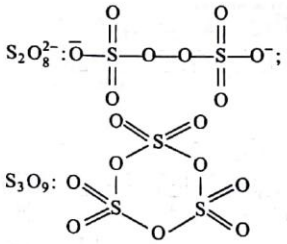
82. (b) $H_t - B - H_t = 120°$, $H_b - H - H_b = 97°$ C;

t = terminal; b = bridge.

83. (b) Chloroprene $CCl_3\cdot NO_2$ is used as tear gas.

84. (a) $P + O_2 \longrightarrow P_2O_5$; the light is released during oxidation of P. The phenomenon of evolution of light as a result of chemical change is chemiluminescence and not phosphorescence. It is wrongly written is books.

85. (c) 



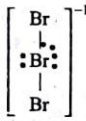
86. (b) Only S has *d*-orbitals.

87. (b) AsO_3^{3-}, ClO_3^- and SO_3^- have sp^3-hybridisation with one lone pair and thus pyramidal.

88. (c) $\underset{\text{Base}}{2K_2MnF_6} + \underset{\text{(Strong Lewis acid)}}{4SbF_5} \longrightarrow 4KSbF_6 + 2MnF_4$

$$2MnF_4 \longrightarrow 2MnF_3 + F_2 \quad \text{(redox)}$$

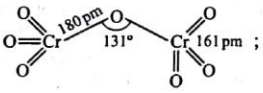
$$2K_2MnF_6 + 4SbF_5 \longrightarrow 4KSbF_6 + 2MnF_3 + F_2$$

89. (a) Br_3^- has 3 lone pairs of electrons 

90. (a) Each has one lone pair of electron but hybridisation is sp^3, sp^3d and sp^3d^3 in XeO_3, $XeOF_4$ and XeF_6 respectively.

91. (b) Thorium series—thoron as ($^{220}_{86}Rn$); actinium series—actinon as ($^{219}_{86}Rn$); uranium series—radon $^{226}_{86}Ra$.

92. (c) SF_4 has see-saw structure.

93. (d) 

It caution two tetrahedron joined together.

94. (a) $$I^- \longrightarrow I^{5+} + 6e$$

$$Mn^{7+} + 3e \longrightarrow Mn^{4+} + 2e$$

$$KI + 2KMnO_4 + H_2O \longrightarrow KIO_3 + 2MnO_2 + 2KOH$$

95. (d) Tl^+ does not exist; Cu^+ disproportionates; Cr^{2+} is less stable than Cr^3.

96. (a) No. of unpaired electron in Mn^{2+}, Cu^{2+}, Fe^{2+} and Ni^{2+} are 5, 1, 4, 2 electrons respectively.

97. (d) $2CuSO_4 + 10KCN \longrightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + \underset{\text{Pseudohalogen}}{C_2N_2}$

98. (c) HgS is insoluble in hot dilute HNO_3.

99. (b) This is due to loss of H_2O molecules to atmosphere.

100. (b) $Fe(CNS)_3$ is red in colour.

101. (b) Solder contains 67% tin + 33% lead.

102. (c) N_2O is called laughing gas.

103. (b) Supercritical CO_2 is liquid below its T_c.

104. (c) Larger is the size of cation, lesser is polarising power, *i.e.*, more ionic character. A compound with more ionic nature is more basic.

$$Ti^{2+} > V^{2+} > Cr^{2+} > Fe^{2+}$$

Ionic radii decrease along the period.

105. (a) Litharge (PbO) is amphoteric oxide and is used in making flint glass, as a drier in paints and varnishes.

106. (a) The hybridisation of Co becomes sp^3d^2 and $[Co(H_2O)_4Cl_2]$ is blue.

107. (a) Follow structure of P_4O_6 and P_4O_{10}.

108. (d) NO_2 is brown.

109. (c) In a spectrochemical series the order is $H_2O < NH_3 < NO_2^-$.

110. (a) Mole of LiH in same mass is lowest (Mole $= \frac{w}{m}$ and m is minimum for LiH).

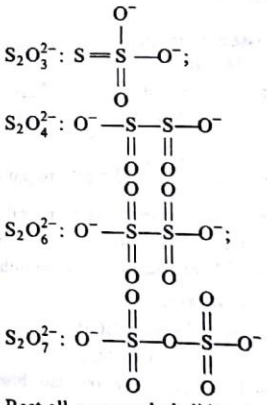
111. (b) Na^+ is replaced by Ca^{2+}

$$Na_2Z + Ca^{2+} \longrightarrow CaZ + 2Na^+$$

112. (d) Pb^{4+} is a strong oxidant and I^- is a strong reductant.

113. (c) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$.

114. (c) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

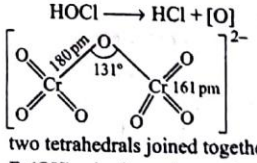
115. (d) 

116. (b) Rest all are pseudo halides, *i.e.*, behave like a halide ion.

117. (a) More is the electronegativity of central atom, more is acidic nature.

118. (b) $Cl_2 + H_2O \longrightarrow HCl + HOCl$; OCl^- acts as oxidant

$$HOCl \longrightarrow HCl + [O]$$

119. (b) 

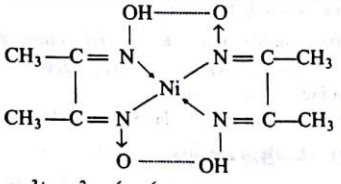
two tetrahedrals joined together

120. (b) $Fe(OH)_3$ is formed as a brown residue with light yellow colour filtrate.

121. (c) $PbCl_2$ and Hg_2Cl_2 are insoluble.

122. (b) Follow hybridisation.

123. (a) It is a fact. (Electrolytic refining)
124. (a) It is so called spring reaction.
125. (a) German silver has Cu, Zn and Ni.
126. (c) Fluorspar is CaF_2.
127. (c) It is a fact; two N atom and four O atoms.
128. (a)



129. (a) $Co^{3+}: 3s^2 3p^6 3d^6$ configuration. It has d^2sp^3 hybridisation having no unpaired electrons in $[Co(NH_3)_6]^{3+}$; In $[CoCl_6]^{3-}$ it has four unpaired electrons and sp^3d^2 hybridisation.
130. (c) Xe^+ and $[Pt\ F_6]^-$
131. (c) l_{2g} of d_{xy}, d_{yz} and d_{zx} is closer to 4*s* and 4*p*. Thus d^3s hybridization.
132. (c) Ag_2CO_3 decomposes on heating to Ag.
133. (b) $NaOH_{(s)} + CO \xrightarrow{200°C} HCOONa$
134. (b) $4KO_2 + 4CO_2 + 2H_2O \xrightarrow{\text{Excess of } CO_2} 4KHCO_3 + 3O_2$
135. (a) $3S + H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$
136. (b) It is a fact.
137. (b) $2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$
138. (d) Tincture of iodine has I_2 + KI dissolved in sprit.
139. (d) $2B_2O_3 + 6Na \longrightarrow 3Na_2O_2 + 4B$
140. (d) I shows + 7 oxidation state with O and F. Large size of Cl resist to get attached 7Cl atoms on I.
141. (a) This reaction shows dissolution of Pb in water.
142. (c) $PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$
$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$
143. (a) Rest all also reacts with NH_3.
144. (d) In solid state N_2O_5 has $NO_2^+NO_3^-$ structure.
145. (d) Thomas slag is $Ca_3(PO_4)_2$
146. (c) $Na_2SO_4 \cdot 10H_2O$ is efflorescent *i.e.*, looses water on exposure to air.
147. (a) It is a fact.
148. (b) Ba imparts green colour to flame.
149. (d) $SF_4(g) + BF_3 \longrightarrow [F_4S \longrightarrow BF_3]$
$SF_4(g) + 2F^- \longrightarrow [SF_6]^{2-}$
150. (b) $PtCl_4 \xrightarrow{374°C} PtCl_2 + Cl_2 \xrightarrow{582°C} Pt + 2Cl_2$
$AuCl_3 \xrightarrow{175°C} 2AuCl + 2Cl_2 \xrightarrow{185°C} 2Au + 3Cl_2$
151. (c) Ox. No. of Xe in perxenates $[XeO_6]^{4-}$ is +8.
152. (d) Malachite is $CuCO_3 \cdot Cu(OH)_2$.
153. (c) Flux ($CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$)
flux slag
154. (a) —do—
155. (c) Al acts as reducing agent.
$2Al + Cr_2O_3 \rightarrow Al_2O_3 + 2Cr$
156. (d) Al, Fe and Sn are more electropositive than H_2 but Al is more electropositive in comparison to Fe and Sn. Therefore, they are reduced from Fe^{3+} to Fe^{2+} and from Sn^{4+} to Sn^{2+} by H_2.
157. (b) CaF_2 is used to lower fusion temperature of fused mixture.
158. (b) Argentite (Ag_2S) and cuprite ($CuFeS_2$) are sulphides not oxides.
159. (c) It is a fact, Na_3AlF_6 is used to decrease the melting point as well as to increase the conductivity of Al_2O_3.
160. (c) Nitrogen has half filled configuration.
161. (d) For isoelectronic ions, as the ENC increases, the size decreases, Ionic size $\propto \frac{1}{Z_{eff}}$
$Z_{eff} = Z - \sigma$
Z = Atomic number, σ = Screening cons.
162. (b) In NH_3 'N' has no '*d*' orbitals. So, lone pair of electron concentrates only on 'N' therefore N can provide easily lone pair of electron. Basic character of hydrides decreases down the gp.
163. (d) Among transition elements, electrons are not filled in *d*-subshell monotonically with increasing atomic number.
164. (b) Heavy *p*-block elements shows inert pair effect in which valence '*s*' electrons become inert. This effect becomes more prominent down the group. Secondly completely filled electronic configurations are comparatively more stable.
$Pb^{2+} \rightarrow 5d^{10}\ 6s^0$ $Fe^{2+} \rightarrow 3d^6$
$Sn^{2+} \rightarrow 4d^{10}\ 5s^0$ $Ag^{2+} \rightarrow$ is not easily obtained.
165. (a) Due to lanthanoid contraction the covalent radii shows the order, $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$. The element Y belongs to Vth period and Lu belongs to VIth period, therefore $Y^{3+} < Lu^{3+}$. The lanthanide contraction is caused by the poor shielding effect of 'f' electrons.
166. (d) $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$
167. (d) N_2O and NO are neutral, while N_2O_3, N_2O_4, N_2O_5 are acidic in nature.
168. (b) N_2 is almost inert due to its high bond dissociation energy. Hence sparingly soluble in water.
169. (a) KNO_3 is called Indian salt peter. $NaNO_3$ is chilie salt petre.
170. (b) H_2S does not form hydrogen bonding, while in water and ammonia, intermolecular hydrogen bonding exists.
171. (d) $CaSO_4 \cdot 2H_2O$ is called gypsum.

172. (c) CuF_2, Cu^{2+} contains one unpaired electron. While in other complexes Cu exists as Cu^+ which has no unpaired electron hence colourless.

173. (c) $Mn + \underset{(dil)}{2HNO_3} \longrightarrow Mn(NO_3)_2 + H_2$

174. (b) $Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

175. (c) $2NO + O_2 \longrightarrow \underset{\text{raddish brown}}{2NO_2}$

176. (a) It is fact.

177. (c) $\underset{(X)}{Cl_2} + H_2O \longrightarrow HCl + HOCl$

$HCl + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl_{(s)}} + HNO_3$

$2HCl + Mg \longrightarrow MgCl_2 + \underset{(Y)}{H_2}$

178. (a) Electrolysis of molten $CaCl_2 \xrightarrow{\text{fused}} Ca^{2+} + 2Cl^-$

At Cathode : $Ca^{2+} + 2e \longrightarrow Ca$

At Anode : $2Cl^- \longrightarrow Cl_2 + 2e$

179. (b) $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$

180. (c) Graphite is used inlead pencil.

181. (d) None of these is coloured.

182. (d) None of these is peroxide.

183. (d) $Pb^{2+} + 2HCl\,(dil) \rightarrow \underset{\text{white ppt}}{PbCl_2}\downarrow 2H^+$

$PbCl_2$ ppts. dissolve on heating

$\underset{\text{hot solution}}{PbCl_2} + H_2S \xrightarrow[\text{medium}]{\text{acidic}} \underset{\text{black ppt.}}{PbS}\downarrow + 2HCl$

Hence, substance is Pb^{2+} salt.

184. (c) Oxidation and reduction (Auto redox)

$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

185. (c) The magnetic moment (μ) of a species is related to its number of unpaired electrons (n).

$Fe^{2+} \rightarrow 3d^6$ (4 unpaired electron)

$Fe^{3+} \rightarrow 3d^5$ (5 unpaired electron)

$\mu = \sqrt{n(n+2)}$ B.M. (B.M. = Bohr Magnetons)

The number of unpaired electrons in the given pairs are as follows :

NO or $\overset{\times\times}{\overset{+}{N}} = \ddot{O}:$ $\quad n = 0$

NO or $\overset{\times}{\underset{\times}{N}} = \ddot{O}:$ $\quad n = 1$

The given combination differs in the unpaired electrons. Hence these can be differentiated by measurement on the solid state magnetic moment of nitroprusside ion.

186. (d) Solvated electrons $Na \longrightarrow Na^+ + e$

$e + x\,NH_3 \longrightarrow \underset{\text{(Blue colour)}}{e(NH_3)_x^-}$

187. (d) None of the above. HF is a weak acid.

188. (c) It sublimes at 100°C under vacuum.

189. (c) Complex forming behaviour.

190. (b) Graphite has mobile free electrons.

191. (d) Sn^{2+} cannot be precipitated out by H_2S and HCl.

192. (c) D_2O. It .s a fact.

193. (b) Chlorine reacts with moisture to give nascent oxygen which bleaches coloured substances

$Cl_2 + H_2O \longrightarrow HCl + HClO$

$HOCl \longrightarrow HCl + O$

194. (a) $2KNO_3 \longrightarrow 2KNO_2 + O_2$

195. (c) It is because SO_2 reacts with water to form H_2SO_4

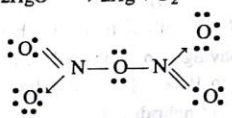
$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$

196. (d) It is a fact.

197. (b) $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$

198. (b) $2HgO \xrightarrow{\Delta} 2Hg + O_2$

199. (b)



200. (c) Na_2CO_3 & NaOH are strong bases.

201. (d) NO_2 is a brown coloured gas.

202. (c) The filtrate is yellow due to CrO_4^{2-} and residue is brown due to $Fe(OH)_3$.

203. (a) NF_3 is least basic because of the high electronegativity of fluorine which give rise to +ve charge on N atom.

204. (b) The reduction potential of Cl_2 is more than Br_2, therefore Cl_2 replaces Br^- from solution.

205. (b) Fe^{3+} is precipitated in its hydroxide form. Cu forms complex with NH_3.

$Fe^{3+} + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4^+$

206. (c) Both Pb^{2+} and Hg_2^{2+} has lower value of K_{sp} than Cd^{2+} and Hg^{2+} hence precipitated as chlorides.

207. (b) $\bar{O}-\overset{O}{\overset{\|}{S}}-O-\overset{O}{\overset{\|}{S}}-\bar{O}$

208. (a) It is an oxide (PbO_2).

209. (b) Because it oxidises HBr to Br_2.

$2HBr + H_2SO_4 \longrightarrow SO_2 + 2H_2O + Br_2$

210. (b) It is a fact.

211. (c) $H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$

212. (b) The thermal stability increases down the group.

213. (a) The acidic strength decreases with the decrease of electronegativity.

214. (b) $Na_2SO_3 + S \xrightarrow[\Delta]{\text{boil}} Na_2S_2O_3$

215. (d) Because Pb^{4+} is a strong oxidant while I^- is a strong reductant. So Pb^{4+} get reduced to Pb^{+2}.

216. (a) It is a fact.

217. (b) Several uninegative groups which show certain characteristic of halide ions, called as pseudohalides.

218. (d) $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$

219. (d) It is due to high lattice energy of $Be(OH)_2$.

220. (a) (i) Both Bi^{3+} and Sn^{4+} (belongs II group) are precipitated by H_2S in presence of dil. HCl hence can

not be separated out while $Al^{3+}, Zn^{2+}, Ni^{2+}$ does not precipitate out by H_2S in presence of dil. HCl.

221. (c) They from soluble complex salt with cationic species.

$$Na_2[Na_4(PO_3)_6] + CaSO_4 \rightarrow \underset{\text{soluble complex salt}}{Na_2[CaNa_2(PO_3)_6]} + Na_2SO_4$$

222. (a) The acidic strength of oxides increases from left to right. CaO = Highly basic; CuO = weak base; H_2O = Neutral; CO_2 = acidic.

223. (a) $HO-\underset{\underset{H}{|}}{\overset{\overset{O}{||}}{P}}-OH$. Dibasic acids have reducing nature.

224. (a) Acidic salt ($NaHCO_3$) and base (NaOH) cannot exist together in solution, because both reacts.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$$

225. (c) Product is linear silicones

$$Me_2SiCl_2 + 2H_2O \rightarrow HO-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-OH$$

$$HO-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-OH + HO-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-OH \longrightarrow$$

$$\left[-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\right]_n$$

Linear Silicones

226. (a) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

In both reactions, the H_2 ratio is 1 : 1.

227. (d) Alkali and alkaline earth metal hydroxides are highly basic as compared to the hydroxides of transition metals.

228. (c) Calcium oxalate is insoluble in acetic acid.

229. (d) Fe is passive in conc. HNO_3 because a thin layer of oxide is formed on its surface.

230. (c) $Cu^{2+} \cdot H_2O\left[O=\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}=O\right]^{2-} \cdot 4H_2O$

Copper sulphate has three types of bonds *i.e.*, electrovalent, covalent and coordinate bond.

231. (a) Zn—Cu couple is obtained by mixing zinc dust and copper gauze.

232. (b) As the number of unpaired electron increases, the paramagnetic character also increases.

In $MnSO_4 \cdot 4H_2O$

Mn^{2+} = $3d^5$ $4s^0$ (Unpaired $e^- = 5$)

In $CuSO_4 \cdot 5H_2O$

Cu^{2+} = $3d^9$ $4s^0$ (Unpaired $e^- = 1$)

In $FeSO_4 \cdot 6H_2O$

Fe^{2+} = $3d^6$ $4s^0$ (Unpaired $e^- = 4$)

In $NiSO_4 \cdot 6H_2O$

Ni^{2+} = $3d^8$ $4s^0$ (Unpaired $e^- = 2$)

Paramagnetic character $\propto$ unpaired electrons

$$\mu = \sqrt{n(n+2)}$$

n = no. of unpaired electron.

233. (c) SO_3 only.

$$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3$$

234. (c)

Ni^{2+} = $3d$ $4s$ $4p$

$[Ni(CN)_4]^{2-}$ = $3d$ $4s$ $4p$ (CN CN CNCN)

dsp^2

(No unpaired electron, diamagnetic)

$[Ni(CO)_4]$ = $3d$ $4s$ $4p$ (CO CO COCO)

dsp^3

(No unpaired electron, diamagnetic)

$[NiCl_4]^{2-}$ = $3d$ $4s$ $4p$ (Cl Cl Cl Cl)

sp^3

(2 unpaired electron, paramagnetic)

A strong field ligand can pair up the unpaired electron of central atom while weak ligand cannot.

CN^- and CO are strong field ligands, hence they bring about the pairing of 3*d*-electrons, whereas, Cl is a weak field ligand and fails to do so.

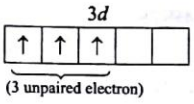
235. (b) Paramagnetic character increases as the number of unpaired electrons in *d*-sub-shells increases.

In these complex ions :

In $[Cr(H_2O)_6]^{3+}$, Cr is present as

Cr^{3+} (O.N. of Cr = + 3)

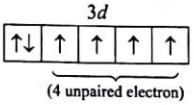
$_{24}Cr^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3$



In $[Fe(H_2O)_6]^{2+}$, Fe is present as

Fe^{2+} (O.N. of Fe = + 2)

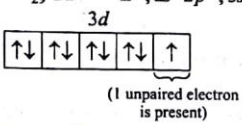
$_{26}Fe^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6$



In $[Cu(H_2O)_6]^{2+}$, Cu is present as

Cu^{2+} (O.N. of Cu = + 2)

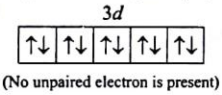
$_{29}Cu^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9$



In $[Zn(H_2O)_6]^{2+}$, Zn is present as

Zn^{2+} (O.N. of Zn = + 2)

$_{30}Zn^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$



So, paramagnetic character is maximum in $[Fe(H_2O)_6]^{2+}$.

236. (c) Solder is an alloy of Pb and Sn.

237. (a) $2KMnO_4 + 6HCl \rightarrow 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$

238. (d) The product is a complex compound

$$CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4$$

$$2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + CN{-}CN$$

(Cyanogen gas)

$$Cu_2(CN)_2 + 6KCN \rightarrow 2K_3[Cu(CN)_4]$$

239. (a) HgS does not dissolved in hot dilute HNO_3.

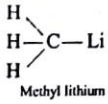
240. (b) The green colour is due to Cr_2O_3

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} \underset{\text{Green}}{Cr_2O_3} + N_2 + 4H_2O$$

241. (b) CuF_2 is coloured because it contains unpaired valence *d* electron.

$$Cu^{2+} = 1s^2 2s^2, 2p^6, 3s^2 3p^6 3d^9$$

242. (d) Organometallic compounds are those compounds in which metal atom is directly bonded with C-atom



Methyl lithium

243. (c) $_{27}Co^{2+} = 2, 8, 15$

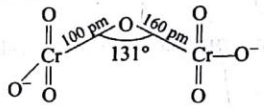
$3s^2, 3p^6, 3d^7$ ⇅ ⇅ 1 1 1

It is paramagnetic and coloured due to presence of unpaired electrons.

244. (d) Cupric chloride

$$CuCl_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{CuS} + 2HCl$$

245. (b) In the dichromate dianions, 6 Cr — O bonds are equivalent



Due to resonace, six Cr — O bonds are equivalent, two bridged Cr — O bonds are equivalent.

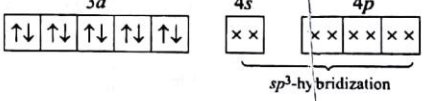
246. (c) Both the complexes have tetrahedral shape and sp^3 hybridisation.

In $Ni(CO)_4$ O.N. of Ni = 0

$Ni = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8, 4s^2$

CO is strong field ligand and thus unpaired electrons in *d*-orbital are paired. Therefore,

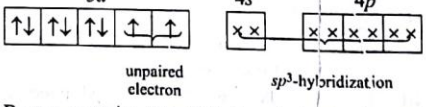
In excitation $Ni = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$



In $Ni(PPh_3)_2Cl_2$, O.N. of Ni = + 2

(Its coordination number = 4)

$Ni^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8$



247. (a) Bones contain $Ca_3(PO_4)_2$. Animal charcoal is obtained from bone ash.

248. (b) SbF_5 has strongest tendency to accept lone pair of electron.

$$SbF_5 + F^- \longrightarrow [SbF_6]^-$$

249. (b) Co exist as Co^{3+}. Since μ = 4.5 B.M.

$\therefore 4.5 = \sqrt{n(n+2)}$

$\therefore n = 4$ *i.e.*, number of unpaired electron = 4.

$_{27}Co^{3+}: 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$

250. (c) It is a fact.

251. (b) Cr in $[Cr(en)_3]^{2+}$ is low spin complex having d^4 configuration of Cr^{2+} ion.

252. (a) MnO_4^{2-} ion is green in colour.

PREVIOUS YEAR OBJECTIVE PROBLEMS (One Answer Correct)

1. The chemical process in the production of steel from haematite ore involves: **(IIT 2000)**
   (a) reduction
   (b) oxidation
   (c) reduction followed by oxidation
   (d) oxidation followed by reduction

2. Electrolyte reduction of alumina to aluminium by Hall-Heroult process is carried out: **(IIT 2000)**
   (a) in the presence of NaCl
   (b) in the presence of fluorite
   (c) in the presence of cryolite which forms a melt with lowers melting temperature
   (d) in the presence of cryolite which forms a melt with higher melting temperature

3. Ammonia can be dried by: **(IIT 2000)**
   (a) conc. H_2SO_4 (b) P_4O_{10}
   (c) CaO (d) anhydrous $CaCl_2$

4. The correct order of acidic nature is: **(IIT 2000)**
   (a) $Cl_2O_7 > SO_2 > P_4O_{10}$
   (b) $CO_2 > N_2O_5 > SO_3$
   (c) $Na_2O > MgO > Al_2O_3$
   (d) $K_2O > CaO > MgO$

5. The number of P — O — P bonds in cyclic meta phosphoric acid is: **(IIT 2000)**
   (a) zero (b) two
   (c) three (d) four

6. The number of S — S bonds in trimer of sulphur trioxide (S_3O_9) is: **(IIT 2001)**
   (a) 3 (b) 2
   (c) 1 (d) 0

7. The chemical composition of slag formed during melting process in the extraction of Cu is: **(IIT 2001)**
   (a) $Cu_2O + FeS$ (b) $FeSiO_3$
   (c) $CuFeS_2$ (d) $Cu_2S + FeO$

8. The complex ion which has no '*d*' electron in the central metal atom is: **(IIT 2001)**
   (a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$
   (c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

9. Which process is used in the extractive metallurgy of Mg? **(IIT 2002)**
   (a) Fused salt electrolysis
   (b) Self reduction
   (c) Aqueous solution electrolysis
   (d) Thermite reduction

10. Polyphosphates are used as water softening agents because they: **(IIT 2002)**
    (a) form soluble complexes with anionic species
    (b) precipitate anionic species
    (c) form soluble complexes with cationic species
    (d) precipitate cationic species

11. Anhydrous ferric chloride is prepared by: **(IIT 2002)**
    (a) heating hydrated ferric chloride at a high temperature in a stream of air
    (b) heating metallic iron in a stream of dry chlorine gas
    (c) reactions of ferric oxide with $HCl_{(aq.)}$
    (d) reaction of metallic iron with $HCl_{(aq.)}$

12. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a: **(IIT 2002)**
    (a) Hg_2^{2+} salt (b) Cu^{2+} salt
    (c) Ag^+ salt (d) Pb^{2+} salt

13. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium: **(IIT 2002)**
    (a) $CuS > ZnS > Na_2S$ (b) $ZnS > Na_2S > CuS$
    (c) $Na_2S > CuS > ZnS$ (d) $Na_2S > ZnS > CuS$

14. A gas '*X*' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas '*Y*'. Identify '*X*' and '*Y*': **(IIT 2002)**
    (a) $X = CO_2, Y = Cl_2$ (b) $X = Cl_2, Y = CO_2$
    (c) $X = Cl_2, Y = H_2$ (d) $X = H_2, Y = Cl_2$

15. $(Me)_2SiCl_2$ on hydrolysis produces: **(IIT 2003)**
    (a) $(Me)_2Si(OH)_2$
    (b) $(Me)_2Si = 0$
    (c) $+O-(Me)_2Si-O+_n$
    (d) $Me_2SiCl(OH)$

16. When MnO_2 is fused with KOH, a coloured compound is formed. The product and its colour is: **(IIT 2003)**
    (a) K_2MnO_4, purple (b) $KMnO_4$, purple
    (c) Mn_2O_3, brown (d) Mn_3O_4, black

17. Between H_3PO_3 and H_3PO_4: **(IIT 2003)**
    (a) H_3PO_3—reductant and monobasic acid
    (b) H_3PO_3—reductant and dibasic acid
    (c) H_3PO_4—not reductant and monobasic acid
    (d) H_3PO_4—reductant and tribasic acid

18. Roasted gold ore $+CN^- + H_2O \xrightarrow{O_2} [X] + OH^- [X] + Zn \longrightarrow [Y] + Au[X]$ and $[Y]$ are: **(IIT 2003)**
    (a) $X = [Au(CN)_2]^-$; $Y = [Zn(CN)_4]^{2-}$
    (b) $X = [Au(CN)_4]^{3-}$; $Y = [Zn(CN)_4]^{2-}$
    (c) $X = [Au(CN)_2]^-$; $Y = [Zn(CN)_6]^{4-}$
    (d) $X = [Au(CN)_4]^{3-}$; $Y = [Zn(CN)_6]^{2-}$

19. Mixture X of 0.02 mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 litre of solution:
1 litre of mixture X + Excess of $AgNO_3 \rightarrow Y$
1 litre of mixture X + Excess of $BaCl_2 \rightarrow Z$
Number of mole of Y and Z respectively are: **(IIT 2003)**
(a) 0.01, 0.01 (b) 0.02, 0.01
(c) 0.01, 0.02 (d) 0.02, 0.02

20. $[X] + H_2SO_4 \longrightarrow [Y]$ a colourless gas with irritating smell, $[Y] = K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ Green solution, $[X]$ and $[Y]$ are: **(IIT 2003)**
(a) SO_3^{2-}, SO_2 (b) Cl^-, HCl
(c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2

21. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-13}, 10^{-18}, 10^{-24} and 10^{-53} respectively, which one will precipitate first: **(IIT 2003)**
(a) FeS (b) MgS
(c) HgS (d) ZnS

22. By which process Pd and Sn are extracted respectively by? **(IIT 2004)**
(a) carbon reduction : self reduction
(b) self reduction : carbon reduction
(c) electrolytic reduction : cyanide process
(d) cyanide process : electrolyte reduction

23. A sodium salt on treatment with $MgCl_2$ gives white precipitate only on heating. The anion of sodium salt is: **(IIT 2004)**
(a) HCO_3^- (b) CO_3^{2-}
(c) NO_3^- (d) SO_4^{2-}

24. The species having tetrahedral shape is: **(IIT 2004)**
(a) $[PdCl_4]^{2-}$ (b) $[Ni(CN)_4]^{2-}$
(c) $[Pb(CN)_4]^{2-}$ (d) $[NiCl_4]^{2-}$

25. The spin magnetic moment of cobalt in $Hg[Co(SCN)_4]$ is: **(IIT 2004)**
(a) $\sqrt{3}$ (b) $\sqrt{8}$
(c) $\sqrt{15}$ (d) $\sqrt{24}$

26. $(NH_4)_2Cr_2O_7$ on heating gives a gas which is also given by: **(IIT 2004)**
(a) heating NH_4NO_2 (b) heating NH_4NO_3
(c) $Mg_3N_2 + H_2$ (d) $Na + H_2O_2$

27. The acid having O — O bond is: **(IIT 2004)**
(a) $H_2S_2O_3$ (b) $H_2S_2O_8$
(c) $H_2S_2O_6$ (d) $H_2S_4O_6$

28. The product of oxidation of I^- with MnO_4^- in alkaline medium is: **(IIT 2004)**
(a) IO_3^- (b) I_2
(c) IO^- (d) IO_4^-

29. Which ore contains both iron and copper? **(IIT 2005)**
(a) Cuprite (b) Chalcocite
(c) Chalcopyrite (d) Malachite

30. Which pair of compounds is expected to show similar colour in aqueous solution? **(IIT 2005)**
(a) $FeCl_2, CuCl_2$ (b) $VOCl_2, CuCl_2$
(c) $VOCl_2, FeCl_2$ (d) $FeCl_2, MnCl_2$

31. Which kind of isomerism is exhibited by octahedral $[Co(NH_3)_4Br_2]Cl$? **(IIT 2005)**
(a) Geometrical and ionization
(b) Geometrical and optical
(c) Optical and ionization
(d) Geometrical only

32. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI converts into orange colour solution. The cation of metal nitrate is: **(IIT 2005)**
(a) Hg^{2+} (b) Bi^{3+}
(c) Pb^{2+} (d) Cu^+

33. When PbO_2 reacts with conc. HNO_3, the gas evolved is: **(IIT 2005)**
(a) NO_2 (b) O_2
(c) N_2 (d) N_2O

34. Name of the structure of silicate in which three oxygen atoms of $[SiO_4]^{4-}$ are shared: **(IIT 2005)**
(a) Pyrosilicate
(b) Sheet silicate
(c) Linear chain silicate
(d) Three dimensional silicates

35. The most thermodynamically stable allotropic form of phosphorus is: **(IIT 2005)**
(a) red (b) white
(c) black (d) yellow

36. Which blue liquid is obtained on reacting equimolar amounts of NO and NO_2 gases at $-30°C$? **(IIT 2005)**
(a) N_2O (b) N_2O_3
(c) N_2O_4 (d) N_2O_5

37. Which of the following is not oxidised by O_3? **(IIT 2005)**
(a) KI (b) $FeSO_4$
(c) $KMnO_4$ (d) K_2MnO_4

38. How the reaction below can be made to proceed in forward direction?
$B(OH)_3 + NaOH \longrightarrow [NaB(OH)_4]$
or $[NaBO_2 + H_2O]$ **(IIT 2006)**
(a) Addition of *cis*-1, 2-diol
(b) Addition of borax
(c) Addition of *trans*-1,2-diol
(d) Addition of Na_2HPO_4

39. A solution is when diluted with H_2O and boiled a white precipitate is obtained. On addition of excess NH_4Cl / NH_4OH, the volume of precipitate decreases

leaving behind a gelatinous precipitate. The precipitate is: **(IIT 2006)**

(a) $Zn(OH)_2$ (b) $Al(OH)_3$
(c) $Mg(OH)_2$ (d) $Ca(OH)_2$

40. If the bond length of C — O in carbon monoxide is 1.128 Å, the bond length of C — O in $Fe(CO)_5$ is: **(IIT 2006)**

(a) 1.15 Å (b) 1.128 Å
(c) 1.72 Å (d) 1.118 Å

41. The species present in solution when CO_2 is dissolved in water are: **(IIT 2006)**

(a) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$
(b) H_2CO_3, CO_3^{2-}
(c) CO_3^{2-}, HCO_3^-
(d) CO_2, H_2CO_3

42. $CuSO_4$ decolourises on addition of KCN. The product is: **(IIT 2006)**

(a) $[Cu(CN)_4]^{2-}$
(b) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$
(c) $Cu(CN)_2$
(d) CuCN

43. $MgSO_4$ on reaction with NH_4OH and Na_2HPO_4 forms a white ppt. It is: **(IIT 2006)**

(a) $Mg(NH_4)PO_4$ (b) $Mg_3(PO_4)_2$
(c) $MgCl_2 \cdot MgSO_4$ (d) $MgSO_4$

44. Among the following, the paramagnetic compound is: **(IIT 2007)**

(a) Na_2O_2 (b) O_3
(c) N_2O (d) KO_2

45. The species having bond order different than CO is: **(IIT 2007)**

(a) NO^- (b) NO^+
(c) CN^- (d) N_2

46. Extraction of zinc from zinc blende is achieved by: **(IIT 2007)**

(a) electrolytic reduction
(b) roasting followed by reduction with carbon
(c) roasting followed by reduction with another metal
(d) roasting followed by self reduction

47. The percentage of *p*-character in the orbitals forming P—P bonds in P_4 is: **(IIT 2007)**

(a) 25 (b) 33
(c) 50 (d) 75

48. Among the following metal carbonyls, the C—O bond order is lowest in: **(IIT 2007)**

(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$
(c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$

49. A solution of metal ion when treated with KI gives a red ppt. which dissolves in excess KI to give a colourless solution. Moreover, the metal ion on treatment with a solution of cobalt (II) this cyanate gives rise to deep blue crystalline ppt. The metal ion is: **(IIT 2007)**

(a) Pb^{2+} (b) Hg^{2+}
(c) Cu^{2+} (d) Co^{2+}

50. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in presence of: **(IIT 2008)**

(a) nitrogen (b) oxygen
(c) CO_2 (d) Ar

51. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives: **(IIT 2008)**

(a) $Na_2S_4O_6$ (b) $NaHSO_4$
(c) NaCl (d) NaOH

52. Among the following, the coloured compound is: **(IIT 2008)**

(a) CuCl (b) $K_3C_4(CN)_4$
(c) CuF_2 (d) $[Cu(CH_3CN)_4]BF_3$

53. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is: **(IIT 2008)**

(a) Tetrachloronickel (II)-tetraamminenickel (II)
(b) Tetraamminenickel (II)-tetrachloronickel (II)
(c) Tetraamminenickel (II)-tetrachloronickelate (II)
(d) Tetrachloronickel (II)-tetraamminenickelate (O)

54. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridization of nickel in the compounds respectively are: **(IIT 2008)**

(a) sp^3, sp^3 (b) sp^3, dsp^2
(c) dsp^2, sp^3 (d) dsp^2, dsp^2

55. The co-ordination number of Al in crystalline state of $AlCl_3$ is: **(IIT 2009)**

(a) 2 (b) 4
(c) 6 (d) 8

56. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is: **(IIT 2009)**

(a) 0 (b) 2.84
(c) 4.90 (d) 5.92

57. The reaction of P_4 with *X* leads selectively to P_4O_6. The *X* is: **(IIT 2009)**

(a) Dry O_2
(b) A mixture of O_2 and N_2
(c) Moist O_2
(d) O_2 in the presence of aqueous NaOH

58. The number of water molecule(s) directly bonded to the metal centre in $CuSO_4 \cdot 5H_2O$ is: **(IIT 2009)**

(a) 5 (b) 4
(c) 1 (d) 3

59. The complex showing a spin only magnetic moment of 2.82 BM is: **(IIT 2010)**

(a) $Ni(CO)_4$ (b) $[NiCl_4]^{2-}$
(c) $Ni(PPh_3)_4$ (d) $[Ni(CN)]_4^{2-}$

60. The ionisation isomer of $[Cr(H_2O)_4ClNO_2]Cl$ is: **(IIT 2010)**

(a) $[Cr(H_2O)_4NO_2]Cl_2$
(b) $[Cr(H_2O)_6Cl_2]NO_2$
(c) $[Cr(H_2O)_4Cl(ONO)]Cl$
(d) $[Cr(H_2O)_3Cl_2NO_2]H_2O$

61. Extra pure N_2 can be obtained by heating : **(IIT 2011)**
(a) NH_3 with CuO (b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

62. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O respectively are : **(IIT 2011)**
(a) Octahedral, tetrahedral and squareplanar
(b) Tetrahedral, squareplanar and octahedral
(c) Squareplanar, tetrahedral and octahedral
(d) Octahedral, squareplanar and octahedral

63. Oxidation state of the metal in the mineral haematite and magnetite respectively are : **(IIT 2011)**
(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite

64. Among the following complexes **(K-P)**, $K_3[Fe(CN)_6]$**(K)**, $[Co(NH_3)_6]Cl_3$**(L)**, $Na_3[Co(oxalate)_3]$**(M)**, $[Ni(H_2O)_6]Cl_2$**(N)**, $K_2[Pt(CN)_4]$**(O)**, and $[Zn(H_2O)_6](NO_3)_2$**(P)** the diamagnetic complexes are : **(IIT 2011)**
(a) K, L, M, N (b) K, M, O, P
(c) L, M, O, P (d) L, M, N, O

65. Passing H_2S gas into a mixture of $Mn^{2+}, Ni^{2+}, Cu^{2+}$ and Hg^{2+} ions in an acidified aqueous solution precipitates : **(IIT 2011)**
(a) CuS and HgS (b) MnS and CuS
(c) MnS and NiS (d) NiS and HgS

66. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is : **(IIT 2012)**
(a) Tetraaquadiaminecobalt (III) chloride
(b) Tetraaquadiamminecobalt (III) chloride
(c) Diaminetetraaquacobalt (III) chloride
(d) Diamminetetraaquacobalt (III) chloride

67. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are : **(IIT 2012)**
(a) O_2 and CO respectively
(b) O_2 and Zn dust respectively
(c) HNO_3 and Zn dust respectively
(d) HNO_3 and CO respectively

68. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively : **(IIT 2012)**
(a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

69. The colour of light absorbed by an aqueous solution of $CuSO_4$ is : **(IIT 2012)**
(a) orange-red (b) blue-green
(c) yellow (d) violet

70. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was : **[JEE (Main) 2013]**
(a) Ammonia (b) Phosgene
(c) Methylisocyanate (d) Methylamine

71. Which of the following complex species is not expected to exhibit optical isomerism ? **[JEE (Main) 2013]**
(a) $[Co(NH_3)_3Cl_3]$ (b) $[Co(en)(NH_3)_2Cl_2]^+$
(c) $[Co(en)_3]^{3+}$ (d) $[Co(en)_2Cl_2]^+$

72. Which of the following is the wrong statement ? **[JEE (Main) 2013]**
(a) Ozone is violet-black in solid state.
(b) Ozone is diamagnetic gas.
(c) $\overset{\gamma}{O}\overset{\gamma}{N}\overset{\gamma}{Cl}$ and $\overset{\gamma}{O}\overset{\gamma}{N}\overset{\gamma}{O}^-$ are not isoelectronic.
(d) O_3 molecule is bent

73. Which of the following arrangements does not represent the correct order of the property stated against it ? **[JEE (Main) 2013]**
(a) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(b) $Sc < Ti < Cr < Mn$: number of oxidation states
(c) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
(d) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size

74. Consider the following complex ions, P, Q and R. $P = [FeF_6]^{3-}, Q = [V(H_2O)_6]^{2+}$ and $R = [Fe(H_2O)_6]^{2+}$, the correct order of the complex ions, according to their spin only magnetic moment values (in B.M.) is : **[JEE (Advanced) I 2013]**
(a) $R < Q < P$ (b) $Q < R < P$
(c) $R < P < Q$ (d) $Q < P < R$

75. Sulphide ores are common for the metals : **[JEE (Advanced) I 2013]**
(a) Ag, Cu and Pb (b) Ag, Cu and Sn
(c) Ag, Mg and Pb (d) Al, Cu and Pb

76. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of : **[JEE (Advanced) I 2013]**
(a) NO (b) NO_2
(c) N_2O (d) N_2O_4

77. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulphide is : **[JEE (Advanced) I 2013]**
(a) Fe(III) (b) Al(III)
(c) Mg(II) (d) Zn(II)

PREVIOUS YEAR OBJECTIVE PROBLEMS SOLUTION

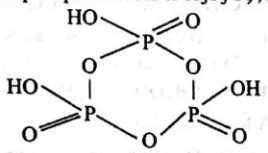
1. (d) Haematite (Fe_2O_3) having little FeO is first oxidised to Fe_2O_3 and then reduced to Fe by CO.

2. (c) Cryolite is added to lower the m. pt. of alumina as well as to make it a good conductor of current.

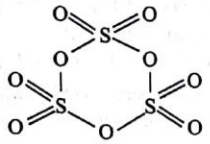
3. (c) Rest all react with NH_3.

4. (a) Acidic character of non-metal oxides increases along the period.

5. (c) Cyclic metaphosphoric acid is $H_3P_3O_9$, *i.e.*,



6. (d) Trimer of SO_3 (S_3O_9) is:



7. (b) The non-fusible mass (basic gangue) FeO is removed by acidic flux SiO_2 in the form of slag $FeSiO_3$.

8. (a) Co^{3+}, Fe^{3+} and Cr^{3+} have 6, 5 and 3 '*d*' electrons respectively.

9. (a) Highly electropositive metals (*e.g.*, alkali metals, alkaline earth metals and aluminium metals) are extracted by the electrolysis of their fused salts. In aqueous state H^+ is discharged.

Anode $\underset{\text{(fused)}}{Mg^{2+}} + 2e \longrightarrow Mg$

10. (a) $Na_2[Na_4(PO_3)_6] + 2Ca^{2+} \longrightarrow 4Na^+ + \underset{\text{Soluble}}{Na_2[Ca_2(PO_3)_6]}$

Ca^{2+} ions are removed from water by reacting with anionic species $Na_4[(PO_3)_6]^2$

11. (b) $2Fe + 3Cl_2 \longrightarrow 2FeCl_3$. In (c) and (d) hydrated ferric chloride ($FeCl_3 \cdot 6H_2O$) is formed.

12. (d) $PbCl_2$ is soluble in hot water but insoluble in cold water.

$$Pb^{2+} + 2HCl \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{soluble on}\\ \text{heating}}}{PbCl_2\downarrow} \longrightarrow \underset{\text{Black ppt.}}{PbS}$$

13. (d) The K_{sp} value of CuS is less than ZnS and thus ZnS is more soluble. Also sodium salts are highly soluble in water.

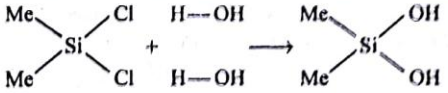
14. (c)

$$\underset{(X)}{Cl_2} + H_2O \longrightarrow HOCl + HCl$$

$$AgNO_3 + HCl \longrightarrow \underset{\text{White ppt.}}{AgCl} + HNO_3$$

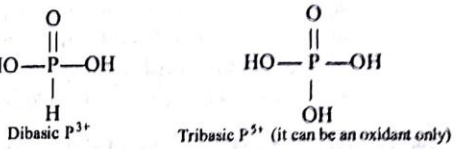
$$Mg + 2HCl \longrightarrow MgCl_2 + \underset{(Y)}{H_2}\uparrow$$

15. (a)



16. (a) $2MnO_2 + 2KOH + O_2 \longrightarrow \underset{\text{Purple}}{2K_2MnO_4} + 2H_2O$

17. (b)



Dibasic P^{3+} Tribasic P^{5+} (it can be an oxidant only)

18. (a) $2Au + 4CN^- + H_2O + \frac{1}{2}O_2 \longrightarrow 2[Au(CN)_2]^- + 2OH^-$

$$2[Au(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Au$$

19. (a) Only primary valencies are ionised. Also normality of each salt = 0.01 *M*

$$[Co(NH_3)_5Br]SO_4 \xrightarrow{BaCl_2} [Co(NH_3)_5Br]^{2+}, BaSO_4$$

$$[Co(NH_3)_5SO_4]Br \xrightarrow{AgNO_3} [Co(NH_3)_5SO_4] + AgBr$$

The mole ratio of complex : *X* or *Y* is 1 : 1.

20. (a) $SO_3^{2-} + H_2SO_4 \longrightarrow \underset{\substack{\text{Burning sulphur smell}\\ \text{(irritating)}}}{SO_2} + SO_4^{2-} + H_2O$

or $S^2 + H_2SO_4 \longrightarrow H_2S + SO_4^{2-}$ Rotten egg smell

SO_2 turns $K_2Cr_2O_7$ solution in acidic medium green.

$$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

21. (c) $[S^{2-}]$ needed for precipitation of

$$MnS = \frac{10^{-13}}{10^{-3}} = 10^{-10}\ M$$

$$FeS = \frac{10^{-18}}{10^{-3}} = 10^{-15}\ M$$

$$ZnS = \frac{10^{-24}}{10^{-3}} = 10^{-21}\ M$$

$$HgS = \frac{10^{-53}}{10^{-3}} = 10^{-50}\ M$$

Thus, minimum $[S^{2-}]$ is for HgS and so it will be precipitated first.

22. (b)

$$\left.\begin{aligned} 2PbS + 3O_2 &\longrightarrow 2PbO + 2SO_2\\ 2PbO + PbS &\longrightarrow 3Pb + SO_2 \end{aligned}\right\} \text{Self reduction}$$

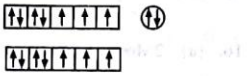
$$SnO_2 + 2C \xrightarrow{\Delta} \underset{\text{Carbon reduction}}{Sn + 2CO_2}\uparrow$$

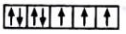
23. (a) $2NaHCO_3 + MgCl_2 \xrightarrow{\Delta} \underset{\text{Insoluble}}{MgCO_3} + 2NaCl + H_2O + CO_2$

24. (d) The magnetic moment of $[NiCl_4]^{2-}$ seveals that the species is paramagnetic having two unpaired electrons,

i.e., Ni^{2+} is $3d^8$. The four electron pairs by Cl^- ligand lead to sp^3-hybridisation in Ni^{2+} and do not disturb Ni^{2+} configuration to give tetrahedral geometry.

25. (c) In $Hg[Co(SCN)_4]$, Co exists as Co^{2+}

$_{27}Co : 3d^7, 4s^2$ or 

$_{27}Co^{2+} : 3d^7$ or 

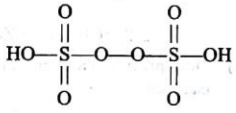
SCN^- ligand provides four electron pairs to show sp^3-hybridisation in $[Co(SCN)_4]^{2-}$ and thus three unpaired electrons exist on Co^{2+}.

Magnetic moment $= \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15}$

26. (a) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

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

27. (b) $H_2S_2O_8$ is:

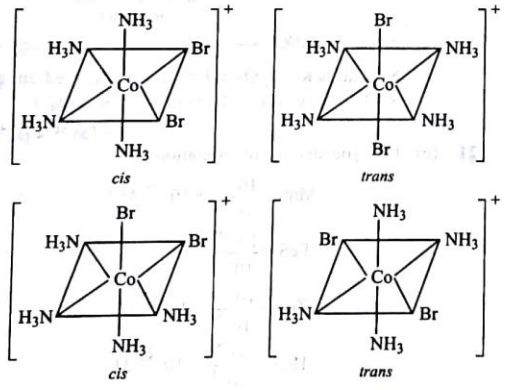


28. (a) $2MnO_4^- + I^- + H_2O \rightarrow 2MnO_2 + IO_3^- + 2OH^-$

29. (c) Cuprite (Cu_2O), chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and malachite $[Cu(OH)_2 \cdot CuCO_3]$.

30. (a) $FeCl_2$ and $CuCl_2$ are green.

31. (a)



cis *trans*

cis *trans*

32. (b) $Bi(NO_3)_{3\,(aq.)} + 3KI_{(aq.)} \longrightarrow BiI_{3(s)} + 3KNO_{3(aq.)}$

$BiI_3 + KI \longrightarrow \underset{\text{Soluble}}{K[BI_4]}$

33. (b) $PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2$

34. (b) Two dimensional sheet structures are formed when three oxygen atoms of each $[SiO_4]^{4-}$ tetrahedral are shared.

35. (c) $\Delta G = 0$ for white P assumed arbitrarily, but most stable form is black P.

36. (b) $NO + NO_2 \longrightarrow N_2O_3$ (blue liquid)

37. (c) Mn in $KMnO_4$ is already in highest oxidation state, *i.e.*, Mn^{7+}.

38. (a) Due to formation of chelated complex, the reaction proceeds in forward direction.

39. (a) Due to the formation of $[Zn(NH_3)_4]^{2+}$.

40. (a) Due to synergic bond formation between metal and CO, the bond order of CO decreases a little.

41. (a) $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

42. (b) $CuSO_4 + KCN \longrightarrow Cu(CN)_2$

$2Cu(CN)_2 \longrightarrow CuCN + (CN)_2$

$3KCN + CuCN \longrightarrow K_3Cu(CN)_4$

43. (a) $Mg^{2+} + NH_4OH + Na_2HPO_4 \longrightarrow Mg(NH_4)PO_4$ (A test of Mg^{2+})

44. (d) KO_2 has O_2^- ion having one unpaired electron.

45. (a) Bond order of CO is 3 and of NO^- is 2.0.

46. (b) ZnO is reduced by carbon.

47. (d) P_4 has sp^3-hybridisation and thus has 75% *p*-character.

48. (d) The carbon metal bond in carbonyls is due to donation of electron pair from C-atom of CO [$:\overset{\cdot\cdot}{C}::\overset{\cdot\cdot}{O}:$], *i.e.*, $M \leftarrow C \equiv O$. The lone pair of electrons of *d*-orbitals left on metal involves back bonding where the metal donates electron pair to empty antibonding orbitals of CO thus forming a π ($M \rightarrow C$) bond. The total bonding with metal is thus $M = C = O$. The partial filling of the antibonding orbitals on C reduces the bond order of C—O bond. The negative charge density on V-atom favours easy donation of an electron pair.

49. (b) $Hg^{2+} + 2I^- \longrightarrow HgI_2$ (scarlet red ppt.)

$HgI_2 + \underset{\text{Excess}}{2I^-} \longrightarrow [HgI_4]^{2-}$ (soluble)

$Hg^{2+} + Co(SCN)_2 \longrightarrow \underset{\text{deep blue ppt.}}{Co[Hg(SCN)_4]}$

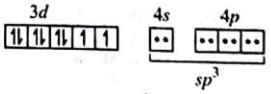
50. (b) $4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$

51. (b) $Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$

52. (c) CuF_2 is blue coloured crystalline solid.

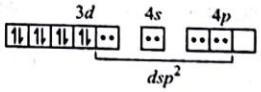
53. (c) Follow IUPAC rules.

54. (b) Ni in $[Ni(CO)_4]$: $...3s^2, 3p^6, 3d^8 4s^2$



sp^3

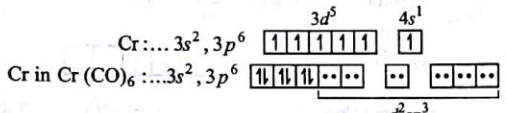
Ni in $[Ni(CN)_4]^{2-}$: $...3s^2, 3p^6, 3d^8 4s^2$



dsp^2

55. (b) $AlCl_3(Al_2Cl_6)$ in solid state has co-ordination number four.

56. (a) CO is strong ligand and thus, Cr possesses no unpaired electron.

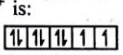


57. (b) $P_4 + \underset{\text{(from air)}}{3O_2} \longrightarrow P_4O_6$

A rapid stream of air (not pure O_2) is passed over phosphorus sticks. N_2 present in air retards further oxidation of P_4O_6 to P_4O_{10}.

58. (b) $[Cu(H_2O)_4]\cdot SO_4H_2O$ Co-ordination no. of Cu is four.

59. (b) Cl is weak ligand and thus, Ni^{2+} is:

Ni^{2+} :[Ar] 

No. of unpaired electron = 2

$\mu = \sqrt{n(n+2)} = \sqrt{8} = 2.82$ B.M.

60. (b) Cl^- is replaced by NO_2^- in ionisation sphere.

61. (d) Except NH_4NO_3 rest all gives N_2 but extra pure N_2 can be obtained by heating $Ba(N_3)_2$.

$$2NH_3 + 3CuO \xrightarrow{\Delta} N_2 + 3Cu + 3H_2O$$

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$$

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

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

62. (b) Ni^{2+} forms $[NiCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$ and $[Ni(H_2O)_6]^{2+}$ complexes.

Ni^{2+} has $3d^8$ configuration, *i.e.,* two unpaired electrons.

In $[NiCl_4]^{2-}$, Cl^- being weak field ligand and thus complex with sp^3-hybridisation has tetrahedral geometry.

In $[Ni(CN)_4]^{2-}$, CN^- being strong field ligand and thus all the eight electrons are paired to give dsp^2 hybridisation leading to square planar geometry.

In $[Ni(H_2O)_6]^{2+}$, H_2O being weak field ligand and thus complex with sp^3d^2 (outer) hybridisation leads to octahedral geometry.

63. (d) **Haematite :** Fe_2O_3; oxidation number of Fe is +3.

Magnetite : Fe_3O_4 or $FeO\cdot Fe_2O_3$; oxidation number of Fe are +2 (in FeO) and +3 in (Fe_2O_3).

64. (c) **[K]** : $K_3[Fe(CN)_6]$: Fe^{3+} has $3d^5$ configuration; CN^- is strong field ligand and thus four electrons are paired leaving one unpaired electron with d^2sp^3 hybridisation and thus **paramagnetic.**

[L] : $[Co(NH_3)_6]Cl_3$: Co^{3+} has $3d^6$ configuration; NH_3 is strong field ligand and thus all the six electrons are paired with d^2sp^3-hybridisation and therefore **diamagnetic.**

[M] : $Na_3[Co(ox)_3]$; Co^{3+} has $3d^6$ configuration; $C_2O_4^{2-}$ is strong field ligand and thus all the six electrons are paired with d^2sp^3-hybridisation and therefore **diamagnetic.**

[N]: $[Ni(H_2O)_6]Cl_2$: Ni^{2+} has $3d^8$ configuration with two unpaired electrons. H_2O is weak field ligand and thus sp^3d^2-hybridisation and **paramagnetic.**

[O] : $K_2[Pt(CN)_4]$: Pt^{2+} has $3d^8$ configuration; CN^- is strong field ligand and thus all the eight electrons are paired with dsp^2-hybridisation and therefore **diamagnetic.**

[P] : $[Zn(H_2O)_6](NO_2)_2$: Zn^{2+} has $3d^{10}$ configuration and thus all are paired showing sp^2d^2 hybridisation and so **diamagnetic.**

65. (a) In presence of HCl, dissociation of H_2S is suppressed (common ion effect) and thus $[S^{2-}]$ ions present in solution are less. K_{sp} of CuS and HgS being low and thus the product of ionic concentrations of $[Cu^{2+}][S^{2-}]$ and $[Hg^{2+}][S^{2-}]$ becomes more than their respective K_{sp}. Thus only CuS and HgS are precipitated. MnS and NiS can be precipitated in presence of higher $[S^{2-}]$, *i.e.,* in alkaline medium.

66. (d) Follow IUPAC rules for complex compounds

$[Co(H_2O)_4(NH_3)_2]Cl_3$

Diamminetetraaquacobalt (III) chloride.

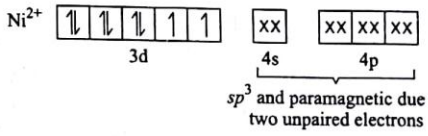
67. (b) The reactions involved in cyanide extraction process are:

$$\underset{\text{(argentite ore)}}{Ag_2S} + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

$$4Na_2S + \underset{\text{(oxidising agent)}}{5[O_2]} + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

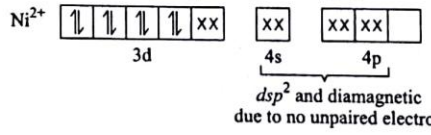
$$2Na[Ag(CN)_2] + \underset{\text{(reducing agent)}}{Zn} \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

68. (c) Ni exists as Ni^{2+} in the complex when paramagnetic showing sp^3 (tetrahedral) hybridization



xx represents electron pair donated in form of pair by the ligands

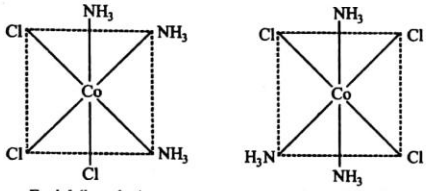
Ni exists as Ni^{2+} in the complex when diamagnetic showing dsp^2 (square planar geometry) hybridization.



69. (a) Aqueous solution of copper sulphate absorbs orange red light and shows complementary colour *i.e.*, blue-green.

70. (c) $CH_3—N=C=O$ (methyl isocyanate) was leaked.

71. (a) $[Co(NH_3)_3Cl_3]$ is MA_3B_3 type and show fac and mer isomers and not optical isomerism.



Facial (inactive) Merdonial (inactive)

72. (c) ONCl has 32 electrons whereas O NO^- has 24 electrons.

73. (c) Sc^{3+} is most stable due to noble gas configuration
Fe^{3+} is more stable due to half filled nature

Mn shows	+7,+6,+5,+4,+3,+2, states
Cr shows	+6,+5,+4,+3,+2,+1, states
Ti shows	+4,+3,+2,
Se shows	+3,+2,

V^{2+}, Cr^{2+}, Mn^{2+} and Fe^{2+} have 3, 4, 5 and 4 unpaired electrons respectively and thus

$$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$$

Ionic size in Å :	Ni^{2+}	Co^{2+}	Fe^{2+}	Mn^{2+}
	0.72	0.74	0.76	0.80

74. (b) $[FeF_6]^{-3} \longrightarrow Fe^{+3} \longrightarrow d^5$ configuration,

(*P*)

F^- is weak field ligand | 1 | 1 | 1 | 1 | 1 |

unpaired electrons = 5; $\therefore \mu = \sqrt{5(5+2)} = 5.92$ B.M.

$[V(H_2O)_6]^{2+} \longrightarrow V^{+2} \longrightarrow d^3$ configuration,

(*R*)

H_2O is weak field ligand | 1 | 1 | 1 | | |

unpaired electron = 3; $\therefore \mu = \sqrt{3(3+2)} = 3.87$ B.M.

$[Fe(H_2O)_6]^{2+} \longrightarrow Fe^{+2} \longrightarrow d^6$ configuration,

(*Q*)

H_2O is weak field ligand | ⇅ | 1 | 1 | 1 | 1 |

unpaired electron = 4; $\therefore \mu = \sqrt{4(4+2)} = 4.90$ B.M.

Therefore only spin magnetic moment $(\mu) = \sqrt{n(n+2)}$ B.M. (n = unpaired electron)

So, μ of $P > R > Q$

75. (a) Metals having high polarising power (Z_{eff}) exist in ore with anions having high polarisibility
Ag, Cu, Pb → Sulphide ores ($Ag_2S, CuFeS_2, PbS$)
Sn → Oxide ore (SnO_2)
Mg → Sea water and dolomite ($CaCO_3, MgCO_3$)
Al → Oxide ore ($Al_2O_3 \cdot 2H_2O$)

76. (b) On standing, HNO_3 decomposes to liberate yellow colour gas NO_2 which dissolves in HNO_3 to impart brown colour to it.

$$HNO_3 \longrightarrow H_2O + NO_2 + 1/2\, O_2$$

77. (d) In analytical chemistry II group and IV group metals ions are precipitated in form of sulphides whereas III group metals (Fe, Al, Cr) are precipitated as hydroxides.
Fe (III) and Al (III) → III group
Zn (II) → IV group (precipitated as sulphide, ZnS)
Mg (II) → V group

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Which are correct for C_{60} form of carbon and other crystalline forms of carbon like C_{50}.
   (a) It is a crystalline state of carbon
   (b) It has 20 hexagons and 12 pentagons having a truncated icosahedron (soccer ball) structure
   (c) It is known as buckminsterfullerene
   (d) Other crystalline forms of C such as C_{50}, etc., have also been discovered
2. Which are correct for the CNT form of carbon?
   (a) It is a crystalline state of carbon
   (b) It has 20 hexagons and 5 pentagons structure and is called carbon nanotube
   (c) It is 100 times stronger than steel
   (d) The size of carbon atoms in CNT ranges from 1 – 10 nm
3. Which of the following are correct statements?
   (a) A reaction between an oxidant and a reductant gives a compound of lower oxidation state if reductant is in excess
   (b) A reaction between an oxidant and a reductant gives a compound of higher oxidation state if oxidant is in excess
   (c) A reaction between an oxidant and a reductant gives a compound of lower oxidation state if oxidant is in excess
   (d) A reaction between an oxidant and a reductant gives a compound of higher oxidation state if reductant is in excess
4. Which of the following are amphoteric oxides?
   (a) Na_2O (b) BaO
   (c) Al_2O_3 (d) ZnO
5. Which of the following are acidic oxides?
   (a) CO_2 (b) P_2O_3
   (c) Mn_2O_7 (d) CrO_3
6. Select the neutral oxides:
   (a) H_2O (b) CO_2
   (c) NO (d) N_2O
7. Which of the followings are named after the names of planets and are radioactive?
   (a) Np (b) Pu
   (c) Po (d) Fr
8. Which properties are correctly matched?
   (a) Ionisation energy : $N > O$ and $N^+ < O^+$
   (b) Electron affinity : $N < O$ and $N^- < O^-$
   (c) Atomic radius : $Ne > F$ and $Al \simeq Ga$
   (d) Electron affinity : $Cl > F$ and $S > O$
9. In which bond angles are correctly matched?
   (a) $PI_3 > AsI_3 > SbI_3$
   (b) $NH_3 > PH_3 > AsH_3$
   (c) $PF_3 > PCl_3 < PBr_3 < PI_3$
   (d) $NO_2^+ > NO_2 > NO_2^-$
10. Which of the following statements are correct?
   (a) PF_3 acts as electron pair donor
   (b) Electron pair donor tendency of NF_3 is lesser than PF_3
   (c) SbF_3 acts as electron pair acceptor
   (d) $SbCl_3$ on dissolving in water gives $Sb(OH)_3$
11. Select the correct statements:
   (a) CO_2 and N_3^- are isoelectronic
   (b) CO_2 and N_3^- are isostructural
   (c) Both have bond order equal to two
   (d) Both have two σ and two π bonds and show *sp*-hybridisation
12. Which of the following in each has more polarising nature?
   (a) $Fe^{3+} > Fe^{2+}$ (b) $Mn^{2+} > Mn^{7+}$
   (c) $Sn^{4+} > Sn^{2+}$ (d) $V^{4+} > V^{3+}$
13. Which of the following do not give NH_3 on heating?
   (a) NH_4NO_3 (b) $(NH_4)_2Cr_2O_7$
   (c) NH_4Cl (d) $(NH_4)_2SO_4$
14. Shielding constant Ne is equal to 4.15. Which of the following have same shielding constant?
   (a) Na (b) Na^+
   (c) F (d) F^-
15. Select the correct statements:
   (a) All of the halogens are oxidised in O_2
   (b) $BiCl_5$ does not exist
   (c) Pb^{4+} salts are better oxidants than Ge^{4+} salts
   (d) EA_1 for Zn is +ve whereas for Cu it is –ve
16. Select the incorrect reactions:
   (a) $CH_3I + H_2O \longrightarrow CH_3OH + HI$
   (b) $CF_3I + H_2O \longrightarrow CF_3OH + HI$
   (c) $SbCl_3 + 3H_2O \longrightarrow Sb(OH)_3 + 3HCl$
   (d) $PCl_3 + 3H_2O \longrightarrow P(OH)_3 + 3HCl$
17. Select the correct reactions:
   (a) $SiO_2 + 2Mg \longrightarrow Si + 2MgO$
   (b) $Si + 2MgO \xrightarrow{1000°C} SiO_2 + 2Mg$
   (c) $SiO_2 + CaO \longrightarrow CaSiO_3$
   (d) $HgS + Fe \longrightarrow FeS + Hg$
18. Which are not used to prepare H_2 by the action over Zn?
   (a) Conc. H_2SO_4 (b) Conc. HCl
   (c) Dil. H_2SO_4 (d) HNO_3

19. Addition of which salt in substantial amount will cause hardness in water?
(a) $Th(NO_3)_4$ (b) $Ca(NO_3)_2$
(c) $Mg(NO_3)_2$ (d) $La(NO_3)_2$

20. Which of the following forms alums?
(a) Li^+ (b) Na^+
(c) Al^{3+} (d) Cr^{3+}

21. Select the correct reactions:
(a) $KF + BrF_3 \longrightarrow K[BrF_4]$
(b) $4KO_2 + 4CO_2 + 2H_2O \longrightarrow 4KHCO_3 + 3O_2$
(c) $2NaNO_3 \xrightarrow{500°C} 2NaNO_2 + O_2$
(d) $4NaNO_3 \xrightarrow{800°C} 2Na_2O + 5O_2 + 2N_2$

22. Which one are correctly represented?
(a) $Ag_2S_2O_3$—white (b) $Fe_2(S_2O_3)_3$—violet
(c) $Cu_2S_2O_3$—white (d) Ag_2S—white

23. Which are correct for the reaction $M^+ + Aq. \longrightarrow M^+_{(aq.)}$?
(a) $\Delta G = -$ ve (b) $\Delta H = -$ ve
(c) $\Delta S = -$ ve (d) $\Delta S = +$ ve

24. The metal bicarbonates which do not exist in solid state are:
(a) $LiHCO_3$ (b) $Ca(HCO_3)_2$
(c) $Zn(HCO_3)_2$ (d) $Ag(HCO_3)$

25. Which orders are correctly matched?
(a) Solubility in water : $BaF_2 < MgF_2 < BeF_2$
(b) Hydrolysis nature : $CaCl_2 < MgCl_2 < BeCl_2$
(c) Covalent nature : $CaCl_2 > MgCl_2 > BeCl_2$
(d) Lattice energy : $BaF_2 < CaF_2 < MgF_2$

26. An element (*A*) burns in N_2 to give ionic compound (*B*). Compound (*B*) reacts with water to give (*C*) and (*D*). Solution of (*C*) becomes milky on boiling CO_2. Element (*A*) may be:
(a) Ca (b) Mg
(c) Ba (d) Be

27. Which of the followings are pseudo alums?
(a) $MnSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(b) $FeSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(c) $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$
(d) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

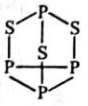
28. Select the correct statements about $B(OH)_3$:
(a) It is a weak Bronsted base
(b) It is a weak Lewis acid
(c) It's acidic nature increases in presence of diols
(d) It's basic nature increases in presence of diols

29. Which of the following are slippery solids?
(a) Boron nitride (b) Graphite
(c) Carborundum (d) Diamond

30. Which are correct about diborane structure?
(a) Boron is approximately sp^3-hybridised
(b) There are two terminal B—H bonds on each boron atom
(c) There are only 12 bonding electrons
(d) It has one 3 centred banana bond (3C—2*e* bond)

31. Select the correct statement about CO :
(a) It acts as Lewis acid in formation of carbonyls
(b) It is a neutral oxide of carbon
(c) It reacts with NaOH at high *P*, *T* to give HCOONa
(d) It acts as π acceptor by accepting electron from the central metal during complex formation

32. Which are correct about P_4S_3?
(a) P is trivalent and S is divalent
(b) It has structure
(c) Average oxidation number of P and S are +3/2 and –2 respectively
(d) It is used in match industry



33. Select the correct statements:
(a) NF_3 and NCl_3 are exothermic compounds
(b) NF_3 and NCl_3 are endothermic compounds
(c) NF_3 is exothermic compound
(d) NCl_3 is endothermic compound

34. Which of the following are known?
(a) SO_2F_2 (b) SO_2Cl_2
(c) SO_2FBr (d) SO_2I_2

35. Which are the characteristics of S_4N_4?
(a) It has two S—S weak bonds
(b) It is thermochromic
(c) It has a cage structure
(d) It detonates on shock, grinding or sudden heating

36. Cyclic trimer of SO_3 has:
(a) 4 (S = O) bonds (b) 3 (S—O—S) bonds
(c) one (S—S) bond (d) 6 (S—O) bonds

37. Which of the following halogen oxides are known?
(a) F_2O (b) Cl_2O_7
(c) Cl_2O_5 (d) I_2O_7

38. Which of the halogen acids have pK_a values –ve?
(a) HF (b) HCl
(c) HBr (d) HI

39. Which of the following are ionic compounds?
(a) $I(CH_3COO)_3$ (b) $I(IO_3)_3$
(c) IPO_4 (d) ICl_3

40. Which of the following are correctly matched?
(a) $XeOF_4$: sp^3d^2, square pyramidal
(b) $XeOF_2$: sp^3d, T-shaped
(c) XeO_3 : sp^3, Trigonal pyramid
(d) XeO_2F_2 : sp^3d, See-saw

41. Which of the following are correct for liquid He?
(a) He (liq.) exists in two forms He (I) and He (II)
(b) He (II) is called superfluid. It is a low conducting and high surface tension liquid
(c) He (II) is used for cryogenic applications
(d) He (I) on cooling at 2.19 K and 38 mm pressure changes to He (II)

42. Select the correct statements:
(a) $[Co(NH_3)_6]^{2+}$ is readily oxidised to $[Co(NH_3)_6]^{3+}$
(b) Co^{2+} is very stable and difficult to oxidise
(c) Ni^{2+} compounds are more stable than Pt^{2+}
(d) Ni^{4+} compounds are less stable than Pt^{4+}

43. CN^- acts as:
(a) reducing agent (b) oxidising agent
(c) complexing agent (d) ligand

44. A square planar complex uses the hybridisation of:
(a) *s*-orbitals (b) p_x-orbitals
(c) d_{z^2}-orbitals (d) $d_{x^2-y^2}$-orbitals

45. Which of the following have EAN equal to next inert gas?
(a) $Fe(CO)_5$ (b) $Co_2(CO)_8$
(c) $H_2Cr(CO)_5$ (d) $Cr(NH_3)_6Cl_3$

46. Which of the following are used in preparing iodised salt?
(a) KIO_3 (b) KI
(c) I_2 (d) HI

47. The chemicals used in preparation of MIC, *i.e.*, methyl isocyanate component of Bhopal gas tragedy are:
(a) CH_3NH_2 (b) $COCl_2$
(c) PH_3 (d) $(CH_3)_2NH$

48. $NaNO_3$ decomposes above 800°C to give:
(a) N_2 (b) O_2
(c) NO_2 (d) Na_2O

49. Addition of high proportions of Mn makes steel useful in making rails of rail roads because manganese:
(a) gives hardness to steel
(b) helps the formation of oxides of iron
(c) can remove oxygen and sulphur
(d) can show highest oxidation state of +7

50. Which of the following statements are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4?
(a) Deep red vapours are evolved
(b) Cl_2 gas is evolved
(c) Chromyl chloride is formed
(d) Evolved vapours on passing in NaOH give yellow solution of Na_2CrO_4

51. Which of the following are coloured?
(a) $Ti(NO_3)_4$ (b) $[Cu(NC\cdot CH_3)_4]^+BF_4^-$
(c) $[Cr(NH_3)_6]Cl_3^-$ (d) $K_3[VF_6]$

52. Nitrogen (I) oxide is produced by:
(a) thermal decomposition of NH_4NO_3
(b) disproportionation of N_2O_4
(c) thermal decomposition of NH_4NO_2
(d) interaction of hydroxyl amine and HNO_2

53. When zeolite (a hydrated sodium aluminium silicate) is treated with hard water, the sodium ions are exchanged with:
(a) H^+ ions (b) Ca^{2+} ions
(c) SO_4^{2-} ions (d) Mg^{2+} ions

54. The materials used in solar cell contains:
(a) Cs (b) Si
(c) Sn (d) Ti

55. Highly pure dilute solution of Na in liquid NH_3:
(a) shows blue colour
(b) exhibits electrical conductivity
(c) produces sodium amide
(d) produces H_2 gas

56. White phosphorus (P_4) has:
(a) six P—P single bonds
(b) four P—P single bonds
(c) four lone pairs of electron
(d) PPP bond angle of 60°

57. NH_3 on reaction with hypochlorite ion, can form:
(a) NO (b) NH_4Cl
(c) N_2H_4 (d) HNO_2

58. Which of the following alloys contains Cu and Zn:
(a) Bronze (b) Brass
(c) Gun metal (d) Type metal

59. The aqueous solution of which salts are coloured:
(a) $Co(NO_3)_2$ (b) $CrCl_3$
(c) $Zn(NO_3)_2$ (d) $CaCl_2$

60. Potassium manganate (K_2MnO_4) is formed when:
(a) Cl_2 is passed in $KMnO_4$ aq.
(b) MnO_2 is fused with KOH in air
(c) HCHO reacts with $KMnO_4$ in presence of strong alkali
(d) $KMnO_4$ reacts with conc. H_2SO_4

61. The statements that are true for the long form of the periodic table are :
(a) It reflects the sequence of filling the electrons in the order of sub-energy level *s*, *p*, *d* and *f*
(b) It helps to predict the stable valency states of the elements
(c) It reflects trends in physical and chemical properties of the elements
(d) It helps to predict the relative ionicity of the bond between any two elements

62. In the electrolysis of alumina, cryolite is added to :
(a) lower the melting point of alumina
(b) increase the electrical conductivity

(c) minimise the anode effect
(d) remove impurities from alumina

63. Of the following the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are :
(a) Ag (b) Mg
(c) Cu (d) Al

64. The compounds used as refrigerant are :
(a) NH_3 (b) CCl_4
(c) CF_4 (d) CF_2Cl_2

65. The major role of fluorspar (CaF_2), which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is :
(a) As a catalyst
(b) To make the fused mixture very conducting
(c) To lower the temperature of the melt
(d) To decrease the rate of oxidation carbon at the anode

66. $MgSO_4$ on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula?
(a) $Mg(NH_4)PO_4$ (b) $Mg_3(PO_4)_2$
(c) $MgCl_2 \cdot MgSO_4$ (d) $MgSO_4$

67. The aqueous solution of the following salts will be coloured in the case of :
(a) $Zn(NO_3)_2$ (b) $LiNO_3$
(c) $Co(NO_3)_2$ (d) $CrCl_3$

68. If the bond length of CO bond in carbon monoxide is 1.128Å, then what is the value of CO bond length in $Fe(CO)_5$?
(a) 11.28 pm (b) 110 pm
(c) 113 pm (d) 120 pm

69. The reagents, NH_4Cl and aqueous NH_3 will precipitate :
(a) Ca^{2+} (b) Al^{3+}
(c) Bi^{3+} (d) Zn^{2+}

70. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions :
(a) Fe^{3+} gives brown colour with potassium ferricyanide
(b) Fe^{2+} gives blue precipitate with potassium ferricyanide
(c) Fe^{3+} gives red colour with potassium thiocyanate
(d) Fe^{2+} gives brown colour with ammonium thiocyanate

71. The species present in solution when CO_2 is dissolved in water are :
(a) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$
(b) H_2CO_3, CO_3^{2-}
(c) CO_3^{2-}, HCO_3^-
(d) CO_2, H_2CO_3

72. In which of the following oxides P-atom has two different oxidation states.
(a) P_4O_6 (b) P_4O_7
(c) P_4O_{10} (d) P_4O_8

73. Select the correct statements :
(a) O_2 is a weak field ligand
(b) ClF_3 is used in enrichment of uranium
(c) ICl is more reactive than I_2
(d) $O_3, CO, CO_2, NO_2, N_2O, CH_4, CFCl_3$ are green house gases

74. Select the correct statements :
(a) oxyhaemoglobin is bright red
(b) deoxyhaemoglobin is purple
(c) oxyhaemoglobin is low spin complex
(d) oxyhaemoglobin absorbs hight of longer wave length

75. Select the correct statements :
(a) Solubility of salts containing anions *i.e.*, Cl^-, SO_4^{2-} that do not hydrolyse are unaffected by pH
(b) Solubility of BaF_2 in water increases in presence of H^+ ions
(c) Solubility of $Mg(OH)_2$ may increase or decrease with pH
(d) On adding lime juice into tea, the colour of tea becomes darker

76. When PbO_2 reacts with conc. HNO_3, the gas evolved is: **(IIT 2005)**
(a) NO_2 (b) O_2
(c) N_2 (d) N_2O

77. A solution of colourless salt H on boiling with excess NaOH produces a non-inflammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salts (H) is/are: **(IIT 2008)**
(a) NH_4NO_3 (b) NH_4NO_2
(c) NH_4Cl (d) $(NH_4)_2SO_4$

78. Which are correct about $[Fe(H_2O)_5NO]SO_4$? **(Modified IIT 2008)**
(a) It is diamagnetic as it has no unpaired electron
(b) It is paramagnetic as it has three unpaired electrons
(c) Ox. no. of Fe is +2
(d) Ox. no. of Fe is +1

79. The nitrogen oxide(s) that contain(s) N—N bond(s) is(are): **(IIT 2009)**
(a) N_2O (b) N_2O_3
(c) N_2O_4 (d) N_2O_5

80. The compound(s) formed upon combustion of sodium metal in excess air is(are): **(IIT 2009)**
(a) Na_2O_2 (b) Na_2O
(c) NaO_2 (d) NaOH

81. The compound(s) that exhibit(s) geometrical isomerism is(are): **(IIT 2009)**
(a) $[Pt(en)Cl_2]$ (b) $[Pt(en)_2]Cl_2$
(c) $[Pt(en)_2Cl_2]Cl_2$ (d) $[Pt(NH_3)_2Cl_2]$

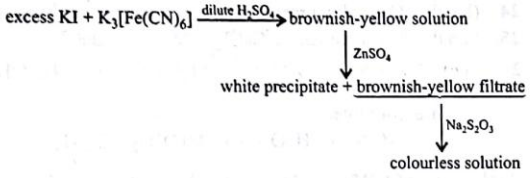
82. The reagents used for softening the temporary hardness of water is (are): **(IIT 2010)**

(a) $Ca_3(PO_4)_2$ (b) $Ca(OH)_2$
(c) Na_2CO_3 (d) NaOCl

83. Extraction of meta from the ore cassiterite involves : **(IIT 2011)**
(a) Carbon reduction of an oxide ore
(b) Self reduction of a sulphide ore
(c) removal of copper impurity
(d) removal of iron impurity

84. Which of the following hydrogen halides react(s) with $AgNO_3(aq)$ to give a precipitate that dissolves in $Na_2S_2O_3(aq)$? **(IIT 2012)**
(a) HCl (b) HF
(c) HBr (d) HI

85. For the given aqueous reactions, which of the statement(s) is (are) true? **(IIT 2012)**



(a) The first reaction is a redox reaction.
(b) White precipitate is $Zn_3[Fe(CN)_6]_2$.
(c) Addition of filtrate to starch solution gives blue colour.
(d) White precipitate is soluble in NaOH solution.

86. With respect to graphite and diamond, which of the statement(s) given below is (are) correct? **(IIT 2012)**
(a) Graphite is harder than diamond.
(b) Graphite has higher electrical conductivity than diamond.
(c) Graphite has higher thermal conductivity than diamond.
(d) Graphite has higher C—C bond order than diamond.

87. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is (are) : **[JEE (Advanced) I 2013]**
(a) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$
(b) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$
(c) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$
(d) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$

88. The correct statement(s) about O_3 is/are : **[JEE (Advanced) II 2013]**
(a) O—O bond lengths are equal
(b) Thermal decomposition of O_3 is endothermic
(c) O_3 is diamagnetic in nature
(d) O_3 has a bent structure

89. The carbon-based reduction method is NOT used for the extraction of : **[JEE (Advanced) II 2013]**
(a) tin from SnO_2
(b) iron from Fe_2O_3
(c) aluminium from Al_2O_3
(d) magnesium from $MgCO_3 \cdot CaCO_3$

SOLUTIONS (More Than One Answer Correct)

1. (a,b,c,d) These are facts.

2. (a,b,c,d) —do—

3. (a,b,c,d) $\underset{\text{red-oxi.}}{\overset{0}{Cl_2}} + 2NaOH \longrightarrow \overset{-1}{Na}\overset{-1}{Cl} + \overset{+1}{Na}\overset{+1}{ClO} + H_2O$

$$\underset{\text{red-oxi.}}{\overset{0}{3Cl_2}} + NaOH \longrightarrow \overset{-1}{Na}\overset{-1}{Cl} + \overset{+3}{Na}\overset{+3}{ClO_3} + 3H_2O$$

4. (c,d) ZnO, Al_2O_3, BeO, SnO_2 and As_2O_3 are amphoteric. Alkali and alkaline earth metal oxides (except BeO) are strong bases.

5. (a,b,c,d) Non-metal oxides (NO_2, N_2O_3, N_2O_5, CO_2, P_2O_3, P_2O_5,...etc.,) are acidic. Mn_2O_7 and CrO_3 are acidic oxides although metal oxides are basic or amphoteric.

6. (a,c,d) CO_2 is acidic but CO is neutral.

7. (a,b) Np is naptunium (Naptune) and Pu is plutonium (Pluto).

8. (a,b,c,d) Follow text.

9. (a,b,c,d) PI_3, AsI_3, SbI_3 : 102°, 100.2°, 99° (P being smallest exerts b.p.-b.p. repulsion strongly)

NH_3, PH_3, AsH_3: 106°51′, 93.5°, 91.5° (Due to decreasing electronegativity of central atom)

PF_3, PCl_3, PBr_3, PI_3 : 102°, 100°, 101.5°, 102° (Due to back bonding in PF_3)

NO_2^+, NO_2, NO_2^- :180°, 134°, 115° (b.p.–b.p. < b.p.–electron < b.p.–1.p.)

10. (a,b,c) $Ni(CO)_4 + 4PF_3 \longrightarrow Ni(PF_3)_4 + 4CO$

Due to small size of N—F bond than P—F bond

$$SbF_3 + 2F^- \longrightarrow (SbF_5)^{2-};$$

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$

11. (a,b,c,d) $\underset{sp}{O=C=O}$ $[\underset{sp}{N=N=N}]^-$; both are linear and have 22 electrons.

12. (a,b,c) More is the charge on cation more is the polarising power. However a metal ion with noble gas configuration has less polarising power due to increased shielding effect in noble gas configuration ion.

13. (a,b) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

14. (b,d) Both have $1s^2, 2s^2, 2p^6$ configuration like Ne.

15. (b,c,d) F_2 is reduced, Bi^{5+} is not possible due to inert pair effect. Stability order of $Pb^{4+} < Ge^{4+}$ due to inert pair effect . Zn has completely filled orbitals and Cu has $3d^{10}, 4s^1$.

16. (b,c) $[CF_3]^{-\delta}I^{+\delta} + H_2O \longrightarrow CF_3H + IOH$

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$

17. (a,b,c,d) All are used in extraction of metals.

18. (a,b,d) Conc. H_2SO_4 and HNO_3 oxidises H_2, conc. HCl forms a coating of $ZnCl_2$ over Zn and thus the reaction stops after little time.

$$Zn + \text{dil. } H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

19. (a,b,c,d) All these cations forms insoluble $(RCOO)_xM$ salt.

20. (b,c,d) Alum is $M_2'(SO_4)\cdot M_2'''(SO_4)_3\cdot 24H_2O$. However, Li does not form alum as it cannot co-ordinate $6H_2O$ molecules due to small size of Li^+.

21. (a,b,c,d) All occurs as shown.

22. (a,b,c) Ag_2S is black.

23. (a,b,c) Hydration of ion is spontaneous and exothermic. Also, randomness decreases.

24. (b,c,d) Only alkali metal bicarbonates exis in solid state.

25. (a,b,d) Covalent nature $CaCl_2 < MgCl_2 < BeCl_2$.

26. (a,c) $3M + N_2 \longrightarrow \underset{B}{M_3N_2}$; $Mg(OH)_2$ and $Be(OH)_2$ are insoluble

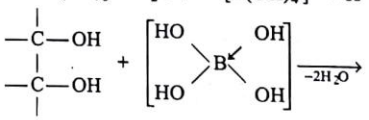
$$M_3N_2 + 6H_2O \longrightarrow \underset{C}{3M(OH)_2} + \underset{D}{2NH_3}$$

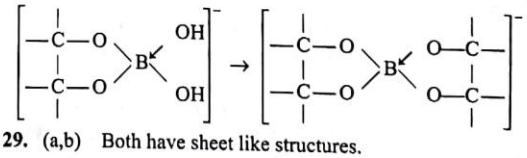
$$M(OH)_2 + CO_2 \longrightarrow \underset{\text{Milky}}{MCO_3} + H_2O$$

27. (a,b) Alums are $M_2'SO_4\cdot M_2'''(SO_4)_3\cdot 24H_2O$. If M' is bivalent then it is pseudo alum.

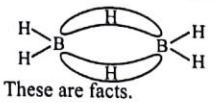
28. (b,c) $B(OH)_3$ is H_3BO_3, *i.e.*, boric acid, a weak Lewis monoboric acid. It forms 1:1 complex with diols.

$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$$





29. (a,b) Both have sheet like structures.

30. (a,b,c,d) 

31. (b,c,d) These are facts.

32. (a,b,c,d) One P has +3 ox. no. and 3P has +1 ox. no.

$$\therefore \quad \text{Aq.} = \frac{1\times 3 + 3\times 1}{4} = +\frac{6}{4} = +\frac{3}{2}$$

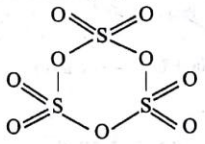
33. (c,d) $\frac{1}{2}N_2 + \frac{3}{2}F_2 \longrightarrow NF_3; \quad \Delta H_f = -109\text{ kJ}$

$$\frac{1}{2}N_2 + \frac{3}{2}Cl_2 \longrightarrow NCl_3; \quad \Delta H_f = +230\text{ kJ}$$

N—F bond energy > F—F bond energy; N — Cl bond energy < Cl—Cl bond energy.

34. (a,b,c) SO_2Br_2 and SO_2I_2 are unstable.

35. (a,b,c,d) All are facts about S_4N_4.

36. (a,b,d) $(SO_3)_3$ is 

37. (a,b) Cl_2O_5 and I_2O_7 are not known. OF_2 is oxygen difluoride.

38. (b,c,d) pK_a for HF, HCl, HBr and HI are 3, −7, − 9, − 10 respectively.

39. (a,b,c) I^{+3} and anions are CH_3COO^-, IO_3^-, PO_4^{3-}.

40. (a,b,c,d) All are facts.

41. (a,b,c,d) — do —

42. (a,b,c,d) — do —

43. (a,c,d) CN^- does not act as oxidant.

44. (a,b,d) Square planar complex involves s, p_x, p_y and $d_{x^2-y^2}$ orbitals.

45. (a,b,c) EAN of Cr = 24 − 3 + (2 × 6) = 33

46. (a,b) It is fact.

47. (a,b) $CH_3NH_2 + COCl_2 \longrightarrow \underset{\text{MIC}}{CH_3N{=}C{=}O} + 2HCl$

48. (a,b,d) $NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$

$2NaNO_3 \longrightarrow Na_2O + N_2 + \frac{5}{2}O_2$

49. (a,c,d) Manganese (Mn) imparts hardness to steel as well as removes oxygen and sulphur from steel by forming slag as $MnSiO_3$.

$Fe_2O_3 + 3Mn \longrightarrow 3MnO + 2Fe$

$MnO + SiO_2 \longrightarrow \underset{\text{(slag)}}{MnSiO_3}$

50. (a,c,d) This is chromyl chloride test

$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 \longrightarrow K_2SO_4 + 2CrO_2Cl_2 + 2Na_2SO_4 + 3H_2O$

51. (c,d) Cu^+ and Ti^{4+} have no unpaired electron, thus colourless.

52. (a,d) $NH_4NO_3 \xrightarrow{\Delta} \mathbf{N_2O} + 2H_2O$

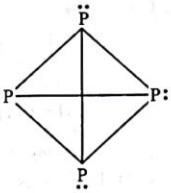
$NH_2OH \cdot HCl + NaNO_2 \longrightarrow NaCl + 2H_2O + \mathbf{N_2O}$

53. (b,d) Ca^{2+} and Mg^{2+} ions are exchanged.

$Na_2Z + Ca^{2+} \longrightarrow CaZ + 2Na$

54. (a) In solar cells **Cs** is used.

55. (a,b) $Na + (X+Y)NH_3(l) \longrightarrow \underset{\text{Solvated cation}}{[Na(NH_3)_x]^+} + \underset{\text{Solvated electron (blue colour)}}{[Y(NH_3)(l)\cdot e]^-}$

56. (a,c,d)  is P_4

57. (c) $2NH_3 + OCl^- \longrightarrow N_2H_4 + H_2O + Cl^-$

58. (b,c) Bronze : Cu + Sn; Type metal : $\underset{60\%}{Pb} + \underset{30\%}{Sn} + \underset{10\%}{Sb}$.

Gun metal : $\underset{90\%}{Cu} + \underset{8-10\%}{Sn} + \underset{4\%}{Zn}$; Brass : Cu + Zn

59. (a,b) Co^{2+} and Cr^{3+} have unpaired electron.

60. (b,c) $2KOH + MnO_2 + O_2 \longrightarrow K_2MnO_4 + H_2O$

$HCHO + 2KMnO_4 + 2KOH \longrightarrow K_2MnO_4 + H_2O + HCOOH$

61. (a,b,c,d) In the long form of periodic table, elements are arranged in increasing order of their atomic number (*i.e.*, increasing order of energy).

Physical and chemical properties are the periodic functions of their electronic configuration (*i.e.*, atomic number) of element.

62. (a,b) Cryolite is added during the electrolysis of alumina. The functions of cryolite are to lower the melting point and to decrease the conductivity as well.

63. (b,d) These metals are not discharged in aqueous solutions as $E^0_{RP}H^+ > E^0_{RP}(M^{n+})$.

64. (a,d) These are facts.

65. (b,c) These are facts.

66. (a) The product is white ppt. of magnesium ammonium phosphate.

$MgSO_4 + Na_2HPO_4 + NH_4OH \rightarrow Mg(NH_4)PO_4 + Na_2SO_4 + H_2O$

67. (c,d) $Co(NO_3)_2$ and $CrCl_3$ has unpaired '*d*' electron, hence they are coloured; while $Zn(NO_3)_2$, $LiNO_3$ and potash alum have no unpaired electron (completely filled shell) hence they are colourless.

68. (c) In Carbonyls double bonding takes place.

$$OC \underset{\pi}{\overset{\sigma}{\rightleftharpoons}} M$$

For this type of back bonding CO should have filled '*sp*' hybrid orbital as well as vacant antibonding Pi molecular orbital (π^x_y or π^x_2) and metal atoms should be in low oxidation state and should have vacant hybrid and filled '*d*' orbitals.

Due to this back bonding CO bond strengthens and so bond order decreases and bond length slightly increases.

69. (b,c) $Al^{3+} + 3NH_4OH \rightarrow Al(OH)_3\downarrow + 3NH_4^+$

$Bi^{3+} + 3NH_4OH \rightarrow Bi(OH)_3\downarrow + 3NH_4^+$

Al^{3+} and Bi^{3+} are precipitated as their hydroxides.

70. (a,b,c) $3FeCl_2 + 2K_3\,Fe(CN)_6 \longrightarrow$

$$\underset{\text{Turn bull's blue}}{Fe_3^{2+}[Fe^{3+}(CN)_6]_2} + 6KCl$$
Femous ferricyanide

$$FeCl_3 + K_3\,Fe(CN)_6 \longrightarrow \underset{\text{Ferric ferricyanide}}{Fe[Fe(CN)_6]} + 3KCl$$
(Brown colour)

The blue, precipitate of Fe^{2+} ions with potassium ferricyanide is due to formation of turnbull's blue.

The red colouration of Fe^{2+} ions with potassium thiocyanate is due to the formation of $[Fe(CNS)Cl_2]$

$$Fe^{3+} + KCNS \longrightarrow \underset{\text{Blood red colour}}{[Fe(CNS)]^{2+}} + K^+$$

71. (a) When CO_2 is dissolved in water, it forms dibasic carbonic acid, which gives HCO_3^- and CO_3^{2-} ions on ionisation. Hence in solution CO_2, H_2CO_3, HCO_3^- and CO_3^{2-} are present.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

72. (b,d) In both these P shows +3 and +5 oxidation state.

73. (b,c,d) Rest all are correct. O_2 is strong field ligand (enrichment of uranium is made by converting uranium to UF_{6g})

$$\underset{(s)}{U} + 3ClF_3 \longrightarrow \underset{(g)}{UF_6} + \underset{(g)}{3ClF}$$

74. (a,b,c) Oxyhaemoglobin is Red and absorbs light of smaller wave length.

75. (a,b,c) Tea contains polyphenols which are weak acids. Lemon juice contains citric acid and thus dissociation of polyphenols decreases in presence of lime juice. The ionised polyphenols are darker in colour and unionised polyphenols are lighter in colour.

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$$
$$F^- + H^+ \longrightarrow HF$$

Weak acid and there for solubility equilibrium shifts to the right.

76. (b) $2PbO_2 \longrightarrow 2PbO + O_2$

$$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$$

77. (a,b) $NH_4NO_3 + NaOH \longrightarrow NH_3\uparrow + NaNO_3 + H_2O$

$NH_4NO_2 + NaOH \longrightarrow NH_3\uparrow + NaNO_2 + H_2O$

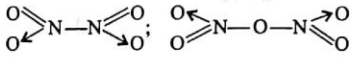
NH_3 is non-inflammable

$NaNO_3 + 4Zn + 7NaOH \longrightarrow 4Na_2ZnO_2 + NH_3 + 2H_2O$

$NaNO_2 + 3Zn + 5NaOH \longrightarrow 3Na_2ZnO_2 + NH_3 + H_2O$

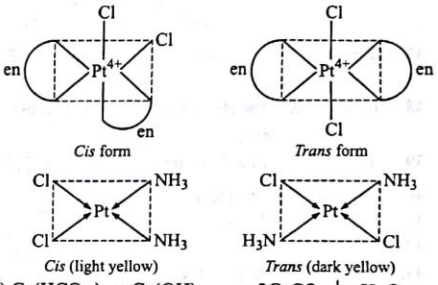
78. (b,d) In iron complex ox. no. of NO = +1 and the Fe is in Fe^+ state, *i.e.*, $3d^6, 4s^1$. 1 electron of *d* is paired by $4s^1$ ⊡•⊡•⊡•⊡•⊡ in presence of NO^+.

79. (a,b,c) $N \equiv N \longrightarrow O$; $O=N-N\overset{O}{\underset{O}{<}}$;



80. (a) $2Na + O_2 \xrightarrow[\text{air}]{} Na_2O_2$

81. (c,d)



82. (b,c,d) $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + H_2O$
(Clark's method)

$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaHCO_3$
(Both permanent and temporary hardness are removed by Na_2CO_3)

$NaOCl + H_2O \longrightarrow HOCl + NaOH$ (–do–)

$2NaOH + Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + Na_2CO_3 + H_2O$ (–do–)

83. (a,c,d) Cassiterite is an ore of SnO_2. The extraction of Sn involves the following steps.

$SnO_2 + 2C \longrightarrow Sn + 2CO$ (Smelting)

The liquid metal Sn contains impurities Cu, iron, tungsten which are removed by flowing liquid metal on inclined plane, leaving behind iron, copper and tungsten. The molten metal is then stirred with a green wood pole to oxidise impurities of S, As.

84. (a,c,d)

$HX + AgNO_3 \longrightarrow AgX\downarrow + HNO_3$ (X = Cl, Br, I)

$$AgX + 2Na_2S_2O_3 \longrightarrow \underset{\substack{\text{sodium argentothiosulphate}\\ \text{coloureless solution}}}{Na_3[Ag(S_2O_3)_2]} + NaX$$

AgF is water soluble.

85. (a,c,d)

$$K_3[\overset{+3}{Fe}(CN)_6] + KI(\text{excess}) \longrightarrow K_4[\overset{+2}{Fe}(CN)_6] + \underset{\text{(Brownish yellow solutions)}}{KI_3}$$ (redox reaction)

$$\underset{\text{(Brownish yellow filterate)}}{I_3^-} + 2Na_2S_2O_3 \longrightarrow \underset{\text{Clear solution}}{Na_2S_4O_6} + 2NaI + I^-$$

$$K_4[Fe(CN)_6] + ZnSO_4 \longrightarrow \underset{\text{(White ppt.)}}{K_2Zn_3[Fe(CN)_6]_3}$$

$$\xrightarrow{NaOH} \underset{\text{Soluble}}{Na_2[Zn(OH)_4]}$$

Starch gives blue colour with I_2 present with I_3^- ($I_2 + I^-$)

86. (b,d)

- Diamond is harder than graphite.
- Graphite is good conductor of electricity as each carbon is attached to three C-atoms involving sp^2 hybridization leaving one p-orbital electron free, which is responsible for electrical conduction, while in diamond, all the four valencies of carbon are satisfied, hence insulator.
- Diamond is better thermal conductor than graphite. Electrical conduction is due to avialability of free p-orbital electrons; whereas thermal conduction is due to transfer of thermal vibrations from atom to atom. A compact and precisely aligned crystal structure of diamond facilitates fast movement of heat.
- In graphite, C—C bond acquires double bond character, hence higher bond order than in diamond.

87. (b,d)

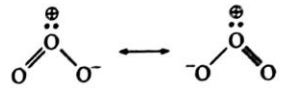
(a) $[Cr(NH_3)_5Cl]Cl_2$ shows ionisation isomerism with $[Cr(NH_3)_4Cl_2]Cl$, but $[Cr(NH_3)_4Cl_2]Cl$ also show geometrical isomerism

(b) Both $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$ show geometrical isomerism

(c) $[CoBr_2Cl_2]^{2-}$ is sp^3 hybridised and does not show any isomerism
$[PtBr_2Cl_2]^{2-}$ is dsp^2 hybridised and show geometrical isomerism

(d) Both $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$ show ionisation isomerism

88. (a,c,d)



both bonds are equal due to resonance, central O-atom is sp^2 hybridised with 2σ and 1π along with one lone pair. Thus O_3 has bent structure. Also it is diamagnetic as it has no unpaired electron.

$\because$ $O_2 \longrightarrow O_3$ $\Delta H = +ve$ (silent electric charge)

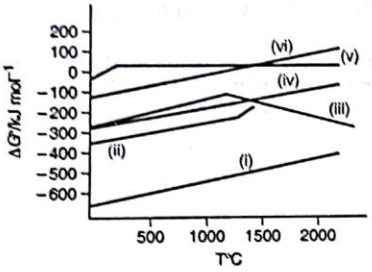
So, $O_3 \longrightarrow O_2$ $\Delta H = -ve$ (exothermic)

89. (c,d)

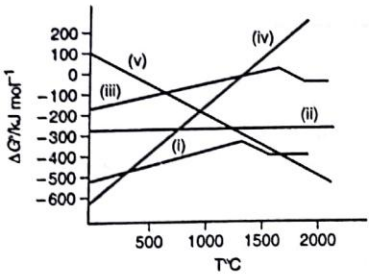
More electropositive metals like Al, Mg, Ca, Na are reduced by electrolytic reductions not by carbon reduction because these forms carbide with carbon.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Some metals e.g., Ag, Au, Pt are found in native state whereas most of the metals are found in nature in their compound state oxides, sulphides, halides, etc. Metals always exhibit positive oxidation states and therefore metals are extracted from their ores either by chemical or electrolytic reduction $M^{n+} + ne \longrightarrow M$. Chemically metal compounds can be reduced by treating them with carbon, CO, H_2, etc. The following two diagrams schematically shows as to which reduction method is suitable for some of the metals. These diagrams are called Ellingham diagrams. The more active metals like Na, K, Mg, Al, etc., are better reduced by electrolysis of their fused salts. Metals which reacts with carbon are easily obtained by reducing their compounds with Al.



(i) $2O_2 + S_2 \longrightarrow 2SO_2$
(ii) $2Zn + S_2 \longrightarrow 2ZnS$
(iii) $2Pb + S_2 \longrightarrow 2PbS$
(iv) $2Fe + S_2 \longrightarrow 2FeS$
(v) $C + S_2 \longrightarrow CS_2$
(vi) $2H_2 + S_2 \longrightarrow 2H_2S$



(i) $2Fe + O_2 \longrightarrow 2FeO$
(ii) $C + O_2 \longrightarrow CO_2$
(iii) $2Pb + O_2 \longrightarrow 2PbO$
(iv) $2Zn + O_2 \longrightarrow 2ZnO$
(v) $C + \frac{1}{2}O_2 \longrightarrow CO$

[1] Which of the following is a suitable method for reduction of galena (PbS)?
(a) $2PbS + C \longrightarrow 2Pb + CS_2$
(b) $PbS + H_2 \longrightarrow Pb + H_2S$
(c) (i) $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$
(ii) $PbO + C \longrightarrow Pb + CO$
(d) Electrolytic reduction

[2] Which of the following is a suitable method for reduction of zinc blende (ZnS)?
(a) (i) $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
(ii) $ZnO + C \longrightarrow Zn + CO$
(b) $2ZnS + C \longrightarrow 2Zn + CS_2$
(c) $ZnS + H_2 \longrightarrow Zn + H_2S$
(d) None of the above

[3] Which of the following set represent maximum true statements?
(I) Zinc blende can be reduced by hydrogen at around 1500°C
(II) The reaction, $PbO + C \longrightarrow Pb + CO$, is feasible only above 500°C
(III) Iron can be produced by the reduction of FeS with Pb above approximately 1400°C
(IV) Alkali metals can be obtained by the electrolysis of their aqueous solution
(V) Under certain conditions Mg can reduce SiO_2 and Si can reduce MgO
(a) I, II, III, V (b) I, II, V
(c) III, V (d) I, III, IV

[4] Which of the following is not correct?
(a) An alloy represents a heterogeneous mixture of two or more metals or a metal and non-metal
(b) Metal ores are rarely found in form of nitrates form
(c) FeO can be reduced by carbon above 1123 K
(d) P_4O_{10} is used in steel manufacture to remove MgO in basic furnace lining

[5] Select the correct statements:
(1) Cr, Mn and Fe oxides can be reduced by carbon or CO
(2) Cr and Mn reacts with carbon to form carbides
(3) Al is used as reducing agent in the reduction of Cr_2O_3 to Cr and Mn_3O_4 to Mn
(4) Galena shows auto-reduction to give lead if heated with oxygen
(a) 1, 2, 3 (b) 3, 4
(c) 1, 2, 4 (d) 1, 2, 3, 4

[6] Select the correct statements:
(1) Ni, Ti, Zr is obtained by vapour phase refining
(2) The vapour phase refining leads to preparation of ultrapure samples of metals
(3) Acidic flux are used to remove the impurities of SiO_2 in ore

(4) In Kroll's process Mg is used as reducing agent for $TiCl_4$ to Ti
(5) In IMI process Na is used as reducing agent for $TiCl_4$ to Ti
(a) 1, 2, 4, 5 (b) 1, 2, 3, 4
(c) 1, 2, 4 (d) 1, 2, 5

Comprehension 2 : Hydrogen resembles in many of its properties with alkali metals as well as halogens. However it also differ markedly in some of its property with these two group elements. H—H bond energy in dihydrogen molecule is maximum. Dihydrogen acts as strong reducing agent. Two oxides of H are known as H_2O, neutral or amphoteric and H_2O_2 a dibasic acid. The strength of H_2O_2 solution is expressed in terms of by volume H_2O_2, *i.e.*, V volume H_2O_2 means 1 mL of H_2O_2 on decomposition gives V mL O_2 or in terms of percentage, *i.e.*, g/100 mL

[1] Reducing power is maximum in case of:
(a) H_2 (b) Atomic H
(c) Nascent H (d) Occluded H_2

[2] Which form of H is produced at elevated temperature?
(a) Atomic H (b) Nascent H
(c) Occluded H_2 (d) None of these

[3] Which are correct statements?
(1) Pure H_2 is obtained by the action of Al on KOH
(2) Pure H_2 is obtained by the action of NaH on H_2O
(3) Electrolysis of warm solution of $Ba(OH)_2$ using Ni electrodes gives pure H_2
(4) Moist H_2 can be dried by H_2SO_4
(a) 1, 2, 3, 4 (b) 1, 4
(c) 1, 2, 3 (d) 2, 3, 4

[4] Which are correct statements?
(1) H_2O_2 is less associated liquid than H_2O
(2) H_2O_2 is paramagnetic in nature
(3) H_2O_2 acts as oxidant and reductant both
(4) H_2O_2 reacts with $K_2Cr_2O_7$ in acidic medium to give blue colour solution
(a) 3, 4 (b) 1, 3, 4
(c) 2, 3, 4 (d) 1, 2, 3

[5] An H_2O_2 solution is labelled as 30 vol H_2O_2. Its strength in terms of % is:
(a) 9.105 (b) 6.07
(c) 3.035 (d) 12.14

[6] The normality of H_2O_2 solution labelled as 6.07% is:
(a) 4.57 N (b) 3.57 N
(c) 2.57 N (d) 5.57 N

[7] In which reaction water acts as catalyst?
(a) $NH_3 + HCl$ (b) $CaO + CO_2$
(c) $F_2 + H_2O$ (d) $Na_2O + CO_2$

Comprehension 3 : *s*-block elements having ns^1 (alkali metals) or ns^2 (alkaline earth metals) include Li, Na, K, Rb, Cs, Fr and Be, Mg, Ca, Sr, Ba, Ra respectively. These metals are soluble in NH_3 and their ammonia solution is strongly conducting, paramagnetic as well as show colour. All of these are reactive metals due to low values of ionisation energy. The physical properties of alkali metals almost describe a regular trend from Li to Cs whereas no such trend is noticed in alkaline earth metals. Also the properties such as density m.pt, b.pt for alkaline earth metals are more than alkali metals. Li in alkali metals and Be in alkaline earth metals differ markedly in many of their properties with their respective group elements.

[1] The conductivity of alkali metals in liq. NH_3 at $-33°C$:
(a) Increases with increase in temperature
(b) Decreases with increase in temperature
(c) Remains same with increase or decrease in temperature
(d) Due to ions furnished by metals

[2] The ΔH_{hyd} is maximum for:
(a) Li^+ (b) Na^+
(c) K^+ (d) Rb^+

[3] Which set of statements are correct?
(I) ΔH_{hyd} for $Sr^{2+} > \Delta H_{hyd}$ for Ag^+
(II) $Ca(OH)_2$ is less soluble in water than $Ba(OH)_2$
(III) Ba^{2+} is more powerful reducing agent than Ca^{2+} in acidic solution
(IV) Ca^{2+} is more powerful reducing agent in alkali medium
(a) I, II, III, IV (b) I, II
(c) I, III, IV (d) II, IV

[4] Which set of statements is correct?
(I) Oxidation number of Cs in $CsCl_3$ and $CsBrCl_2$ is +1
(II) Density of K < density of Na
(III) Alkali metals except Li and Na form superoxide on combustion
(IV) Ash obtained by burning Mg in air on dissolution in water gives odour of NH_3
(a) I, II (b) II, III, IV
(c) II, III (d) I, II, III, IV

[5] Which set of statements is correct?
(I) All alkaline earth metals gives characteristic flame colour
(II) IE_2 for alkaline earth metals are lower than IE_2 of alkali metals
(III) Addition of NaCl to fused $MgCl_2$ lowers the fusion point
(IV) Baking powder is a mixture of pot hydrogen tartarate and Na_2CO_3
(a) I, II, III, IV (b) II, III, IV
(c) II, III (d) I, IV

[6] Which set of statements is correct?
(I) Bicarbonates of alkali and alkaline earth metals are known in solid state
(II) SO_2 gives white precipitate on passing through baryta water
(III) Thermal decomposition of $CaCO_3$ is reversible in closed vessel but irreversible in lime kiln
(IV) American baking powder is $Ca(H_2PO_4)_2$

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

[7] Select the wrong statements:
(a) Hydration energy : $Mg^{2+} > Mg^{+} > Na^{+}$
(b) λ released during flame colour :
$Li > Na > K > Rb > Cs$
(c) Conducting power in solution :
$Cs^{+} > Rb^{+} > K^{+} > Na^{+} > Li^{+}$
(d) Density : Be > Mg > Ca > Sr > Ba > Ra

[8] $Be(NO_3)_2$ on heating to 125° gives:
(a) $BeO + NO_2 + O_2$
(b) $BeO + NO_2$
(c) $[Be_4O(NO_3)_6] + N_2O_5$
(d) $BeO + N_2O_5$

[9] Which statement is not correct?
(a) Be_2C gives CH_4 on dissolution in water
(b) Mg_2C_3 gives propyne on dissolution in water
(c) CaC_2 gives acetylene on dissolution in water
(d) Mg_2C_3 is called magnesium acetylide

Comprehension 4 : Group 13 of periodic table consists of boron or aluminium family. Boron being the first member, shows anomalous behaviour due to its small size and high nuclear charge/size ratio, high electronegativity and non availability of *d*-electrons. All the group 13 members forms hydrides, hydroxides, halides showing +3 covalency, however boron forms electron deficient species.

[1] Boron and aluminium differ from each other except:
(I) Both B and Al forms anionic hydrides
(II) Both form alkaline hydroxide of formula $M(OH)_3$
(III) Both B and Al forms a series of polymeric hydrides
(IV) Both forms monomeric halides MX_3
(a) I, IV (b) I, II, III
(c) II, III (d) I, II, IV

[2] Which one is not correct chemical change?
(a) $H_3BO_3 + 3NaOH \longrightarrow Na_3BO_3 + 3H_2O$
(b) $H_3BO_3 + 3ROH \longrightarrow R_3BO_3 + 3H_2O$
(c) $4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$
(d) $3B_2H_6 + 6NH_3 \xrightarrow{450\ K} 2B_3N_3H_6 + 12H_2$

[3] Diborane does not have in its structure:
(a) A three centre electron pair bond
(b) A multi centre bond or banana bond
(c) Two bridging H-atom below or above the plane of four B—H bonds
(d) Two bridging H-atom in the same plane of four B—H bonds

[4] Which set of statements is correct among group 13 members?
(I) Boron does not decompose steam while other members do it
(II) Boron shows a maximum covalency of four while others members exhibit a covalency of six
(III) Borates are more stable than aluminates
(IV) Borax is $Na_2B_4O_7 \cdot 7H_2O$
(a) I, III (b) I, IV
(c) III, IV (d) I, II, IV

[5] The correct order for acidic strength of boron trihalides is:
(a) $BF_3 < BCl_3 < BBr_3 < BI_3$
(b) $BI_3 < BBr_3 < BF_3 < BCl_3$
(c) $BF_3 > BCl_3 > BBr_3 > BI_3$
(d) $BF_3 > BBr_3 > BCl_3 > BI_3$

Comprehension 5 : Group-14 of periodic table includes C, Si, Se, Te and Po. Carbon forms two oxides CO (neutral) and CO_2 (acidic) whereas other members of group 14 forms amphoteric oxides. Both CO and CO_2 are covalent compounds. Si does not form monoxide.

[1] The bond energy is maximum in:
(a) CO (b) O_2
(c) H_2 (d) N_2

[2] CO although neutral acts as acid as well as π-electron acceptor in the reactions respectively:
(I) $CO + NaOH \xrightarrow{High\ P,T} HCOONa$
(II) $Ni + 4CO \xrightarrow{80°C} Ni(CO)_4$
(III) $PbO + CO \longrightarrow Pb + CO_2$
(IV) $I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$
(a) I, II (b) II, III
(c) III, II (d) I, IV

[3] Which of the following reaction in not correct?
(a) $PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$
(b) $PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2$
(c) $PbO_2 + 2HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$
(d) $2CO_2 + 2Na \longrightarrow Na_2CO_3 + CO$

[4] Which statement is not correct?
(a) The CO_2 molecule possesses *sp*-hybridization and also shows resonating structure
(b) The structure of CO is $[:C \rightleftharpoons O:]$
(c) Ammoniacal CuCl absorbs CO and forms adduct product
(d) Asphyxia is low level poisoning produced in a atmosphere of CO_2

[5] Which statement is not correct?
(a) CO is isoelectronic with N_2 but less reactive than N_2
(b) CO is isoelectronic with N_2 and possesses more bond energy
(c) CO is isoelectronic with N_2 and more reactive than N_2
(d) CO is isoelectronic with N_2 and required for respiration

[6] The mole ratio of gases obtained on dehydration of $H_2C_2O_4$ and HCOOH respectively is:
(a) 2 : 1 (b) 1 : 2
(c) 3 : 1 (d) 1 : 3

Comprehension 6 : Group 15 includes pnicogens *i.e.*, N, P, As, Sb and Bi elements with ns^2np^3 configuration. N_2 is gas. All these elements except Bi shows allotropy. Phosphorus exists in three allotropic forms, white phosphorus, red phosphorus and black phosphorus. The later being most stable (thermodynamically) form of P. Each member of this forms hydrides of the molecular formula MH_3. Nitrogen however forms three hydrides NH_3, N_3H and N_2H_4. The thermal stability, basic nature and solubility in water of hydrides (MH_3) however decreases from N to Bi.

[1] Which one is wrong statement?
(a) White phosphorus possesses P_4 molecular state having P—P—P angle 60°
(b) White phosphorus is most reactive form because of maximum strain
(c) Red P neither shows chemiluminescence nor reacts with alkalies
(d) White P is insoluble in CS_2 but red phosphorus is soluble in CS_2

[2] For which form of phosphorus the standard enthalpy has been assumed to be zero?
(a) Red (b) Black
(c) White (d) Yellow

[3] The correct order for acidic nature is:
(a) $NH_4^+ < PH_4^+ < AsH_4^+$ (b) $NH_4^+ > PH_4^+ > AsH_4^+$
(c) $AsH_4^+ > NH_4^+ > PH_4^+$ (d) $AsH_4^+ < NH_4^+ < PH_4^+$

[4] Which hydride of groups 15 is most powerful reducing agent?
(a) NH_3 (b) PH_3
(c) AsH_3 (d) SbH_3

[5] The correct order of bond angles is:
(a) $NH_3 > PH_3 > AsH_3 > SbH_3$
(b) $SbH_3 > AsH_3 > PH_3 > NH_3$
(c) $SbH_3 > PH_3 > AsH_3 > NH_3$
(d) $PH_3 > NH_3 < SbH_3 < BiH_3$

[6] Which reaction is not possible?
(a) $NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$
(b) $PCl_5 + Cl^- \longrightarrow [PCl_6]^-$
(c) $PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$
(d) $CuSO_4 + 2PH_3 \longrightarrow Cu(PH_3)_2SO_4$

Comprehension 7 : Group 16 includes chalcogens O, S, Se, Te and Po each showing different allotropic forms. Both oxygen and sulphur shows catenation but it is more pronounced in sulphur. Each member of this forms oxides of the formula MO_2, MO_3 (except O), MO (except Se). The acidic nature of oxides of these metals decreases down the group, *i.e.*, from O to Po. Each di and tri oxide involves $p\pi$-$d\pi$ bonding in addition to $p\pi$-$p\pi$ bonds.

[1] The thermodynamically more stable form of Se is:
(a) Red monoclinic
(b) Grey hexagonal
(c) Grey polymeric hexagonal
(d) Se_8 staggered

[2] Which forms of sulphur has been proposed boat and chair structure respectively?
(a) S_8-Rhombic, S_8-staggered
(b) S_8-Rhombic, Cyclo-S_6
(c) Cyclo-S_6, S_8-staggered
(d) Cyclo-S_6, Catena-S_n

[3] Number of S—S bonds present in poly sulphuric acid ($H_2S_nO_6$) is:
(a) n (b) $n-1$
(c) $n-2$ (d) $n+1$

[4] Which element of group 15 forms only two series of oxides?
(a) Po (b) S
(c) Se (d) Te

[5] $p\pi$-$p\pi$ and $p\pi$-$d\pi$ bonds are not present in:
(a) PCl_5 (b) SO_2
(c) NCl_3 (d) SO_3

[6] Colloidal sulphur is not obtained by:
(a) $2HNO_3 + H_2S \longrightarrow 2NO_2 + 2H_2O + S$
(b) $SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$
(c) $Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O + S$
(d) $3SO_2 \longrightarrow 2SO_3 + S$

(7) The hybridization of S in SO_2 and H_2SO_3 is respectively:
(a) sp^2, sp^3 (b) sp^2, sp^2
(c) sp^3, sp^2 (d) sp, sp^2

Comprehension 8 : Ionic character of metallic halides tends toward covalent nature as per Fajan's rule. Such covalent halides behave as non-metallic in their higher oxidation states. The property to hydrolyse to give oxo-acids of the element and corresponding hydro halogen acid for most non-metallic elements proceeds exceptionally in the way keeping oxidation number of element and halide same.

$$MX_a + aH_2O \longrightarrow MH_a + aHOX$$
$$MH_a + HOX \rightleftharpoons MH_{a+1}^+ + OX^-$$

If element M is more electronegative than halogens.

Non-polar halides are immiscible in water, it does not undergoes hydrolysis, but halides of some elements with empty d-orbital undergo hydrolysis. Stability of halides of higher oxidation state are governed by inert-pair effect.

Pseudohalides are anions having resemblance with halide ions. Group IA metals can formed salts with pseudohalides. Pseudohalides can act as ligands and form co-ordinate complexes. Their hydrides are weakly acidic and can be prepared in analogous way as halogen hydrides are prepared. Azides, cyanides, selenocyanides are examples of pseudo halides. Interhalogen compounds are the compounds in which

two halogens interact covalently due to difference in electronegativity giving AB, AB_3, AB_5 and AB_7 compounds where B is more electronegative.

[1] Which halide undergoes hydrolysis to give oxo-acids of underlined elements?
(a) $\underline{C}Cl_4$ (b) $\underline{P}Cl_3$
(c) $\underline{N}I_3$ (d) $\underline{Sb}Cl_3$

[2] Which one undergoes hydrolysis to form oxo-acids of the underlined element?
(a) $\underline{N}F_3$ (b) $\underline{N}Cl_3$
(c) $\underline{N}I_3$ (d) $\underline{B}Cl_3$

[3] Which one is not correct?
(a) $SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$
(b) $SbCl_5 + 4H_2O \longrightarrow (OH)_3SbO + 5HCl$
(c) $SbCl_3 + 3H_2O \longrightarrow Sb(OH)_3 + 3HCl$
(d) $XeF_2 + H_2O \longrightarrow Xe + 2HF + \frac{1}{2}O_2$

[4] Which one is stable and known?
(a) $PbCl_2$ (b) $PbCl_4$
(c) $GeCl_4$ (d) CCl_2

[5] Which one does not exist and not known?
(a) $PbCl_4$ (b) PbF_4
(c) PbI_4 (d) $PbBr_4$

[6] The reaction of cyanogens with alkali gives:
(a) CN^-, OCN^- (b) NH_3, H_2CO_3
(c) $HCOO^-, NH_3$ (d) HCN, H_2O

[7] When sodium cyanide reacts with H_2SO_4. The products are:
(a) HCN and Na_2SO_4 (b) HCN and $NaHSO_4$
(c) $(CN)_2$, Na_2SO_4, H_2O (d) none of these

[8] When sodium pseudohalide salts are dissolved in water it resembles with:
(a) NaCl (b) NaBr
(c) NaF (d) NaI

[9] When CN_2 reacts with Na metal, the product is:
(a) NaCN (b) Na_2C, N_2
(c) NaN_3, carbon black (d) $[Na(CN)_2]^-$

[10] When sodium azide reacts with conc. sulphuric acid, the product is:
(a) $(NH_4)_2SO_4, Na_2SO_4$
(b) NH_3, Na_2SO_4
(c) $N_3H, NaHSO_4$
(d) none of the above

[11] Which compound does not exists?
(a) IF_7 (b) IF_5
(c) IF_3 (d) ClF_7

[12] Which the species is not a pseudohalide?
(a) CNO^- (b) $RCOO^-$
(c) OCN^- (d) NNN^-

[13] $KICl_2$ on heating gives:
(a) $KI + Cl_2$ (b) $KCl + ICl$
(c) no effect (d) $K^+ + ICl_2^-$

[14] Which halogen acid forms two series of salts?
(a) HF (b) HCl
(c) HBr (d) HI

[15] Interhalogen compounds are:
(a) hydrolysed easily
(b) acts as oxidant
(c) volatile and fumes in air
(d) all of the above

Comprehension 9. Group 18 includes noble gases He, Ne, Ar, Kr, Xe and Rn. The credit of discovery for maximum number of this group element goes to Ramsay. Dorn discovered the last member Rn as one of the disintegration product of Ra. Xe having nearly same ionisation energy as oxygen forms a large number of compounds like xenon fluorides, oxy fluorides, oxides and perxenates. Coconut charcoal adsorbs noble gases at different temperature and thus used to separate them from each other. Liquid He exist in two forms He(I) and He(II). Inversion temperature of liquid He is 35 K.

[1] The first noble gas compound prepared was ..... by .....:
(a) Xe PtF_6, Bartlet (b) XeF_2, Bartlet
(c) XeO_3, Bartlet (d) XeF_4, Bartlet

[2] In addition to Xe, the fluorides of noble gas known are:
(a) Ar (b) Kr
(c) Ne (d) He

[3] The number of lone pairs of electrons in XeF_2, XeF_4, XeF_6 and $XeOF_2$ are respectively:
(a) 3, 2, 1, 2 (b) 2, 1, 1, 2
(c) 3, 2, 1, 1 (d) 3, 2, 2, 2

[4] The hybridization of Xe in XeO_2F_2 and shape of XeO_2F_2 respectively as:
(a) sp^3d^2, T-shaped (b) sp^3d, seasaw
(c) sp^3, tetrahedral (d) sp^3d, V-shape

[5] Liquid He is obtained by Joule-Thomson effect at:
(a) 2.19 K (b) 37 K
(c) 40 K (d) 42 K

[6] The wrong statement is:
(a) Perxenates are XeO_6^{4-}
(b) Perxenates are yellow and powerful oxidants
(c) Perxenates are yellow and powerful reductants
(d) Oxidation number of Xe in perxenates is +8

[7] Which reaction does not take place?
(a) $XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$
(b) $XeF_6 + 2NOF \longrightarrow [NO_2]^+[XeF_8]^2$
(c) $2HXeO_4^- + OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$
(d) $XeO_3 + 2H^+ \longrightarrow XeO_2 + H_2O$

[8] Which statement is wrong about He?
(a) He(II) is super fluid having no thermal motion of atoms
(b) He(II) has negligible interatomic forces

(c) He(II) has 600 times more conductance than Cu
(d) He(II) has high surface tension

Comprehension 10 : $KMnO_4$ and $K_2Cr_2O_7$ are strong oxidant in acidified medium:

$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$; $E^\circ_{RP} = +1.51\,V$

$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$; $E^\circ_{RP} = +1.31\,V$

Both are important reagents for analytical chemistry. $KMnO_4$ acts as self indicator in titration against oxalic acid and $FeSO_4$ solution. It also acts as oxidant in alkaline medium as $MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 2OH^-$ as well as in neutral medium as:

$$MnO_4^- + 4H^+ + 3e \longrightarrow MnO_2 + 2H_2O$$

H_2O_2 and O_3 also acts as oxidant as:

$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e$; $E^\circ_{OP} = -0.68\,V$

$2OH^- + H_2O_2 \longrightarrow 2H_2O + O_2 + 2e$; $E^\circ_{OP} = -0.22\,V$

$O_3 + 2H^+ + 2e \longrightarrow O_2 + H_2O$; $E^\circ_{RP} = +2.07\,V$

[1] Addition of Zn to acidified $K_2Cr_2O_7$ solution show change in colour on standing for some time:
(a) Green to blue and then orange and finally blue
(b) Orange to green and then blue and finally green
(c) Orange to blue and then green and finally blue
(d) Orange to yellow and then green and finally blue

[2] The reaction,
$3CrO_4^{3-} + 8H^+ \longrightarrow 2CrO_4^{2-} + Cr^{3+} + 4H_2O$ shows:
(a) oxidation of Cr^{5+}
(b) intermolecular redox
(c) intramolecular redox
(d) disproportionation reaction

[3] $KMnO_4$ dissolution in conc. H_2SO_4 results in explosion due to:
(a) formation of Mn_2O_7 which explodes
(b) formation of MnO_2 which explodes
(c) formation of MnO_4^{2-} which explodes
(d) formation of $MnSO_4$ gives violent reaction

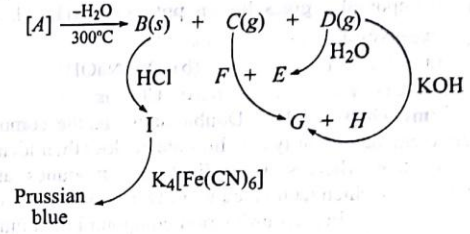
[4] On passing CO_2 to green solution of K_2MnO_4 gives:
(a) purple colour with brown solid
(b) brown colour with yellow solid
(c) purple colour with green solid
(d) pink colour with green solid

[5] Eq. mass of $KMnO_4$ in its reaction with KI in alkaline medium and the I^- are oxidized to:
(a) $M/3, IO_3^-$ (b) $M/6, I_2O_3^-$
(c) $M/1, IO_3^-$ (d) $M/2, I_2$

[6] The best oxidant in acidified medium is:
(a) $KMnO_4$ (b) $K_2Cr_2O_7$
(c) H_2O_2 (d) O_3

[7] Which one is wrong reaction?
(a) $2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$
(b) $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O + K_2SO_4$
(c) $2CrO_4^{2-} + 2H^+ \underset{\text{Base}}{\overset{\text{Acid}}{\rightleftharpoons}} Cr_2O_7^{2-} + H_2O$
(d) $2KOH + 2MnO_2 + 2H_2O + 3O_2 \longrightarrow 2KMnO_4 + 3H_2O_2$

Comprehension 11 : A sequence of reaction has been represented in the given chart. A hydrated salt [*A*] is heated strongly.



(I) *F* is an oxidizing agent which gives colloidal sulphur with H_2S gas and it also gives reddish brown gas with NaCl and H_2SO_4
(II) *C* gives temporary bleaching action with moisture
(III) *G* is a white ppt. and *H* is a green colour substance

[1] The number of hydrated water molecules in [*A*] is:
(a) 7 (b) 10
(c) 5 (d) 2

[2] The nature of compound *C* is:
(a) oxidant
(b) reductant
(c) oxidant and reductant
(d) solvent

[3] Aqueous solution of [*A*] does not acts as reducing agent for:
(a) $AuCl_3$ (b) $HgCl_2$
(c) $KMnO_4$ (d) NO

[4] Prussian blue compound has molecular formula:
(a) $K_2Fe[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$
(c) $KFe[Fe(CN)_6]$ (d) (b) and (c) both

[5] Bleaching action of compound *C* is because of liberation of:
(a) nascent H (b) nascent O
(c) nascent Cl (d) O_3

[6] Compound *F* is:
(a) HNO_3 (b) $K_2Cr_2O_7$
(c) $KMnO_4$ (d) H_2SO_4

[7] Compound *E* is:
(a) H_2SO_4 (b) Cl_2
(c) HNO_3 (d) H_2CO_3

[8] Aqueous solution of compound [*A*] is slightly acidic due to:
(a) hydrolysis of SO_4^{2-}
(b) reducing nature

(c) hydrolysis of Fe^{2+} ion
(d) oxidizing nature

[9] Compound $K_4[Fe(CN)_6]$ is formed when excess KCN reacts with:
(a) *D* (b) *A*
(c) *E* (d) *G* + *H*

[10] When gas '*C*' is heated with *K* metal, it gives:
(a) K_2SO_3 (b) K_2CO_3
(c) K_2SO_4 (d) $K_2SO_3 + K_2S_2O_3$

[11] Compound *I* gives brown ppt. with NH_4OH, which dissolves in:
(a) Dil. HCl (b) Dil. NaOH
(c) Cl_2 gas (d) CO gas

Comprehension 12 : Double salts are the compounds which retain their identity in solid state but lose their identity in solution state whereas. Co-ordination compounds are the complex salts which retain their identity in solid state as well as in solution state. In a co-ordination compound the number of ions or molecules (ligand) attached to the central metal atom or ion (central atom) is beyond the number possible, on the basis of electrovalent or covalent bonding. The extra groups or ions are linked to the metal by co-ordination bonds in which the linked group (*L*) is the donor and the metal (*M*) is the acceptor. *i.e.*, $M \leftarrow L$. Co-ordination compounds are mainly of two types:

(i) Neutral compounds like $[Fe(CO)_5]$.

(ii) Ionic compounds, which consists of ions in which atleast one is a complex ion, *e.g.*, cationic complex $[Ag(NH_3)_2]Cl$ or anionic complex $Na[BH_4]$.

Complex ion: A complex ion is an electrically charged radical which consists of a metal atom or ion surrounded by a group of ions or neutral molecules. For example, $[Cu(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{3-}$.

Ligand : Ligands are defined as molecules or ions having atleast one pair of electrons for donation. Ligands are also known as Lewis bases. There are two main classes of ligands:

(a) Classical or simple donor ligands: These are the ligands which act as electron pair donor to acceptor ions or molecules and form complexes with all types of Lewis acids, metal ions or molecules.

(b) Non-classified ligands, π-bonding or π-acid ligands: These refer to those ligands which form compounds largely with transition metal atoms. This type of interaction is possible due to special properties of both metal and ligand. The metal has *d*-orbitals that can be used in bonding and the ligand has not only donor capacity but also has acceptor orbitals. Ligand can be negative ions, positive ions or neutral molecules.

Co-ordination number : The total number of ligands attached to the central metal atom in co-ordination sphere is called co-ordination number. The species out side the co-ordination number are ionizable species.

[1] How many ions are produced by $[Co(NH_3)_6]Cl_3$ in solution?
(a) 6 (b) 4
(c) 3 (d) 2

[2] Which of the following is non-ionizable?
(a) $[Co(NH_3)_3Cl_3]$ (b) $[Co(NH_3)_4Cl_2]Cl$
(c) $[Co(NH_3)_5Cl]Cl_2$ (d) $[Co(NH_3)_6]Cl_2$

[3] The complex $CoCl_3 \cdot 3NH_3$ ionizes to give:
(a) $2Cl^-$ ions (b) $1Cl^-$ ion
(c) $3Cl^-$ ions (d) zero Cl^- ion

[4] AgCl dissolves in NH_4OH due to the formation of:
(a) $[Ag(NH_4)_2Cl]$ (b) $[Ag(NH_4)_3]Cl$
(c) $[Ag(NH_3)_2]Cl$ (d) $[Ag(NH_3)_2OH]$

[5] Which is not π-bonded complex?
(a) Zeise's salt (b) Ferrocene
(c) Dibenzene chromium (d) Tetraethyl lead

[6] The correct IUPAC name for $K_3[Fe(C_2O_4)_3]$ is:
(a) Potassium trioxalatoferrate (II)
(b) Potassium trioxalatoferrate (I)
(c) Potassium trioxalatoferric (III)
(d) Potassium trioxalatoferrate (III)

[7] The oxidation number, co-ordination number and effective atomic number respectively of central metal atom in $K_2[HgI_4]$ is:
(a) 0, 2, 86 (b) +2, 4, 86
(c) +2, 2, 84 (d) +2, 2, 86

[8] Maximum co-ordination number of a central atom can be:
(a) 2 (b) 4
(c) 6 (d) > 6

[9] The numerical value of '*X*' in $H_XCr(CO)_4$ is:
(a) 0 (b) 1
(c) 2 (d) 3

[10] Which of the following is ambidentate ligand?
(a) NO_2 (b) $C_2O_4^{2-}$
(c) CO (d) N_2

Comprehension 13: The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, + 4 and + 6. XeF_4 reacts violently with water to give XeO_3. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. **(IIT 2007)**

[1] Argon is used in arcwelding because of its:
(a) low reactivity with metal
(b) ability to lower the melting point of metal
(c) flammability
(d) high calorific value

[2] The structure of XeO_3 is:
(a) linear (b) planar
(c) pyramidal (d) T-shaped

[3] XeF_4 and XeF_6 are expected to be:
(a) oxidising (b) reducing
(c) unreactive (d) strongly basic

Comprehension 14 : Ni^{2+} ions form the following complexes.

$$Ni^{2+} \xrightarrow{KCN} \text{Complex I}$$

$$Ni^{2+} \xrightarrow[\text{excess}]{KCl} \text{Complex II}$$

Both the complexes have co-ordination number 4. **(IIT 2008)**

[1] The IUPAC names of the complexes respectively are:
(a) potassium tetracyanonickel(II) and potassium tetrachloronickelate(II)
(b) potassium tetracyanonickelate(II) and potassium tetrachloronickel(II)
(c) potassium tetracyanonickel(II) and potassium tetrachloronickel(II)
(d) potassium tetracyanonickelate(II) and potassium tetrachloronickelate(II)

[2] Which of the following statements is correct?
(a) The cyano complex is diamagnetic and the chloro complex is paramagnetic.
(b) The cyano complex is paramagnetic and the chloro complex is diamagnetic.
(c) Both the complexes are diamagnetic
(d) Both the complexes are paramagnetic

[3] Nickel ion involves:
(a) dsp^2-hybridization in both complexes
(b) sp^3-hybridization in both complexes
(c) dsp^2-hybridization in cyano complex and sp^3 - hybridization in chloro complex
(d) sp^3-hybridization in cyano complex and dsp^2 - hybridization in chloro complex

Comprehension 15 : There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms larger number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorus. **(IIT 2008)**

[1] Among the following, the correct statement is:
(a) Phosphates have no biological significance in humans
(b) Between nitrates and phosphates, phosphates are less abundant in earth's crust
(c) Between nitrates and phosphates, nitrates are less abundant in earth's crust
(d) Oxidation of nitrates is possible in soil

[2] Among the following, the correct statement is:
(a) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional
(b) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(c) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(d) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional

[3] White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a:
(a) dimerization reaction
(b) disproportionation reaction
(c) condensation reaction
(d) precipitation reaction

Comprehension 16. *P*-Amino-*N*, *N*-dimethylaniline is added to a strongly acidic solution of **X**. The resulting solution is treated with a few drops of aqueous solution of **Y** to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of **Y** with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of **Y** with the solution of potassium hexacyanoferrate(III) leads to a brown colouration due to the formation of **Z.** **(IIT 2009)**

[1] The compound **X** is:
(a) $NaNO_3$ (b) NaCl
(c) Na_2SO_4 (d) Na_2S

[2] The compound **Y** is:
(a) $MgCl_2$ (b) $FeCl_2$
(c) $FeCl_3$ (d) $ZnCl_2$

[3] The compound **Z** is:
(a) $Mg_2[Fe(CN)_6]$ (b) $Fe[Fe(CN)_6]$
(c) $Fe_4[Fe(CN)_6]_3$ (d) $K_2Zn_3[Fe(CN)_6]_2$

Comprehension 17 : Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ($CuSO_4 \cdot 5H_2O$), atacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($Cu_2(OH)_2CO_3$). However, 80% of the world copper production comes from the ore chalcopyrite ($CuFeS_2$). The extraction of copper from

chalcopyrite involves partial roasting, removal of iron and self-reduction. **(IIT 2010)**

[1] Partial roasting of chalcopyrite produces:
(a) Cu_2S and FeO (b) Cu_2O and FeO
(c) CuS and Fe_2O_3 (d) Cu_2O and Fe_2O_3

[2] Iron is removed from chalcopyrite as:
(a) FeO (b) FeS
(c) Fe_2O_3 (d) $FeSiO_3$

[3] In self-reduction, the reducing species is:
(a) S (b) O^{2-}
(c) S^{2-} (d) SO_2

Comprehension 18 : When a metal rod *M* is dipped into an aqueous colourless concentrated solution of compound *N*, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate *O*. Addition of aqueous NH_3 dissolves *O* and gives an intense blue solution. **[IIT 2011]**

[1]. The final solution contains :
(a) $[Pb(NH_3)_4]^{2+}$ and $[CoCl_4]^{2-}$
(b) $[Al(NH_3)_4]^{3+}$ and $[Cu(NH_3)_4]^{2+}$
(c) $[Ag(NH_3)_2]^{+}$ and $[Cu(NH_3)_4]^{2+}$
(d) $[Ag(NH_3)_2]^{+}$ and $[Ni(NH_3)_6]^{2+}$

[2]. The compound *N* is :
(a) $AgNO_3$ (b) $Zn(NO_3)_2$
(c) $Al(NO_3)_3$ (d) $Pb(NO_3)_2$

[3]. The metal rod *M* is :
(a) Fe (b) Cu
(c) Ni (d) Co

Comprehension 19 : The reactions of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, *P* and *Q*, respectively. The Cl_2 gas reacts with SO_2 gas, in presence of charcoal, to give a product *R*. *R* reacts with white phosphorus to give a compound *S*. On hydrolysis, *S* gives an oxoacid of phosphorus, *T*. **[JEE (Advanced) II 2013]**

[1]. *R*, *S* and *T*, respectively, are :
(a) SO_2Cl_2, PCl_5 and H_3PO_4
(b) SO_2Cl_2, PCl_3 and H_3PO_3
(c) $SOCl_2$, PCl_3 and H_3PO_2
(d) $SOCl_2$, PCl_5 and H_3PO_4

[2]. *P* and *Q*, respectively, are the sodium salts of :
(a) hypochlorus and chloric acids
(b) hypochlorus and chlorus acids
(c) chloric and perchloric acids
(d) chloric and hypochlorus acids

Comprehension 20 : An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (*P*) and a filtrate (*Q*). The precipitate *P* was found to dissolve in hot water. The filtrate (*Q*) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (*R*) with H_2S in an ammoniacal medium. The precipitate *R* gave a coloured solution (*S*), when treated with H_2O_2 in an aqueous NaOH medium. **[JEE (Advanced) II 2013]**

[1]. The coloured solution *S* contains :
(a) $Fe_2(SO_4)_3$ (b) $CuSO_4$
(c) $ZnSO_4$ (d) Na_2CrO_4

[2]. The precipitate *P* contains :
(a) Pb^{2+} (b) Hg_2^{2+}
(c) Ag^{+} (d) Hg^{2+}

SOLUTIONS

Comprehension 1

[1] (c) Galena (PbS) is first converted to PbO.
$\Delta G = -$ ve at high temperature for reduction of PbO to Pb

[2] (a) $\Delta G = -$ ve for reduction of ZnO to Zn at high temperature

[3] (a) Alkali metals cannot be reduced from their aqueous salt solution. Also

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

$$2MgO + Si \xrightarrow{1000°C} 2Mg + SiO_2$$

[4] (d) MgO is used to remove acidic impurities such as P_4O_{10} in basic furnace lining. Nitrates of all metals are water soluble and thus metals never found in form of nitrates.

[5] (b) These are facts

[6] (a) Acidic flux are used to remove basic impurities.

Comprehension 2

[1] (b) $H_2 \xrightarrow[\text{high temp}]{\text{electric arc}} 2H;\ \Delta H = 104.0$ kcal

[2] (a) Follow answer [1]

[3] (c) Moist H_2 cannot be dried by H_2SO_4;

$$H_2SO_4 + H_2 \longrightarrow SO_2 + 2H_2O$$

[4] (a) H_2O_2 is more associated liquid, diamagnetic and form blue CrO_5 with acidified $K_2Cr_2O_7$

$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O$$

[5] (a) $\% = \frac{17}{56} \times \text{Volume strength} = \frac{17}{56} \times 30 = 9.105$

[6] (b) $\text{Normality} = \frac{\text{Volume strength}}{5.6}$

$$= \frac{56}{17} \times \frac{\%}{5.6} = \frac{56}{17} \times \frac{6.07}{5.6} = 3.57$$

[7] (a) NH_3 and HCl combines only in presence of moisture.

Comprehension 3

[1] (b) The passage of current in the system is due to electronic conduction.

[2] (a) Li^+ is smaller cation. Smaller is cation more is hydration.

[3] (c) Sr^{2+} has more charge, $Ca(OH)_2$ is more soluble than $Ba(OH)_2$ in water. The reducing nature depends upon E°_{OP} values in acidic and alkaline solution.

[4] (d) Alkali metal has +1 oxidation state $Cs^+Cl_3^-$, $Cs^+BrCl_2^-$; density of K, Na are 0.86, 0.97 respectively Li forms Li_2O and Na form Na_2O_2, ash contains Mg_3N_2 and MgO

[5] (b) These all are facts

[6] (a) Bicarbonates of alkaline earth metals are known only in solution state.

[7] (d) Density order

Be	Mg	Ca	Sr	Ba	Ra
1.84	1.74	1.55	2.54	3.75	6.00 g / cm^3

[8] (c) $4Be(NO_3)_2 \xrightarrow{125°C} [Be_4O(NO_3)_6] + N_2O_5$

[9] (d) Mg_2C_3 is magnesium allylide containing C_3^{4-} ion (allylide ion)

Comprehension 4

[1] (a) $NaBH_4$ and $LiAlH_4$ are anionic hydrides. Al does not form a series of polymeric hydride. Only one hydride of Al as $(AlH_3)_n$ is known. $B(OH)_3$ is acid. AlX_3 exists as dimer.

[2] (a) $H_3BO_3 + NaOH \longrightarrow NaB(OH)_4 \longrightarrow NaBO_2 + 2H_2O$

[3] (d) Rest all are facts about B_2H_6.

[4] (a) Borax is $Na_2B_4O_7 \cdot 10H_2O$

[5] (a) BF_3 is least acidic due to back bonding.

Comprehension 5

[1] (a) CO has highest bond energy among all diatomic molecules.

[2] (a) CO reacts with alkali to form salt. CO is π-electron pair acceptor in $Ni(CO)_4$

[3] (d) $4Na + CO_2 \longrightarrow 2Na_2O + C$

[4] (d) Asphyxia is due to CO which combines with haemoglobin to form cherry coloured carbon haemoglobin complex and reduces the capacity of O_2 to be absorbed.

[5] (a) CO and N_2 are isoelectronic. No doubt bond energy of CO > bond energy of N_2 but because of lower nuclear charge on carbon (compared to N or O), the lone pair on carbon is loosely held in CO.

[6] (a) $H_2C_2O_4 \xrightarrow{H_2SO_4} H_2O + CO + CO_2$

$$HCOOH \xrightarrow{H_2SO_4} H_2O + CO$$

Comprehension 6

[1] (d) White P is soluble in CS_2 but red P is not.

[2] (c) Black phosphorus is most stable form but for P_w, $H° = 0$ has been assumed.

[3] (a) The basic character of hydrides decreases from N to Bi because of increasing size of central atom and thus electron density of lone pair is diffused over larger region. Stronger is base, weaker is its conjugate acid.

[4] (d) The reducing character of hydrides increases from N to Bi because of decrease in M—H bond strength with decrease in electronegativity from N to Bi.

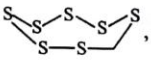
[5] (a) The decrease in bond angle down the group is due to increasing size of central atom having lone pair which reduces repulsion between bond pair-lone pair.

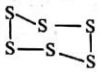
NH_3	PH_3	AsH_3	SbH_3
106.5°	93.5°	91.5°	90.3°

[6] (d) $3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$

Comprehension 7

[1] (c) It is a fact.

[2] (b) S_8-Rhombic is  ,

cyclo-S_6 is 

[3] (b) $HO_3S—S_{(n-2)}—SO_3H$ [$(n-1)$ only S—S bonds]

[4] (c) S forms SO, SO_2, SO_3; Te forms TeO, TeO_2 and TeO_3; Po forms PoO, PoO_2, PoO_3, Se forms SeO_2, SeO_3

[5] (c) N has no *d*-orbitals.

[6] (d) In this sulphur powder is formed. Note that H_2O or medium is necessary for getting colloidal sulphur.

[7] (b) In both S is sp^2-hybridised.

Comprehension 8

[1] (b) $PCl_3 + 3H_2O \longrightarrow \underset{\text{Oxo-acid}}{H_3PO_3} + 3HCl$;

$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$

[2] (d) $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$

[3] (c) $SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$

[4] (a) $PbCl_2$ is stable and known.

[5] (c) PbI_4 has Pb^{4+} (strong oxidant) and I^- (strong reductant) and thus does not exist.

[6] (a) $(CN)_2 + NaOH \longrightarrow NaOCN + HCN$

[7] (a) $2NaCN + H_2SO_4 \longrightarrow 2HCN + Na_2SO_4$

[8] (c) $NaCN + H_2O \longrightarrow NaOH + \underset{\text{Weak acid}}{HCN}$;

$NaF + H_2O \longrightarrow NaOH + \underset{\text{Weak acid}}{HF}$;

HCl., HBr, HI are strong acids

[9] (a) $2Na + (CN)_2 \longrightarrow 2NaCN$

[10] (c) $NaN_3 + H_2SO_4 \longrightarrow NaHSO_4 + N_3H$

[11] (d) Heptavalent nature of halogen (iodine) is shown in IF_7.

[12] (b) Rest all are pseudo halide.

[13] (b) $KICl_2 \longrightarrow KCl + ICl$ (smaller halogen forms anionic part)

[14] (a) HF exists as H_2F_2 and forms KHF_2 and KF.

[15] (d) These are characteristics of inter halogen compounds.

Comprehension 9

[1] (a) On the formation of $O_2^+ [PtF_6]^-$, Bartlet prepared $Xe^+ [PtF_6]^-$

[2] (b) KrF_2 is known.

[3] (a) XeF_2, XeF_4, XeF_6 and $XeOF_2$ have sp^3d (linear), sp^3d^2 (square planar), sp^3d^3 (pentagonal pyramidal) and sp^3d (T-shaped) with 3, 2, 1 and 2 lone pairs respectively.

[4] (b) sp^3d-hybridisation with one lone pair at equatorial position and thus sea saw structure.

[5] (a) Ti of He is 35 K; For cooling by J.T. effect $T_{He} < T_I$

[6] (c) XeO_6^{4-} have Xe in highest oxidation state of +8 and can act as oxidant only.

[7] (d) Rest all are correct.

[8] (d) He (II) has flat maniscus due to low surface tension as intermolecular forces are negligible.

Comprehension 10

[1] (b)

$$Zn \longrightarrow Zn^{2+} + 2e$$

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 14H^+ + 6e \longrightarrow \underset{\text{Green}}{2Cr^{3+}} + 7H_2O$$

$$\underset{\text{Green}}{Cr^{3+}} + e \longrightarrow \underset{\text{Blue}}{Cr^{2+}}$$

$$4Cr^{2+} + O_2 + 4H^+ \longrightarrow \underset{\text{Green}}{4Cr^{3+}} + 2H_2O$$

[2] (d) $Cr^{5+} + 2e \longrightarrow Cr^{3+}$ and $Cr^{5+} \longrightarrow Cr^{6+} + e$

[3] (a) $2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + Mn_2O_7 + H_2O$

$$2Mn_2O_7 \xrightarrow{\text{Explodes}} 4MnO_2 + 3O_2$$

[4] (a) $CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$3MnO_4^{2-} + 4H^+ \longrightarrow \underset{\text{Purple}}{2MnO_4^-} + \underset{\text{Brown solid}}{MnO_2} + 2H_2O$$

[5] (a) $2KMnO_4 + KI + H_2O \longrightarrow KIO_3 + MnO_2 + 2KOH$

[6] (d) E°_{RP} for $KMnO_4$ or $K_2Cr_2O_7$, H_2O_2 and O_3 are +1.51 V, +1.31 V, +0.68 V and +2.07 V. More is E°_{RP} more is the tendency to get reduced and more is oxidising power.

[7] (d) The $KMnO_4$ oxidises H_2O_2 as E°_{RP} of $KMnO_4$ is more

$$2KMnO_4 + 3H_2O_2 \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3O_2$$

Comprehension 11

The reaction sequence is:

$$\underset{[A]}{2FeSO_4 \cdot 5H_2O} \xrightarrow{-5H_2O} \underset{[B]}{Fe_2O_3}(s) + \underset{[C]}{SO_2}(g) + \underset{[D]}{SO_3}(g)$$

$$\underset{[B]}{Fe_2O_3} + 6HCl \longrightarrow \underset{[I]}{2FeCl_3} + 3H_2O$$

$$\underset{[I]}{4FeCl_3} + 3K_4Fe(CN)_6 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

$$\underset{[C]}{3SO_2} + \underset{(F)\text{ Oxidant}}{K_2Cr_2O_7} + \underset{[E]}{H_2SO_4} \longrightarrow \underset{(G)\text{ White}}{K_2SO_4} + \underset{(H)\text{ Green}}{Cr_2(SO_4)_3} + H_2O$$

$$\underset{[D]}{SO_3} + H_2O \longrightarrow \underset{[E]}{H_2SO_4}$$

$$\underset{[C]}{3SO_2} + 4K \longrightarrow K_2SO_3 + K_2S_2O_3$$

$$\underset{[D]}{SO_3} + 2KOH \longrightarrow \underset{[G]}{K_2SO_4} + H_2O$$

[1] (a) The compound is $FeSO_4 \cdot 7H_2O$

[2] (c) SO_2 acts as oxidant and reductant both as ox no. of S is +4 (between) +6 (max) and −2 (min)

[3] (d) Fe^{2+} reduces Au^{3+} to Au, Hg^{2+} to Hg_2^{2+}, Mn^{7+} to Mn^{2+}. It absorbs NO to form $FeSO_4 \cdot NO$.

[4] (b) Prussian blue is $Fe_4[Fe(CN)_6]_3$

[5] (a) $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$

[6] (b) Follow sequence of reaction.

[7] (a) do

[8] (c) $Fe^{2+} + 2H_2O \longrightarrow Fe(OH)_2 + \underset{\text{Strong acid}}{4H^+}$

[9] (b) $FeSO_4 + \underset{\text{Excess}}{6KCN} \longrightarrow K_4Fe(CN)_6 + K_2SO_4$

[10] (d) Follow sequence of reaction.

[11] (a) $\underset{[I]}{FeCl_3} + NH_4OH \longrightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3} \xrightarrow{HCl} \text{Soluble}$

Comprehension 12

[1] (b) $[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$

[2] (a) All ligands (NH_3 and Cl) are in side co-ordination sphere.

[3] (d) Co^{2+} has six co-ordination number thus it is $[Co(NH_3)_3Cl_3]$.

[4] (c) $AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$

[5] (d) Tetra ethyl lead $[(C_2H_5)_4Pb]$ has no π-bonding in it.

[6] (d) Follow IUPAC rule.

[7] (b) $K_2[HgI_4] \rightleftharpoons 2K^+ + [HgI_4]^{2-}$

$\therefore$ Oxidation no. of $Hg^{2+} = +2$, no. of ligands = 4.

EAN = Atomic number of Hg − electrons lost in the formation of $Hg^{2+} + 4 \times$ Number of electrons in co-ordination $= 80 - 2 + 4 \times 2 = 86$

[8] (d) It is a fact.

[9] (b) In carbonyls, the effective atomic number = Atomic number of next noble gas

EAN of Cr = 36 [EAN of Cr]

$\therefore$ In $H_X\ Cr(CO)_4$; $X + 27 + 4 \times 2 = 36$

$\therefore \quad X = 1$

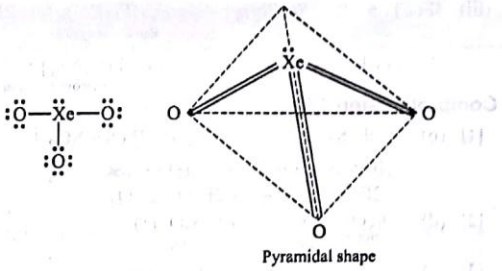
[10] (a) An ambidentate ligand possesses two donor atoms, but in forming complex only one atom is involved.

$\leftarrow NO_2$ or $\leftarrow ONO$

Comprehension 13

[1] (a) Argon is used to provide an inert atmosphere in arc welding.

[2] (c) XeO_3 is sp^3-hybridized with one lone pair on Xe. Hence, these electrons acquire tetrahedral orientations. The shape of the molecule is pyramidal.



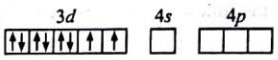
Pyramidal shape

[3] (a) XeF_4 and XeF_6 are oxidising agents. These can oxidise H_2 to H^+, Cl^- to Cl_2, I to I_2 and Ce(III) to Ce(IV).

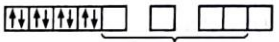
Comprehension 14

[1] (d) The complexes are $K_2[Ni(CN)_4]$ and $K_2[Ni(Cl)_4]$. Hence, their names are potassium tetracyanonickelate(II) and potassium tetrachloro nickelate(II).

[2] (a) $_{28}Ni^{2+}(3d^8)$



Ni^{2+} in cyano complex



dsp^2-hybridization

Ni^{2+} in chloro complex

sp^3-hybridization

[3] (c) See solution of [2].

Comprehension 15

[1] (c) Between nitrates and phosphates, nitrates are less abundant in earth's crust because all nitrates are soluble in water.

[2] (c) NH_3 is a better electron donor than PH_3 because the lone pair of electrons occupies sp^3 orbital formed from the more compact $2s$ and $2p$ orbitals as compared to $3s$ and $3p$ orbitals of phosphorus in PH_3.

[3] (b) The reaction of

$$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$$

The oxidation state of phosphorus in P_4, PH_3 and $H_2PO_2^-$ are 0, −3 and +1, respectively, thus, the reaction is disproportionation reaction.

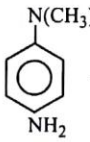
Comprehension 16

[1] (d)

[2] (c)

[3] (b)

(i) $\underset{(X)}{Na_2S} + 2H^+ \longrightarrow 2Na^+ + H_2S$

(ii) 

$+ H_2S + 6Fe^{3+} \longrightarrow 6Fe^{2+} + NH_4^+ + 4H^+$ + methylene blue (a dye)

(iii) $4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Ferri ferrocyanide}}{Fe_4[Fe(CN)_6]_3} + 2KCl$

Or $FeCl_3 + K_3[Fe(CN)_6] \longrightarrow \underset{(Z)\text{ Brown colour}}{Fe[Fe(CN)_6]} + 3KCl$

Comprehension 17

[1] (b) $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2\uparrow$

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

[2] (d) $\underset{\text{gangue}}{FeO} + \underset{\text{flux}}{SiO_2} \longrightarrow \underset{\text{slag}}{FeSiO_3(l)}$

[3] (c) $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

$\underset{\text{Reductant}}{S^2} \longrightarrow \underset{\text{Oxidant}}{S^{4+}}$

Comprehension 18

[1] (c)

[2] (a)

[3] (b)

The paragraph given and the problems asked suggests that the following changes are possible.

$\underset{(M)}{Cu} + 2\underset{(N)}{AgNO_3} \longrightarrow \underset{\text{(Blue)}}{Cu(NO_3)_2} + 2Ag$

On addition of aqueous NaCl to blue aqueous solution a white precipitate of AgCl is formed.

$AgNO_3 + NaCl \longrightarrow \underset{\text{White}}{AgCl\downarrow} + NaNO_3$

As the blue solution contains $Cu(NO_3)_2$ and left $AgNO_3$, addition of NH_3 to this solution, AgCl and $Cu(NO_3)_2$ form complexes of $[Ag(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$

$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ + Cl^-$

$Cu(NO_3)_2 + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + 2NO_3^-$

Comprehension 19

[1] (a)

[2] (a) $\underset{\text{cold dil.}}{Cl_2 + NaOH} \longrightarrow \underset{(P)}{NaCl + NaOCl}$

$\underset{\text{hot conc.}}{3Cl_2 + 6NaOH} \longrightarrow \underset{(Q)}{5NaCl + NaClO_3 + 3H_2O}$

Sodium hypoclorite (NaOCl) is salt of hypochlorous acid (HOCl)

Sodium chlorate ($NaClO_3$) is salt of chloric acid ($HClO_3$)

$Cl_2 + SO_2 \xrightarrow{\text{charcoal}} \underset{(R)}{SO_2Cl_2}$

$10SO_2Cl_2 + P_4 \longrightarrow \underset{(S)}{4PCl_5} + 10SO_2$

$PCl_5 + 4H_2O \longrightarrow \underset{(T)}{H_3PO_4} + 5HCl$

Comprehension 20

[1] (d) Cr^{3+} does not give precipitate with dil. HCl, also does not give precipitate with H_2S in acid medium but gives green coloured precipitate with H_2S in alkaline medium of $Cr(OH)_3$, The green precipitate being soluble in NaOH which on reacting with H_2O_2 gives yellow coloured solution of Na_2CrO_4.

$Cr(OH)_3 + 2NaOH + H_2O_2 \longrightarrow \underset{\substack{(S)\\ \text{green colour}}}{Na_2CrO_4} + 3H_2O$

[2] (a) Pb^{2+} gives precipitate with dil HCl, which is soluble in hot water but insoluble in cold water. Among Pb^{2+}, Hg_2^{2+}, Ag^+, Hg^{2+}only Pb^{2+}

also give precipitate with dil. H^+ / H_2S

$Pb^{2+} + H_2S \xrightarrow{H^+} \underset{\substack{(P)\\ \text{precipitate}}}{PbS} + 2H^+$

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (**S**) and explanation (**E**) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) **S** is correct but **E** is wrong
(b) **S** is wrong but **E** is correct
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**

1. S : F atom has a less negative electron affinity than Cl atom.
E : Additional electrons are repelled more effectively by 3*p* electrons in Cl atom than by 2*p* electrons in F.

2. S : The first ionization energy of Be is greater than that of B.
E : 2*p* orbital is lower in energy than 2*s*.

3. S : Although PF_5, PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.
E : Phosphorus has lower electronegativity than nitrogen.

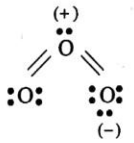
4. S : The alkali metal can form ionic hydrides which contain the H^-.
E : The alkali metals have low electronegativity, their hydrides conduct electricity when fused and liberate hydrogen at the anode.

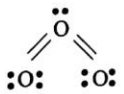
5. S : F—F bond in F_2 molecule is strong.
E : F-atom is small in size.

6. S : $Al(OH)_3$ is amphoteric in nature.
E : Al—O and O—H bonds can be broken with equal ease in $Al(OH)_3$.

7. S : Sulphate is estimated as $BaSO_4$ and not as $MgSO_4$.
E : Ionic radii of Mg^{2+} is smaller than Ba^{2+}.

8. S : The electronic structure of O_3 is



E :  structure is not allowed because octet around O cannot be expanded.

9. S : LiCl is predominantly a covalent compound.
E : Electronegativity difference between Li and Cl is too small.

10. S : HNO_3 is a stronger acid than HNO_2.
E : In HNO_3 there are two nitrogen to oxygen bonds where as in HNO_2 there is only one.

11. S : A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow ppt. of CdS on passing H_2S.
E : Solubility product of CdS is more than that of NiS.

12. S : To a solution of potassium chromate if a strong acid is added it changes its colour from yellow to orange.
E : The colour changes is due to the oxidation of potassium chromate.

13. S : A very dilute solution of Cd^{2+} and Ni^{2+} gives yellow ppt. on passing H_2S.
E : Solubility product of CdS is less than of NiS.

14. S : NH_3 can be dried by $CaCl_2$.
E : $CaCl_2$ is a good dehydrating agent.

15. S : Both H_3PO_4 and H_3PO_3 possess the same number of hydrogen atoms, but H_3PO_4 is tribasic acid and H_3PO_3 is dibasic.
E : In oxyacids only those H atoms are replaceable which are attached to O atom.

16. S : HF forms two series of salts but HCl not.
E : F atom is more electronegative than Cl atom.

17. S : Among alkali metal cations, $Li^+(aq)$ has highest electrical conductance.
E : $Li^+(aq)$ is largest alkali metal cation because of greater degree of hydration.

18. S : CO is neutral molecule.
E : CO forms salt with NaOH at high *P* and high *T*.

19. S : LiCl is predominantly covalent compound.
E : Electronegativity difference between Li and Cl is too small.

20. S : HNO_3 is a stronger acid than HNO_2.
E : In HNO_3, there are two N—O bonds whereas in HNO_2 there is only one.

21. S : Sulphate is estimated as $BaSO_4$ and not $MgSO_4$.
E : Ionic radius of Mg^{2+} is smaller than that of Ba^{2+}.

22. S : Iodine does not displace Cl_2 or Br_2 from their chloride and bromides but displaces them from their oxy salts.
E : E°_{OP} of $I_2 > E^\circ_{OP}$ of Cl_2 or Br_2.

23. S : H_2 molecule is more stable than He—H molecule.
E : The antibonding electron in He—H molecule decreases the bond order and thereby the stability.

24. S : Super oxide ion is paramagnetic whereas peroxide ion is diamagnetic.

E : Super oxide ion $[O{=}O]^-$ has one unpaired electron whereas peroxide ion $[O{=}O]^{2-}$ has no unpaired electron.

25. S : Graphite is thermodynamically more stable than diamond.

E : $C_D \longrightarrow C_G$; $\Delta H = -1.9$ kJ/mol.

26. S : PCl_3 $\left[\begin{array}{c} Cl \\ | \\ Cl-P-Cl \end{array}\right]$ on hydrolysis gives

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-OH \text{ and not } HO-\underset{\underset{OH}{|}}{P}-OH$$

E : H_3PO_3 exists in two tautomeric forms:

$$HO-\underset{\underset{OH}{|}}{P}-OH \rightleftharpoons HO-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{P}}-OH$$ and the latter is more stable due to resonance.

27. S : On throwing aluminium powder in air, it catches fire.

E : $2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3$; $\Delta H = -$ve.

The reaction is highly exothermic and once started continues to develop fire.

28. S : Equivalent mass of H_2SO_4 in lead storage battery is 49.

E : In lead storage battery, H_2SO_4 acts both as oxidant and reductant.

29. S : Magnesium and oxygen do not react at 0°C but on heating to 200°C, an exothermic reaction occurs.

E : The heat is used to cross the energy barrier of the reaction of Mg and oxygen.

30. S : Sometimes a white precipitate is obtained when a solution is prepared in conc. HCl and then diluted, even if first group is absent.

E : This is due to insoluble nature of $PbCl_2$.

31. S : Ba^{2+} ion is poisonous, yet $BaSO_4$ is given to patient prior to taking stomach X-ray.

E : $BaSO_4$ is extremely insoluble and does not pass from digestive systems into circulatory system.

32. S : C_3O_2 has linear structure.

E : Each C atom in C_3O_2 is *sp*-hybridised.

33. S : Phosphine is prepared in an inert atmosphere of CO_2 and H_2.

E : Phosphine is highly inflammable in air.

34. S : During diazotisation, excess of HCl is used with $NaNO_2$.

E : Excess of HCl prevents the hydrolysis of diazonium salt.

35. S : The formula of iron (III) ferro-cyanide is $Fe_4[Fe(CN)_6]_3$.

E : 860 g of iron (III) ferro-cyanide contains 7 atoms of iron.

36. S : Li resembles with Mg.

E : Both have nearly same charge/size ratio.

37. S : Boron does not show univalent nature but unipositive nature of thallium is quite stable.

E : Inert pair effect predominates in thallium.

38. S : $BeCl_2$ cannot be easily hydrolysed.

E : $BeCl_2$ is electron deficient compound.

39. S : The melting point of LiCl is lower than that of NaCl.

E : LiCl has predominantly covalent nature, whereas NaCl is ionic.

40. S : Pb^{4+} is easily reduced to Pb^{2+}.

E : Pb^{4+} is strong oxidant.

41. S : LiCl is soluble in organic solvent.

E : LiCl is a covalent compound.

42. S : A fresh stain of iodine is washed with hypo solution.

E : Hypo is a bleaching agent and it oxidises I_2 to I^-.

43. S : Iodine is sparingly soluble in water but fairly soluble in KI.

E : Iodine is non-polar in nature.

44. S : H_2SO_4 is more viscous than water.

E : In H_2SO_4, S has highest oxidation state.

45. S : White phosphorus is less stable whereas red phosphorus is more stable.

E : White phosphorus exist as individual P_4 having more strained geometry while red phosphorus has P_4 tetrahedron structure linked together.

46. S : Iodine is liberated when KI is added to Cu^{2+} ions but Cl_2 is not liberated when KCl is added to Cu^{2+} ions.

E : The reducing power of I^- is more than Cl^-.

47. S : Sulphur (IV) oxide can act as reducing as well as oxidising agent.

E : S in SO_2 has its oxidation number +4 lying between –2 (minimum) and +6 (maximum).

48. S : $HgCl_2$ and $SnCl_2$ exist together in an aqueous solution.

E : $SnCl_2$ is a strong reducing agent.

49. S : $AgNO_3$ produces a black stain on the skin.

E : $AgNO_3$ is a dye.

50. S : The surface of aluminium metal get tarnished when exposed to air for long time.

E : The aluminium metal is coated with Al_2O_3.

51. **S :** Sodium fire in laboratory cannot be extinguished by pouring water.
E : Sodium reacts with water violently.

52. **S :** Ores of metals are not found as nitrates.
E : All the metal nitrates are insoluble in water.

53. **S :** The IUPAC name of $K_3[Cr(CN)_6]$ is potassium hexacyanochromate (III).
E : It is an anion complex.

54. **S :** $Ti(H_2O)^{3+}$ is coloured ion while $Sc(H_2O)_6^{3+}$ is colourless.
E : Ti^{3+} has $3d^1$ configuration whereas Sc^{3+} has no unpaired electron and thus *d-d* transition is not possible.

55. **S :** Mn_2O_7 is acidic oxide of manganese.
E : Mn_2O_7 reacts with water to give $HMnO_4$.

56. **S :** $FeSO_4(aq)$ is not a primary standard.
E : In aqueous medium Fe^{2+} ions are not present.

57. **S :** $[Al(NH_3)_6]^{3+}$ does not exist in aqueous solution.
E : Al^{3+} being smaller ion possesses high degree of hydration.

58. **S :** H_2S can be dried by H_2SO_4.
E : A basic drying agent absorbs moisture from basic substance and an acidic drying agent is needed for acidic substance to be dried.

59. **S :** $BeCl_2$ is linear but $SnCl_2$ is angular.
E : $BeCl_2$ has *sp*-hybridised Be atom whereas $SnCl_2$ has sp^3-hybridised Sn atom.

60. **S :** NH_3 is more basic than PH_3 as well as H_2O is less acidic than H_2S.
E : Basic character of hydrides decreases along the period as well as down the group.

61. **S :** H_2 exists in two isomeric forms known as ortho and para forms.
E : The ortho and para H_2 differ in the spin of their electron.

62. **S :** Helium (II) is unique liquid with properties of gas.
E : He (II) is super fluid having so low energy that thermal motion of atom do not take place, however, interatomic forces are also so weak that it does not occupy solid state.

63. **S :** Fe_3O_4 is paramagnetic at room temperature and becomes ferrimagnetic at 850 K.
E : The randomisation of spin takes place with temperature.

64. **S :** In fused state, calcium chloride can not be used to dry alcohol or NH_3.
E : $CaCl_2$ is not a good dessicant.

65. **S :** Lead and bismuth are purified by liquation method.
E : Lead, tin and bismuth have low m.pt. as compared to impurities.

66. **S :** $NH_2—NH_2$ is a chelating ligand.
E : A chelating ligand must have two or more lone pairs of electrons at such a distance that it may from suitable strain free jumps at the metal ions.

67. **S :** Order of H—*X* bond length : HI > HBr > HCl > HF
Order of dipole moment : HF > HCl > HBr > HI.
E : The increase in partial charge from F to I predominates over the increase in bond length from HF to HI.

68. **S :** The stability order for Co^{2+} complex with halides shows the order $Cl^- > Br^- > I^-$ but for Pt^{2+} complex it is $I^- > Br^- > Cl^-$.
E : A blue coloured complex $K[CoCl_4]$ on treatment with $HgCl_2$ gives another blue coloured complex.

69. **S :** Electrolysis of $CaH_2(s)$ is made in eutectic mixture of LiCl/KCl.
E : $CaH_2(s)$ decomposes on heating before its melting.

70. **S :** Nitrates ores are less abundant in the earth crust.
E : Nitrates of all the metal are water soluble.

71. **S :** P_2O_5 is acidic anhydride of many oxoacids of phosphorus.
E : H_3PO_3 is stronger acid than H_3PO_4.

72. **S :** $:NH_2\overset{\bullet\bullet}{N}H_2$ although possesses two electron pair for donation but does not act as chelating agent.
E : The coordination of $NH_2 \cdot NH_2$ leads to a highly unstable three membered strained ring.

73. **S :** $Al(NH_3)_6^{3+}$ exists in aqueous solutions.
E : Al^{3+} ion has lesser tendency for NH_3 than H_2O and thus ligand NH_3 is repaced by H_2O.

74. **S :** A small quantity of H_2SO_4 is added during preparation of standard solution of ferrous ammonium sulphate.
E : It Prevents hydrolysis of sulphate ions and provides a clear solution.

75. **S :** CrO_4^{2-} is yellow coloured anion.
E : The colour is due to *d-d* transition.

76. **S :** Cu^+ is more stable than Cu^{2+} in solid state, whereas $Cu^+_{aq.}$ is less stable than $Cu^{2+}_{aq.}$.
E : $CuI_2(aq.)$ is less stable than $Cu_2I_2(aq.)$ but $CuCl_2(aq.)$ is more stable than $Cu_2Cl_2(aq.)$.

77. **S :** Between $SiCl_4$ and CCl_4, only $SiCl_4$ reacts with water. **(IIT 2001)**
E : $SiCl_4$ is ionic and CCl_4 is covalent.

78. **S :** In water, orthoboric acid behaves as a weak monobasic acid. **(IIT 2007)**
E : In water, orthoboric acid acts as a proton donor.

79. **S :** Boron always forms covalent bond. **(IIT 2007)**

E : The small size of B^{3+} favours formation of covalent bond.

80. **S :** Alkali metals dissolved in liquid ammonia to give blue solutions. **(IIT 2007)**

E : Alkali metals in liquid ammonia give solvated species of the type $[M(NH_3)_n]^+$ (M = alkali metals).

81. **S :** $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.

E : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons. **(IIT 2008)**

82. **S :** The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.

E : Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry. **(IIT 2008)**

83. **S :** Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.

E : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'. **(IIT 2008)**

ANSWERS (Statement Explanation Problems)

1. (a) It is due to higher interelectronic repulsion forces. The additional electrons are repelled more effectively by $2p$-electrons in F-atom (due to small size) than by $3p$-electrons in Cl-atom.

2. (a) Statement is correct but explanation is incorrect because a large amount of energy is required for the removal of $2s$ electrons in comparison to $2p$ electron, *i.e.*, energy level of $2s$ is less than $2p$-orbital.

3. (d) Both are the facts.

4. (d) Both are the facts.

5. (c) Explanation is correct explanation.

6. (a) Statement is correct but explanation is incorrect.

7. (d) Both are correct but the explanation is not the correct explanation.

8. (d) Both are correct.

9. (a) Statement is correct but explanation is incorrect.

10. (a) $H—O—N\begin{matrix}O\\O\end{matrix}$; $H—O—N=O$

11. (a) Statement is correct but explanation is wrong.

$$K_{sp} \text{ of NiS} > K_{sp} \text{ of CdS}$$

12. (a) $\underset{\text{yellow}}{CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O$

13. (c) $[Cd^{2+}][S^{2-}] > K_{sp}$ CdS, then only CdS can give yellow precipitate. The dissociation of H_2S provides appreciable $[S^{2-}]$ to precipitate CdS. NiS can be precipitated only in alkaline medium because K_{sp} of NiS is high.

14. (b) No doubt $CaCl_2$ is a dehydrating agent but it reacts with NH_3 and thus it cannot be used by drying NH_3, NH_3 can be dried by CaO.

15. (c) $HO—\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{P}}—OH$ and $HO—\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}—OH$

16. (d) HF forms $NaHF_2$ and NaF salts due to its dimerised formula H_2F_2 on account of H-bonding. No doubt F is more electronegative than Cl.

17. (b) Explanation is correct and thus, conductance of Li^+ is lowest among alkali metal cations.

18. (d) CO is neutral but the only reaction where it acts as acid is $CO + NaOH \xrightarrow{P,T} HCOONa$.

19. (a) LiCl is predominantly covalent because small cation (Li^+) causes more polarisation of Cl^- to develop covalent nature.

20. (a) N in HNO_3 has higher oxidation state (+5) than in HNO_2(+3). More is oxidation number of central atom in oxyacid, more is acidic nature.

21. (d) $MgSO_4$ is water soluble; $BaSO_4$ is insoluble, thus estimation can be made by $BaSO_4$. The insoluble nature of $BaSO_4$ is due to its higher lattice energy inspite of larger size of Ba^{2+}.

22. (d) $2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$

$KCl + I_2 \longrightarrow$ No reaction $\longrightarrow E^\circ_{op}$ of Cl < E°_{op} of I;

Thus,

I will oxidise and Cl will reduce.

23. (c) Bond order for $H_2 = 1$

Bond order for $He—H = \frac{1}{2}$

24. (c) $[O=O]^-$ has M.O. configuration

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \sigma 2p^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^2 \pi^* 2p_y^1$$

$[O=O]^{2-}$ has M.O. configuration

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \sigma 2p^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^2 \pi^* 2p_y^2$$

25. (c) Graphite form of carbon possess lower energy level.

26. (c) Explanation is correct reason for statement.

27. (c) Explanation is correct reason for statement.

28. (b) Anode:

$Pb(s) + HSO_4^- + H_2O \longrightarrow PbSO_4 + 2e + H_3O^+$

Cathode :

$PbO_2(s) + HSO_4^- + 3H_3O^+ + 2e \longrightarrow PbSO_4(s) + 5H_2O$

Net $Pb + 2HSO_4^- + 2H_3O^+ + PbO_2 \longrightarrow PbSO_4 + 4H_2O$

Thus, $2H_2SO_4$ consumes 2 electrons

$\therefore$ Equivalent mass $= \frac{\text{Molar mass}}{1} = 98$

29. (c) A reaction occurs only when threshold energy barrier is crossed.

30. (a) The white precipitate formed is due to the formation of oxychlorides of Bi or Sb.

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$

31. (c) Explanation is correct reason for statement.

32. (c) C_3O_2 has O=C=C=C=O geometry.

33. (c) Explanation is correct reason for statement.

34. (c) Explanation is correct reason for statement.

35. (a) 1 mole of $Fe_4[Fe(CN)_6]_3$ has 7 g atoms of Fe.

36. (c) Explanation is correct reason for statement.

37. (c) Explanation is correct reason for statement.

38. (d) Salts of strong acid and strong base cannot be hydrolysed. Also $BeCl_2$ is electron deficient compound.

39. (c) Explanation is correct reason for statement.

40. (c) Explanation is correct reason for statement.

41. (c) Explanation is correct reason for statement.

42. (c) Explanation is correct reason for statement.

43. (d) Iodine is more soluble in KI due to complex (KI_3) formation.

44. (d) H_2SO_4 shows extensive H-bonding and thus more viscous.

45. (c) Explanation is correct reason for statement.

46. (c) Explanation is correct reason for statement.

47. (c) Explanation is correct reason for statement.

48. (b) $SnCl_2$ will reduce $HgCl_2$ to Hg_2Cl_2 and finally to Hg.

49. (a) $AgNO_3$ reduces to Ag on coming in contact with protein.

50. (c) Explanation is correct reason for statement.

51. (c) Explanation is correct reason for statement.

52. (a) All the metal nitrates are water soluble.

53. (d) $[Cr(CN)_6]^{3-}$ is an anionic complex.

54. (c) Explanation is correct reason for statement.

55. (c) Explanation is correct reason for statement.

56. (a) A standard solution of $FeSO_4(aq)$ cannot be prepared by simple weighing as some of the Fe^{2+} are readily oxidised to Fe^{3+} ions.

57. (c) Al^{3+} ion being smaller possess high degree of hydration and therefore, the ligand H_2O takes position of NH_3.

$$[Al(NH_3)_6]^{3+} + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 6NH_3$$

58. (b) H_2S (acid) can not be dried by H_2SO_4 (acid) as the later oxidises H_2S. However, given explanation is correct.

$$3H_2S + H_2SO_4 \longrightarrow 4H_2O + 4S$$

59. (a) Be atom in $BeCl_2$ is *sp*-hybridised whereas Sn atom in $SnCl_2$ has sp^2-hybridisation.

60. (c) The given statement and explanation both are correct and explanation is correct for given statement.

61. (a) The two forms ortho and para hydrogen differ from each other in spin of their proton or nucleus.

62. (c) The given statement and its explanation are correct.

63. (b) Fe_3O_4 is ferrimagnetic at room temperature and becomes paramagnetic at 850K due to randomisation of spin with temperature.

64. (a) $CaCl_2$ is good dessicant and forms addition product with NH_3 and alcohol. It also absorbs water.

65. (c) Explanations is correct reason for statement.

66. (b) $NH_2 \cdot NH_2$ leads to 3-membered highly unstable strained ring.

67. (c) $\mu = \delta \times \overrightarrow{d}$.

68. (a) $K_2[CoCl_4] + HgCl_2 \longrightarrow Co[HgCl_4] + 2KCl$; $Co^{2+}(aq.)$ is pink.

69. (a) CaH_2 is ionic hydride.

70. (c) Explanantion is correct order for statement.

71. (d) Both are correct due to different explanation.

72. (c) Explanation is correct reason for statement.

73. (b) $[Al(NH_3)_6]^{3+} + H_2O \longrightarrow [Al(H_2O)_6]^{3+} + NH_3$

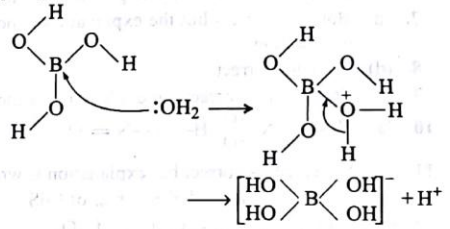
74. (c) Explanation is correct reason for statement.

75. (a) The color is not due to *d-d* transition.

76. (d) Both are correct and have different explanation.

77. (a) Both are covalent. $SiCl_4$ hydrolyses due to presence of *d*-orbitals.

78. (a) H_3BO_3 is weak monobasic Lewis acid.



79. (c) Boron always forms covalent bond because boron requires very high energy to form B^{3+} and again B^{3+} due to its very small size having high polarising power thus cause greater polarisation and eventually significant covalent characteristics. (Fajans rule).

80. (d) Alkali metals with ammonia give blue colour due to ammoniated e^-

$$Na + (x+y)NH_3 \longrightarrow [Na(NH_3)_y]^+ + [e(NH_3)_x]^-$$

solvated (blue colour) electron.

81. (c) Iron in $[Fe(H_2O)_5NO]SO_4$ exists in +2 oxidation state having electronic configuration $(3d)^6$. The unpaired electron of NO is shifted to Fe^{2+} changing it to Fe^+ and also changes NO to NO^+. The electronic configuration of iron in the complex thus, becomes $(3d)^7$ with three unpaired electrons as in the complex, sp^3d^2 hybridization exists.

82. (c) Both statements are correct and explanation is correct reason for statement.

83. (a) Due to inert-pair effect, the higher oxidation states for the group 14 elements are less stable for the heavier members of the group and have a tendency to reduce to lesser oxidation state (*i.e.*, these are stronger oxidizing agent).

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

Name	Formula
1. Orthosilicate	a. $[Si_2O_7]^{6-}$
2. Pyro silicate	b. $[SiO_4]^{4-}$
3. Cyclic silicate	c. $[Si_nO_{3n}]^{2n-}$
4. Infinite chain silicate	d. $[Si_4O_{11}]^{6-}$
5. Infinite sheet silicate	e. $[SiO_3^{2-}]_n$

2.

List A	List B
(a) Magnetite	(i) Fe_2O_3
(b) Haematite	(ii) Fe_3O_4
(c) Limonite	(iii) $FeCO_3$
(d) Siderite	(iv) $Fe_2O_3 \cdot 3H_2O$

3.

List A	List B
(a) Amatol	(i) Explosive
(b) Bronsted acid	(ii) $B(OH)_3$
(c) Hypo	(iii) H_3PO_4
(d) Lewis acid	(iv) Photography

4.

Column-I	Column-II
(a) Lignite	(p) Bhilai
(b) Ammonium sulphate	(q) Copper
(c) Blast furnance	(r) Neyveli
(d) Chalcopyrite	(s) Sindri

5.

Column-I	Column-II
(a) Silver	(p) Fused-salt electrolysis
(b) Calcium	(q) Carbon reduction
(c) Zinc	(r) Carbon monoxide reduction
(d) Iron	(s) Amalgamation
(e) Copper	(t) Self-reduction

6.

Column-I	Column-II
(a) $KCl \cdot MgCl_2 \cdot 6H_2O$	(p) Cassiterite
(b) SnO_2	(q) Carnallite

7.

X	Y
(a) Al	(p) Calamite
(b) Cu	(q) Cryolite
(c) Mg	(r) Malachite
(d) Zn	(s) Carnallite

8.

Column-I	Column-II
(a) Spinel	(p) $MgAl_2O_4$
(b) Felspar	(q) $PbCO_3$
(c) Cerussite	(r) $K_2O \cdot Al_2O_3 \cdot 6SiO_2$
(d) Malachite	(s) $MgSO_4 \cdot H_2O$
(e) Kisserite	(t) $Cu(OH)_2 \cdot CuCO_3$

9.

Column-I	Column-II
(a) Anhydrous $AlCl_3$	(p) Air pollutant
(b) Carbon monoxide	(q) Lubricant
(c) Graphite	(r) Deliquescent

10.

Column-I	Column-II
(a) Bleaching agent	(p) Carbon
(b) Smelling salt	(q) Tin
(c) Bell metal	(r) Ammonium carbonate
(d) Fluorspar	(s) Calcium
(e) Fertilizer	(t) Chlorine
(f) Anthracite	(u) Ammonium phosphate

11.

Column X	Column Y
(a) $(NaPO_3)_n$	(p) Cassiterite
(b) NO_3^-	(q) Producer gas
(c) SnO_2	(r) Water softener
(d) $KCl \cdot MgCl_2 \cdot 6H_2O$	(s) Brown ring test
(e) $CO + N_2$	(t) Carnallite

Type II : More Than One Match Are Possible

12.

Column-I	Column-II
(A) Cu + dil. HNO_3	(p) NO
(B) Cu + conc. HNO_3	(q) NO_2
(C) Zn + dil. HNO_3	(r) N_2O
(D) Zn + conc. HNO_3	(s) $Cu(NO_3)_2$
	(t) $Zn(NO_3)_2$

[IIT 2009]

13.

Column-I	Column-II
(A) B_2	(p) Paramagnetic
(B) N_2	(q) Undergoes oxidation
(C) O_2^-	(r) Undergoes reduction
(D) O_2	(s) Bond order ≥ 2
	(t) Mixing of '*s*' and '*p*' orbitals

[IIT 2009]

14.

Column-I	Column-II
(A) $(CH_3)_2SiCl_2$	(p) Hydrogen halide formation
(B) XeF_4	(q) Redox reaction
(C) Cl_2	(r) Reacts with glass
(D) VCl_5	(s) Polymerization
	(t) O_2 formation

[IIT 2010]

15.

Column-I	Column-II
(a) Self reduction	(p) Lead
(b) Carbon reduction	(q) Silver
(c) Complex formation and displacement by metal	(r) Copper
(d) Decomposition of iodide	(s) Boron

16.

Column-I	Column-II
(a) $Bi^{3+} \rightarrow (BiO)^+$	(p) Heat
(b) $[AlO_2]^- \rightarrow Al(OH)_3$	(q) Hydrolysis
(c) $[SiO_4]^{4-} \rightarrow [Si_2O_7]^{6-}$	(r) Acidification
(d) $[B_4O_7]^{2-} \rightarrow [B(OH)_3]$	(s) Dilution by water

17.

Column-I	Column-II
(a) $[Co(NH_3)_4(H_2O)_2]Cl_2$	(p) geometrical isomers
(b) $[Pt(NH_3)_2Cl_2]$	(q) paramagnetic
(c) $[Co(H_2O)_5Cl]Cl$	(r) diamagnetic
(d) $[Ni(H_2O)_6]Cl_2$	(s) metal ion with +2 oxidation state

Type III : One Match From Each List

18.

Column *X*	Column *Y*	Column *Z*
A. Invar	p. Co, Ni	a. Cutlery
B. Nichrome	q. Fe, Ni	b. Heating element
C. Stainless steel	r. Fe, Cr, Ni	c. Watch spring

19. Each entry in column *X* is in some way related to the entries in column *Y* and *Z*. Match the appropriate entries :

Column *X*	Column *Y*	Column *Z*
A. Yeast	p. Fermentation	a. Ethanol
B. Mica	q. Graphite	b. Abrasive
C. Superphosphate	r. Crystallite cubic	c. Insulator
D. Carbon fibres	s. Layer structure	d. Fertilizer
E. Rock salt	t. Diamond structure	e. Reinforced plastics
F. Carborundum	u. Bone ash	f. Preservative

20. The unbalanced chemical reactions given in List I show missing reagent or condition (?) which are provided in List II. Match List I with List II and select the correct answer using the code given below the lists :

List I	List II
(*P*) $PbO_2 + H_2SO_4 \xrightarrow{?} PbSO_4 + O_2 +$ other product	(1) NO
(*Q*) $Na_2S_2O_3 + H_2O \xrightarrow{?} NaHSO_4 +$ other product	(2) I_2
(*R*) $N_2H_4 \xrightarrow{?} N_2 +$ other product	(3) Warm
(*S*) $XeF_2 \xrightarrow{?} Xe +$ other product	(4) Cl_2

[JEE (Advanced) II 2013]

Codes:

	P	*Q*	*R*	*S*
(a)	4	2	3	1
(b)	3	2	1	4
(c)	1	4	2	3
(d)	3	4	2	1

ANSWERS

1. 1–b; 2–a; 3–c; 4–d; 5–e
2. a–ii; b–i; c–iv; d–iii
3. a–i; b–iii; c–iv; d–ii
4. a–r; b–s; c–p; d–q
5. a–s; b–p; c–q; d–r; e–t
6. a–q; b–p
7. a–q; b–r; c–s; d–p
8. a–p; b–r; c–q; d–t; e–s
9. a–r; b–p; c–q
10. a–t; b–r; c–q; d–s; e–u; f–p
11. a–r; b–s; c–p; d–t; e–q
12. A–p, r, s; B–q, s; C–p, r, t; D–q, t

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

Cold dil. 1 : 1 $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

Cold dil. $4Cu + 10HNO_3 \rightarrow 4Cu(NO_3)_2 + 5H_2O + N_2O$

Hot conc. $Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

Cold dil. $3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 2H_2O + 2NO$

Cold V dil.

$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$

$\hookrightarrow N_2O + 2H_2O$

13. A–p, q, r, t;

(i) B_2 has bond order 1, two unpaired electrons.

(ii) $3Mg + B_2 \longrightarrow Mg_3B_2$

(iii) $B_2 + N_2 \xrightarrow{\Delta} 2BN$

B–q, r, s, t;

(i) N_2 has bond order 3, no unpaired electron.

(ii) $N_2 + 3H_2 \longrightarrow 2NH_3$

(iii) $3Mg + N_2 \longrightarrow Mg_3N_2$

(iv) $N_2 + O_2 \xrightarrow{arc} 2NO$

C–p, q, r, t;

(i) O_2^- has bond order 1.5, one unpaired electron.

(ii) $KO_2 + 2H_2O \longrightarrow KOH + H_2O_2 + \frac{1}{2}O_2$

(disproportionation of O_2^{-1})

D–p, q, r, s, t

(i) O_2 has bond order 2, two unpaired electrons.

(ii) $2F_2 + O_2 \longrightarrow 2F_2O$

(iii) $2Mg + O_2 \longrightarrow 2MgO$

14. A–p, s; B–p, q, r, t; C–p, q; D–p
15. a–p, r; b–p, r; c–q; d–s
16. a–q, s; b–s; c–r; d–q, r
17. a–p, q, s; b–p, r; c–q; d–q, s
18. A–q–c; B–p–b; C–r–a
19. A–p–a; B–s–c; C–u–d; D–q–e; E–r–f; F–t–b
20. (d)

(*P*) $PbO_2 + H_2SO_4 \xrightarrow{\Delta} PbSO_4 + \frac{1}{2}O_2 + H_2O$

(*Q*) $Na_2S_2O_3 + 5H_2O \xrightarrow{4Cl_2} 2NaHSO_4 + 8HCl$

(*R*) $N_2H_4 \xrightarrow{2I_2} N_2 + 4HI$

(*S*) $XeF_2 \xrightarrow{NO} Xe + NOF$

IIT-JEE MODEL PAPER CHEMISTRY 1-A

Time : 60 Minutes **M.M. : 73**

Section A : Single Correct Answer [2×9 = 18]

1. Select the incorrect statement :
   (a) All the Al—Cl bonds are not identical in Al_2Cl_6
   (b) Both BF_4^- and CH_4 have regular tetrahedron geometry
   (c) Ionic radius of a cation decreases with increase in ox. no.
   (d) Ionic radius of a cation increases with increase in co-ordination number
2. Select the incorrect statement :
   (a) Adiabatic process can not be made in isolated systems
   (b) Isolated system does not allow exchange of mass or energy with the surroundings
   (c) The process occuring in an open system are always isobaric
   (d) In an open system, the system remains in equilibrium with atmospheric pressure
3. Select the incorrect statement :
   (a) Rate of evaporation of a liquid is directly proportional to surface area and temperature
   (b) Vapour pressure of a liquid does not depends upon surface area
   (c) Vapour pressure is the pressure exerted by liquid vapours when rate of evaporation = rate of condensation
   (d) Higher is the rate of evaporation of a liquid more will be its vapour pressure
4. Select the incorrect statement :
   (a) Ionisation energy of lithium is higher than sodium
   (b) It is easier to oxidise Li(*s*) to $Li^+(aq.)$ as compared to Na(*s*) to $Na^+(aq.)$
   (c) Hydration energy of Li^+ is lesser than Na^+
   (d) I_2 can replace Cl from $KClO_3$
5. Which one is incorrect about nitrogen(II) oxide :
   (a) It is diamagnetic in liquid state but paramagnetic in gaseous state
   (b) NO acts only as oxidant
   (c) It works as ligand in complex formation
   (d) It has bond order equal to NO^{2+} (*i.e.* 2.5) but bond length greater than NO^{2+}
6. Which of the following has maximum dipole moment :
   (a) *trans*-1,2-dichloro ethene
   (b) *cis*-1,2-dichloro ethene
   (c) *cis*-2,3-dichloro-2-butene
   (d) *cis*-1,2-dibromo-1,2-dichloro ethene
7. The major product formed on reaction of $(CH_3)_3 \cdot C \cdot CH_2OH$ with acid is :
   (a) 2-methyl but-1-ene
   (b) 2-methyl but-2-ene
   (c) 2,2-dimethyl but-1-ene
   (d) 2-methyl propene
8. In which of the following reactions in sulphonation of benzene, equilibrium is far to the left :
   (a) $2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$
   (b) $SO_3 + C_6H_6 \rightleftharpoons C_6\overset{+}{H}_5\!<\!\begin{matrix}H\\SO_3^-\end{matrix}$
   (c) $C_6\overset{+}{H}_5\!<\!\begin{matrix}H\\SO_3^-\end{matrix} + HSO_4^- \rightleftharpoons C_6H_5SO_3^- + H_2SO_4$
   (d) $C_6H_5SO_3^- + H_3O^+ \rightleftharpoons C_6H_5SO_3H + H_2O$
9. 0.1 *M* solution of weak acid *HA* is 1% dissociated at 25°C. If this solution is with respect to Na*A* 0.2 *M*, what is degree of dissociation of *HA* :
   (a) 2×10^{-5} (b) 10^{-4}
   (c) 4×10^{-5} (d) 5×10^{-5}

Section B : More than One Correct Answers [3×5 = 15]

10. Which of the following are true about the reaction :
    $CH_2 = CH-CH = CH_2 + HBr \longrightarrow$
    $CH_3-CHBr-\underset{(P)}{CH=CH_2} + CH_3-\underset{(Q)}{CH=CH}\cdot CH_2Br$
    (a) At low temperature ($\simeq -80°C$) product (*P*) is major product
    (b) At high temperature ($\simeq 40°C$) product (*Q*) is major product
    (c) At low temperature, the rate of addition is responsible for major product
    (d) At high temperature, major product is decided by the equilibrium between the two isomers
11. Select the correct statements :
    (a) O_2 and N_2^{2-} have same number of electrons and same MO configuration
    (b) O_2 and N_2^{2-} have bond order equal to two
    (c) N_2 is almost inert at room temperature but becomes reactive at high temperature or in presence of catalyst
    (d) There occurs extensive delocalisation of π-electrons in N_2 molecule
12. Select the correct statements :
    (a) P_4 molecule is tetrahedral with P–P–P angle of 60°
    (b) P_4 molecule has sp^3 hybridization
    (c) Black phosphorus is good conductor of current
    (d) Red phosphorus is good conductor of current
13. Which of the following gas on addition in air will decrease average molar mass of air ?

(a) Ar (b) He
(c) $H_2O_{(v)}$ (d) Ne

14. Which of the following are not correct ?
(a) The ratio of molar gas constant and Avogadro's no. is called Boltzman constant
(b) 1 equivalent of $K_2Cr_2O_7$ has seven equivalent of oxygen
(c) The ratio of mole and equivalent for a substance is called valence factor
(d) The value of $\frac{RT}{PV}$ at critical conditions is 3/8

Section C : Matrix Match Type Problems: **[4×2 = 8]**

More than one choice are possible:

15.

List A	List B
A. Sweating	P. Evaporation
B. Hoar frosting	Q. Endothermic
C. Roasting	R. $H_2O_{(v)} \longrightarrow H_2O_{(s)}$
D. Sintering	S. High temperature

16.

List A	List B
A. Thermal decomposition of $KClO_3$	P. Intramolecular redox
B. Thermal decomposition of $KClO_4$	Q. Inter molecular redox
C. Thermal decomposition of $(NH_4)_2Cr_2O_7$	R. Auto redox
D. Thermal decomposition of H_3PO_2	S. Disproportionation

Sintering is roasting with incipient fusion at comparatively high *T*. Black *P* consists of coagulated sheet each *P* bonded to neighbours in sheet.

Section D: Statement- Explanation **[2×4 = 8]**

Read the given statement and explanation and answer accordingly to choices given below :
(a) **S** is correct, but **E** is wrong
(b) **S** is wrong, but **E** is correct
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**

17. **S:** N_2O_3 is pale blue liquid at –30°C.
E: At room temperature N_2O_3, gives NO and NO_2 and dissociation increases with temperature.

18. **S:** NH_2OH is a weaker base than NH_3.
E: NH_2OH acts as oxidant in acid medium and mild reductant in alkaline medium.

19. **S:** Water of water fall is more cooler at the top rather than at the bottom.
E: During fall of water from top to bottom, the potential energy is converted into kinetic energy as it just hits the surface of bottom to give rise an increase in temperature.

20. **S:** Hypohalites are used to bring in oxidation as well as halogenation.
E: Hypohalite have halogens in +1 oxidation state.

Section E: Single Integer Answer Type **[3×8 = 24]**

S-1 : Ratio of P— O and P═O bonds in $H_4P_2O_7$ is :

S-2 : Number of tetrahedrals involved in $Cr_2O_7^{2-}$ structure

S-3 : A sample of SF_n mass 54 mg is supposed to contain 3×10^{20} molecules. Assuming Av. no. $=6\times10^{23}$, calculate the value of *n* (Atomic mass of F is 19)

S-4 : Number of water molecules associated with crystal hydrate of NaCl.

S-5 : A simplest alkene showing isomerism on monosubstitution has number of carbon atoms.

S-6: 0.22 g of organic compound C_xH_yO which occupied 112 mL at NTP and on combustion gave 0.44 g CO_2. The ratio of *y* to *x* is.....

S-7: 500 mL of 2 *M* K_2SO_4 and 500 mL of 4 *M* KCl are mixed. The solution is now diluted to 2 litre. The molarity of K^+ ions in the resultant solution is.....

S-8: 15 g impure sample of $Ba(MnO_4)_2$ is used to completely oxidise 10 mL of 11.2V H_2O_2 solution. What is percentage purity of $Ba(MnO_4)_2$?

SOLUTION OF MODEL PAPER 1-A

Section A

1. (b) BF_4^- does not possess regular tetrahedron structure due to the presence of co-ordinate bond.

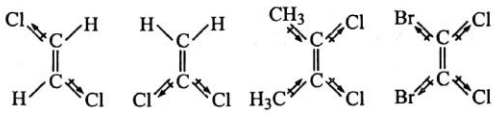
2. (c) The atmospheric pressure may be disturbed at any time due to sudden weather change or due to temperature.

3. (d) Vapour pressure is characteristic constant at given temperature. Larger surface area shows higher rate of evaporation then smaller surface area at constant *T*.

4. (c) $2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$
Hydration energy: $Li^+ > Na^+$ due to smaller size.

5. (b) $10NO + 2CS_2 \longrightarrow 2CO + 4SO_2 + 5N_2$ (as oxidant)
$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O$ (as oxidant)
$3MnO_4^- + 5NO + 4H^+ \longrightarrow 3Mn^{2+} + 5NO_3^- + 2H_2O$ (as reductant)

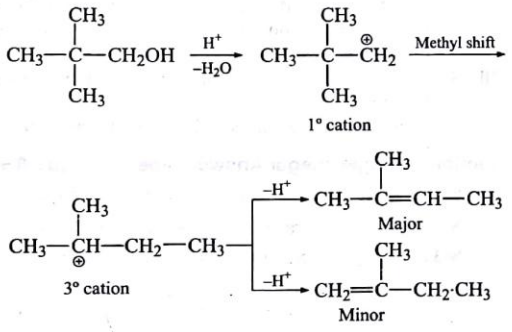
6. (c)



(a) $\mu = 0$ (b) $\mu \neq 0$ (c) $\mu \neq 0$ (d) $\mu \neq 0$

$\mu_{(c)} > \mu_{(b)}$ because dipole moment of CH_3 and Cl are additive (in same direction). Also $\mu_{(c)} > \mu_{(d)}$ because dipole moment of Br and Cl are subtractive (in opposite direction)

7. (b)



8. (d) $C_6H_5SO_3H$ is strong acid and exist as ions in water.

9. (d) $K_a = C\alpha^2 = 0.1\times(0.01)^2 = 10^{-5}$

Also, In NaA: $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{C\cdot\alpha\times 0.2}{C(1-\alpha)} = 10^{-5}$

$\therefore \quad \alpha = 5\times10^{-5}$

Section B

10. (a,b,c,d) Follow point c,d for the results in (a) and (b).

11. (b,c) Both N_2^{2-} and O_2 have different M.O.

12. (a,b,c) Red phosphorus is bad conductor of current.

13. (b,c,d) Argon has molar mass 40, higher than air (28.8).

14. (b, d) 1 *eq.* of $K_2Cr_2O_7$ = 1*eq.*K^+ = 1*eq.*Cr^{6+} = 1*eq.*O^{2-} ;

$\dfrac{P_cV_c}{RT_c} = \dfrac{3}{8}$ and $\dfrac{RT_c}{P_cV_c} = \dfrac{8}{3}$

Section C

15. A : P, Q
B : R
C : Q, S
D : Q, S

16. A : P, R, S $2KClO_3 \longrightarrow KClO_4 + KCl + 2O_2$
$\quad\quad\quad

IIT-JEE MODEL PAPER CHEMISTRY 1-B

Time : 60 Minutes **M.M. : 73**

Section A : Single Correct Answer **[2×8 = 16]**

1. Which of the following is not known ?
   (a) SO_2F_2 (b) SO_2Cl_2
   (c) SO_2FBr (d) SO_2I_2

2. The C—$\ddot{\underset{\cdot\cdot}{O}}$—C bond angles in ether is :
   (a) >109.5° (b) 109.5°
   (c) 105° (d) 107°

3. Select the correct statement :
   (a) For each 10° rise of temperature, the specific reaction rate constant is nearly doubled.
   (b) Rate of reaction decreases with rise in temperature for exothermic reaction.
   (c) Rate of reaction decreases with rise in temperature for endothermic reaction.
   (d) The reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$ having rate constant $3.0\times10^{-5}\,sec^{-1}$ goes for completion in 3.0×10^{4} sec.

4. Which of the following statement is correct ?
   (a) pH of 1.0×10^{-8} *M* NaOH is 8
   (b) Autoprotolysis constant of water is 3.23×10^{-18}
   (c) Equilibrium constant for dissociation of water is 1.0×10^{-14}
   (d) 10 mL of 0.1 *M* H_2SO_4+20 mL of 0.1 *M* NH_4OH mixture is buffer

5. Which of the following are mass independent ?
   (a) *P* (b) *V*
   (c) $\frac{PV}{n}$ (d) *PV*

6. If the energy of H-atom in the ground state is $-E$, the velocity (u) of photo-electron emitted when a photon having energy E_p strikes a stationary Li^{2+} ion in ground state is given by :
   (a) $u=\sqrt{\frac{2(E_P-E)}{m}}$ (b) $u=\sqrt{\frac{2(E_P+9E)}{m}}$
   (c) $u=\sqrt{\frac{2(E_P-9E)}{m}}$ (d) $u=\sqrt{\frac{2(E_P-3E)}{m}}$

7. Aqueous solution of two compounds M_1-O-H and M_2-O-H are prepared in two different beakers. If the electronegativity of $M_1=3.4$, $M_2=1.2$, O = 3.5 and H = 2.1, then the nature of two solutions will be respectively :
   (a) acidic, basic (b) acidic, acidic
   (c) basic, acidic (d) basic, basic

8. $(C_6H_5)_2—C=CHBr \xrightarrow{KNH_2}$ Product formed is :
   (a) Diphenyl ether
   (b) Diphenyl ethyne
   (c) $C_6H_5CH=CBrC_6H_5$
   (d) None of these

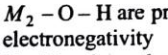
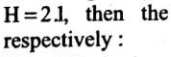
Section B: More Than One Correct Answer **[3 x 5 = 15]**

9. Which of the following are correct ?
   (a) In Cr atom, 15 electrons have a spin of one type and 9 electrons of the opposite type
   (b) All the four quantum numbers were proposed before the origin of quantum theory
   (c) The azimuthal quantum number of a poly electronic atom is related to shape and energy of orbital.
   (d) The azimuthal quantum number of a one electron system is related to shape and energy level

10. Select the correct statement :
    (a) The pH of a buffer mixture obtained by 1 *M* NH_4OH and 1 *M* $(NH_4)_3PO_4$ is equal to (pK_w-pK_b) where K_b is dissociation constant of NH_4OH
    (b) The amount of adsorbate per unit mass of adsorbent is a function of temperature at constant pressure.
    (c) For free radical combination rate constant is independent of temperature.
    (d) Molar heat capacity of water in equilibrium with vapour at constant pressure is infinite.

11. Which one is not correct about N_2O_3 ?
    (a) It is pale blue compound
    (b) It exists only in solid state
    (c) It disproportionates on heating ($N_2O_3 \rightarrow NO + NO_2$)
    (d) The degree of dissociation increases with temperature

12. Select the correct chemical changes :
    (a) $2NH_4F \xrightarrow{\Delta} NH_3 + NH_4HF_2$
    (b) $NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$
    (c) $(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$
    (d) $3NH_2OH \xrightarrow{\Delta} N_2 + NH_3 + 3H_2O$

13. Hydration of cyclobutyl ethene in dil. H_2SO_4 gives :
    (a) *cis*-2-methyl pentanol
    (b) *trans*-2-methyl pentanol
    (c) 
    (d) 

Section C : Single Integer Answer Problem **[3×8 = 24]**

14. A mixture of NaOH and Na_2CO_3 was first neutralised with 25 mL of *N*/10 HCl in presence of phenolphthalein as indicator. The same amount of mixture required 30 mL of

$N/10$ HCl using methyl orange as indicator. The ratio of milli equivalent NaOH and Na_2CO_3 in the mixture is:

15. The ratio of vertices in truncated octahedron and truncated tetrahedron is :

16. If $T_1 = 800$ K and $T_2 = 300$ K, the ratio of U_{rms} : U_{mp} at T_1, T_2 respectively for He is :

17. λ_{He^+} for a transition is 22.8 nm. The λ_H for the corresponding transition will be ..... times of λ_{He^+}.

18. Number of regular hexagonal faces in a truncated tetrahedron.

19. How much of the following will reduce $-CONH_2$ to $-NH_2$
Br_2 + NaOH, H_2 / Ni, Na / C_2H_5OH,
$LiAlH_4$ / ether, $NaOBr_{aq.}$?

20. How much of the following are condensation polymers : terelene, bakelite, glyptal, malamine, polyacrolonitrile, polyvinyl chloride ?

21. How much of the following leaves no residue on strong heating: dryice, NH_4NO_3, NH_4NO_2, NH_4Cl, $(NH_4)_2Cr_2O_7$?

Section D : **[4×2 = 8]**

Match the following (one or more matches are possible) :

22.

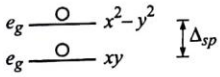
A. Zone refining	(a) Boron
B. Van Arkel method	(b) Silicon
C. Pyrometallurgy	(c) Hg
D. Self reduction	(d) Cu
	(e) Pb

23.

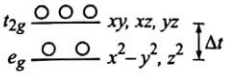
A. E_1 elimination reactions	(a) II order
B. E_2 elimination reactions	(b) *trans* chloro fumaric acid $\xrightarrow{NaOH}$ But-2-yne-1, 4-di oic acid
C. $S_{N}1$ reaction	(c) $(CH_3)_3C-X \xrightarrow{KOH} (CH_3)_2C=CH_2$
D. $S_{N}2$ reaction	(d) $CH_3CH_2OH \xrightarrow[\text{agent}]{\text{Dehydrating}} CH_2=CH_2$
	(e) I order
	(f) $R-X + :Nu \rightarrow \text{Product} + \bar{X}$

Section E : Comprehension **[2×5 = 10]**

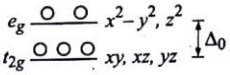
d-orbital configuration in transition metals is the key to understand many properties of these metal ions. In complex transition metal ions, electrons are placed into the set of *d*-orbitals according to Hund's rule and the values of Δ_0. The value of Δ_0 and the ligand determine whether a *d*-electron configuration will be low spin or high spin. A schematic diagram for the splitting patterns of the *d*-orbitals in square planar (*SP*) tetrahedral complex and octahedral complex are given ahead :



Square planar complex



Tetrahedral complex



24. Select the incorrect statement about Fe (II) complex in haemoglobin :
(a) It is square planar complex
(b) $e_g > t_{2g}$
(c) It is high spin complex
(d) Δ_{sp} is large

25. If Δ_0 is large compared to the pairing energy then which one is correct :
(a) The *d*-electrons will fill e_g orbitals completely before they occupy t_{2g} level in high spin complex
(b) The *d*-electrons will fill t_{2g} orbitals completely before they pair up in the e_{2g} orbital in low spin
(c) The high spin configuration has the maximum number of unpaired *d*-electrons
(d) The high spin configuration has the minimum number of unpaired *d*-electrons

26. Select the incorrect fact :
(a) All d^8 square planar complex are low spin
(b) All d^8 square planar complex has Δ_{sp} relatively high
(c) There are no low spin tetrahedral complexes
(d) In tetrahedral complex Δ_t is relatively large

27. Select the incorrect statement :
(a) The t_{2g} set of orbitals can accommodate a maximum of six electrons
(b) The five *d*-orbitals in a metal ions develops non-degeneracy in presence of ligand
(c) The value of Δ_0 depends upon the nature of ligand in an octahedral complex
(d) A high spin d^6 complex is diamagnetic

28. For the reaction :
$[Pb_2Fe(CN)_6]_{(s)} + 4I^- \rightleftharpoons 2PbI_{2s} + [Fe(CN)_6]^{4-}_{aq.}$,
equilibrium constant is given by K_1. If K_{sp_1} and K_{sp_2} are solubility product of PbI_2 and $Pb_2[Fe(CN)_6]$, respectively then :

(a) $K_1 = \dfrac{K_{sp_2}}{K_{sp_1}}$ (b) $K_1 = \dfrac{K_{sp_1}}{K_{sp_2}}$

(c) $K_1 = \dfrac{K_{sp_2}}{(K_{sp_1})^2}$ (d) $K_1 = \dfrac{(K_{sp_1})^2}{(K_{sp_2})}$

SOLUTION OF MODEL PAPER (Part 1- B)

Section A

1. (d) SO_2I_2 is unstable.
2. (a) As size of alkyl group bonded to O increases, the repulsive forces between them increases, causing an expansion of the angle.
3. (a) Rate of reaction always increases with temperature as $r = KC_R{}^n$. Also $K = Ae^{-Ea/RT}$. I order reaction never goes for completion.
4. (b) $(H_2O + H_2O \rightleftharpoons \overset{+}{H_3O} + OH^-)$

$$K_{a.p.} = \frac{K_w}{[H_2O]^2} = \frac{10^{-14}}{(55.6)^2} = 3.23 \times 10^{-18}$$

Also $K_c = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{55.6}$

$= 1.8 \times 10^{-16}$

Rest all are wrong.

5. (c) $PV = nRT$

$\frac{PV}{n} = RT$ = constant since T is mass independent

6. (c) $h\nu = h\nu^0 + \frac{1}{2}mu^2$

$E_p = 9E + \frac{1}{2}mu^2$ [For $Li^{+2}, E_1 = E_{1_H} \times z^2$]

$u = \sqrt{\frac{2(E_p - 9E)}{m}}$

7. (a) M_2 is metal and M_1 is non metal.

M_2OH is base; (*e.g.*, NaOH); M_1OH is acid (*e.g.*, HOCl).

8. (b) $(C_6H_5)_2C{=}C(H)Br \xrightarrow[-HBr]{KNH_2} C_6H_5{-}C{\equiv}C{-}C_6H_5$

Section B

9. (a,c) $_{24}Cr: 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$; Also signifies for shape and energy level for poly electronic atom.
10. (b,c,d) $\frac{x}{m}$ is $f(T)$ at constant; P; E_a for free radical combination is zero;

At equilibrium $C_p = \infty, C_p = \frac{\Delta H}{\Delta T}; \Delta T = 0;$

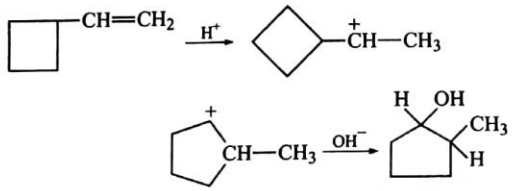
Also $pOH = pK_b + \log\frac{[C\cdot A]}{[Base]}; [C.A.] = [NH_4^+] = 3M$

and [Base] = 1 M

11. (a,c,d) All are facts.
12. (a, b, d) $(NH_4)_2SO_4 \longrightarrow NH_3 + NH_4HSO_4$

$NH_2OH \longrightarrow N_2 + NH_3 + 3H_2O$

13. (a, b)



cis and *trans*

Section C

14. Two : *Meq.* of NaOH + 1/2 *Meq.* of $Na_2CO_3 = 25 \times 0.1 = 2.5$ (HPh is indicator)

Meq. of NaOH + *Meq.* of $Na_2CO_3 = 30 \times 0.1 = 3.0$ (MeOH is indicator)

$\therefore$ *Meq.* of $Na_2CO_3 = 0.5 \times 2 = 1.0$

Meq. of NaOH = 2

15. Two : A truncated octahedron has 24 vertices and 36 edges whereas a truncated tetrahedron has 12 vertices and 18 edges.
16. Two : $\frac{u_{rms}}{u_{Av.}} = \sqrt{\frac{3 \times 800}{2 \times 300}} = 2$
17. Four : $\lambda_H = \lambda_{He^+} \times Z^2_{He}$
18. Four
19. Two
20. Four
21. Four

Section D

22. A-a, b; B-b, c; C-c, d, e; D-c, d, e
23. A-c, d, e; B-a, b; C-e, f; D-a, f

Section E

24. (d)
25. (c)
26. (d)
27. (d)
28. (c)

IIT-JEE MODEL PAPER CHEMISTRY 2-A

Time : 60 Minutes **M.M. : 72**

Section A : One Answer Correct **[2×9 = 18]**

1. Which one is not correct about the reaction :
   $RC \equiv CLi + R'X \longrightarrow RC \equiv CR'$
   (a) C—C bond formed in product is heterolytically
   (b) Carbon atom attached to Li in $RC \equiv CLi$ acts as nucleophilic
   (c) Carbon atom attached to X in $R'X$ acts as electrophilic
   (d) Carbon atom attached to X is electron rich
2. Select the incorrect statement :
   (a) Lithium acetylide is stronger base than water
   (b) $LiNH_2$ is stronger base than lithium acetylide
   (c) Acetylene is stronger acid than NH_3
   (d) $Li^+NH_2^-$ is a salt of strong acid
3. The value of molal ebullioscopic constant for a solvent determined using solution of solute A is found to be 5.12 K molality^{-1}. The value of molecular ebullioscopic constant for same solvent using solution of solute B in same solvent will be:
   (a) 51.2 $K^{-1}mol^{-1}$, 0.1 kg solvent
   (b) 512 K^{-1} mol^{-1}, 0.1 kg solvent
   (c) 5.12 K^{-1} mol^{-1}, 0.1 kg solvent
   (d) cannot be predicted
4. Which of the following is strongest oxidant :
   (a) FeO_4^{2-} (b) MnO_4^{2-}
   (c) VO_4^{3-} (d) CrO_4^{2-}
5. $AlCl_3 \cdot 6H_2O$ on heating liberates :
   (a) Cl_2 (b) HCl
   (c) H_2O (d) None of these
6. Which reaction occurs if Fe rod is placed in $Fe(NO_3)_3$ solution :
   (a) $Fe^{3+} + 3e \longrightarrow Fe$
   (b) $Fe \longrightarrow Fe^{3+} + 3e$
   (c) $2Fe^{3+} + Fe \longrightarrow 3Fe^{2+}$
   (d) $Fe^{2+} \longrightarrow Fe^{3+} + e$
7. The complex $[Co(NH_3)_5Br]^{2+}$ having purple colour, in presence of acidic water produces the solution having colour:
   (a) Pink (b) Blue
   (c) Red (d) Green
8. Which of the following is incorrect :
   (a) Na_3BO_3 exist but Na_3PO_3 not
   (b) H_3BO_3 is monobasic but H_3PO_3 is dibasic
   (c) H-atoms attached on the O-atom in oxoacids usually represents their 'n' factor
   (d) n-factor of a substance is independent of chemical reaction.
9. Select the incorrect statement :
   (a) $\left[\frac{\partial T_f}{\partial m}\right]_{m\to 0}$ depends on the characteristic of solvent.
   (b) For solvents obeying Trouton's rule $K_b \propto MT_b$.
   (c) The classification of solute and solvent in a solution is a matter of convenience only.
   (d) Trouton's rule = $\frac{\Delta_f H}{T_f}$

Section B: More Than One Answer Correct **[3 x 4 = 12]**

10. Which of the following metal chlorides does not give chromyl chloride test :
    (a) $HgCl_2$ (b) $SnCl_2$
    (c) $SbCl_3$ (d) AgCl
11. Which of the following gases turns KI-soaked starch paper blue :
    (a) NO_2 (b) F_2
    (c) Cl_2 (d) O_3
12. Select the correct statements :
    (a) In the electrolytic cell cathode works as electron sink like electrochemical cell
    (b) In the electrolytic cell electrons are sucked out of the anode by the positive terminal of external battery
    (c) In the electrolytic cells the electrons flow from cathode to anode through external wires
    (d) Cathode of electrolytic cell is negative electrode
13. Select the correct statements about hexagonal closest packed structure and cubic closest packed structure for a given element :
    (a) Both have same density
    (b) Both have the same co-ordination number
    (c) Both have the same packing fraction
    (d) Both have different co-ordination number

Section C : Matrix Match Type Problems : **[4×2 = 8]**

14. Match the following :

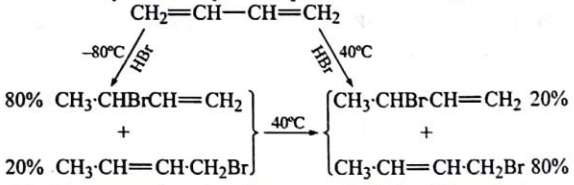
A. BrF_5	1. Distorted geometry
B. PCl_5	2. Non polar
C. SF_6	3. Polar
D. $XeOF_4$	4. One lone pair

15. Match the following :

A. CH_3^+	1. sp
B. $CH_3^\bullet$	2. sp^2
C. CH_3^-	3. sp^3
D. CH_4	4. sp^3d

Section D : Comprehension

Addition of HBr to 1,3-butadiene yields both 1,2- and 1,4-products. The proportion in which 1,2- and 1,4-products are markedly affected by the temperature : [5×2 = 10]



16. The proportion of products actually isolated from the low temperature addition is determined by :
    (a) Equilibrium between two isomers
    (b) Higher value of rate constant for 1,4-addition
    (c) Higher value of rate constant for 1,2-addition
    (d) None of the above
17. The proportion of products for the high temperature addition is determined by :
    (a) Equilibrium between two isomers
    (b) Higher value of rate constant of 1,4-addition
    (c) Higher value of rate constant of 1,2-addition
    (d) None of the above

Section E : Single digit answer [3×8 = 24]

18. Total number of structural isomers of the compound $C_5H_{10}O$.
19. Total number of stereoisomers of the compound $C_5H_{10}O$.
20. How much salts given below during electrolysis will produce a solution of pH > 7 ?
    $NaCl(aq.)$; $(NH_4)_2SO_4(aq.)$; $FeCl_3(aq.)$; CH_3COONa
    $CuSO_4(aq.)$; $KNO_3(aq.)$; $Ni(NO_3)_2(aq.)$; KCN
21. How much compounds possess weak electrolyte nature ?
    CH_3COONH_4; Phenolphthalein; $H_2C_2O_4$; CCl_3COOH
    NH_4CN; Methyl orange; NH_4OH; CH_3COOH
22. Number of compounds which can be used only as oxidant from the given list :
    $HClO_4$; HNO_3; H_2S; SO_3; CO_2;
    SO_2; H_3PO_4; F_2; CO; HNO_2
23. What is the value of X in $H_XCr(CO)_5$?
24. Number of positrons given out during nuclear fusion of ^1_1H to produce one particle of ^4_2He.
25. How much of the following salts will show an increase in their solubility in presence of $1N$ HNO_3?
    AgCN, AgCl, AgBr, CaF_2, AgF, Ag_2CO_3, AgI, $CaCl_2$

SOLUTION OF MODEL PAPER 2-A

Section A

1. (d) Carbon atom attached to X (electronegative) becomes electron deficient because X pulls electron pair towards it self.
2. (d) $Li + NH_3 \longrightarrow Li^+NH_2^-$ (Salt of weak acid H—NH_2)
3. (a) Molecular ebullioscopic constant = 10× molal ebullioscopic constant.
4. (a) Fe normally exist in +2 or +3. In ferrate it exists as +6 and thus easily reduced to Fe^{3+}.
   Also stability order $VO_4^{3-} > CrO_4^{2-} > MnO_4^{2-}$
   $> FeO_4^{2-} > CoO_4^{2-}$
5. (b) $AlCl_3 \cdot 6H_2O \rightarrow AlCl_3 + 6H_2O \rightarrow Al(OH)_3 + 3HCl$
6. (c) $2Fe^{3+} + Fe \rightarrow 3Fe^{2+}$ $E^0 = 1.21$ V a miniature cell is formed.
7. (a)
   $\underset{\text{Purple}}{[Co(NH_3)_5Br]^{2+}} + H_2O_{(l)} \longrightarrow \underset{\text{Pink-orange}}{[Co(NH_3)_5H_2O]^{3+}_{aq.}} + Br^-_{aq.}$
8. (d) $HNO_3 \longrightarrow H^+ + NO_3^-$ (n factor = 1)
   $2HNO_3 \longrightarrow H_2O + 2NO + 3O$ (n factor = 3)
9. (d) Trouton's rule is : $\frac{\Delta_v H}{T_b} = 10.5R$ and
   $$K_b = \frac{RT_b^2 \times M}{\Delta H_v \times 1000} = \frac{RMT_b}{1000 \times 10.5R} \propto MT_b$$

Section B

10. (a,b,c) All these are covalent chlorides. Only ionic chlorides gives chromyl chloride test.
11. (b, c, d) gives $2KI + X_2 \longrightarrow 2KX + I_2$ (X is F, Cl, Br)
    $NO_2 + H_2SO_4 + 2KI \longrightarrow K_2SO_4 + H_2O + NO + I_2$
    (only in acid medium)
    $O_3 + 2KI + H_2O \longrightarrow 2KOH + I_2 + O_2$
12. (a, b, d) Electrons sucked out from anode and flow towards cathode through external wire.
13. (a, b, c) b, c are explanations to a.

Section C

14. A-1, 3, 4; B-2; C-2; D-1, 3, 4
15. A-2; B-3; C-3; D-3

Section D

16. (c) The fact that 1,2-product is more than 1,4-product at −80° C that formation of 1,2-product is faster, since each compound remains unchanged at −80°C.The proportion in which they are isolated shows the proportion in which they are formed.
17. (a) As the temperature rises, the conversion of 1,2-product into 1,4-product becomes more to attain equilibrium. There occurs faster conversion of products initially formed into the equilibrium mixture at higher temperature.

Section E

18. Seven
19. Two
20. Two
21. Five
22. Six
23. Two : EAN of Cr = 36
    $\therefore 36 = 24 + (2 \times 5) + x$
    $\therefore x = 2$
24. Two : $4^1_1H \longrightarrow ^4_2He + 2^0_{+1}e + h\nu$
25. Four : AgCN, AgF, Ag_2CO_3, CaF_2 (These which possess strong basic nature of anion.)

IIT-JEE MODEL PAPER CHEMISTRY 2-B

Time : 60 Minutes **M.M. : 72**

Section A : Single Correct Answer **[2×8 = 16]**

1. Acid dehydration of cyclobutyl carbinol is :

(a) (b)

(c) (d) None of these

2. Arrange the following in the increasing order of *s*-character in central atom (hybrid orbital) :

(a) $PH_3 = NH_3 = NCl_3 > N_3^-$

(b) $PH_3 < NCl_3 < NH_3 < N_3^-$

(c) $NH_3 < PH_3 < NCl_3 < N_3^-$

(d) $PH_3 = NCl_3 = NH_3 < N_3^-$

3. The correct order of bond length of Si–O, P–O, S–O and Cl–O in SiO_4^{4-}, PO_4^{3-}, SO_4^{2-} and ClO_4^- is :

(a) $ClO_4^- > SO_4^{2-} > PO_4^{3-} > SiO_4^{4-}$

(b) $PO_4^{3-} > SiO_4^{4-} > SO_4^{2-} > ClO_4^-$

(c) $SiO_4^{4-} > PO_4^{3-} > SO_4^{2-} > ClO_4^-$

(d) $SO_4^{2-} > SiO_4^{4-} > PO_4^{3-} > ClO_4^-$

4. In O_2F_2, which of the following statement is correct?

(a) O-F bond length in O_2F_2 is longer than O-F bond length in OF_2

(b) The O.N. of oxygen in O_2F_2 is +1

(c) The O—O bond length in O_2F_2 is shorter than O—O bond length in H_2O_2

(d) All of the above

5. Select the incorrect reaction :

(a) $CH_2 = CH_2 + Br_2 \xrightarrow[H_2O]{NaCl} BrCH_2{\cdot}CH_2Br + BrCH_2{\cdot}CH_2Cl + BrCH_2{\cdot}CH_2OH$

(b) $CH_2 = CH_2 + Br_2 \xrightarrow{NaI_{aq.}} BrCH_2CH_2Br + BrCH_2{\cdot}CH_2I$

(c) $CH_2 = CH_2 + I_2 \xrightarrow{CCl_4} CH_2I - CH_2I$

(d) $CH_2 = CH_2 + I_2 \xrightarrow{CCl_4} CH_2Cl - CH_2I$

6. A sample of H_2O_2 solution labelled as 33.6 volume has density (d)g litre^{-1}. Mark the incorrect option representing concentration of same solution in other units. (Assume that solution contains only H_2O and H_2O_2).

(a) Mole fraction of H_2O_2 in the solution $= \frac{54}{(1000d - 102)}$

(b) Normality = $6N$

(c) Molarity (M) = $6M$

(d) Molality (m) $= \frac{3000}{(1000d - 102)}$

7. Number of regular hexagonal faces and regular tetrahedral faces in truncated tetrahedron are respectively :

(a) 2, 4 (b) 4, 4

(c) 6, 4 (d) 4, 6

8. Virial equation of state for one mole of real gas $Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} .....$

Where B = IInd virial coefficient

C = IIIrd virial coefficient

D = IVth virial coefficient

Find out the value of $\frac{B}{Z}$ at Boyle's temperature :

(a) 0 (b) 1

(c) $\left(b - \frac{a}{RT}\right)$ (d) $\frac{a}{bR}$

Section B : More than One Correct Answer **[4×5 = 20]**

9. Which of the following statements is incorrect ?

(a) All C—O bonds in CO_3^{2-} are equal but not in H_2CO_3

(b) All C—O bonds in HCO_2H are equal but not in HCO_2^-

(c) C—O bond length in HCO_2^- is longer than C—O bond length in CO_3^{2-}

(d) C—O bond length in HCO_2^- and C—O bond length in CO_3^{2-} are equal.

10. In I_3^- :

(a) I_2 is Lewis acid and I^- is Lewis base

(b) I_2 is Lewis base and I^- is Lewis acid

(c) I_3^- itself behaves as amphoteric anion

(d) I_3^- is linear

11. Which of the following have non zero dipole moment ?

(a) 1,4-dihydroxy benzene

(b) 1,4-dichloro benzene

(c) 1,4-dinitro benzene

(d) 1,4-dimethoxy benzene

12. Which of the following are correct?

(a) For a reaction involving only condensed phase $\Delta_r H = \Delta_r U$

(b) Bond enthalpy and bond dissociation energy of a triatomic molecule are identical

(c) Enthalpy of an ideal gas is a function of temperature only

(d) There is no entropy change during allotropic change

13. Select the correct reaction :

(a) $CH_3 \cdot CH_2 \cdot CH = CHCHO \xrightarrow{Zn/Hg\text{-}HCl} CH_3CH_2CH_2 \cdot CH_2CHO$

(b) $CH_3 \cdot CH_2 \cdot CH = CHCHO \xrightarrow{Zn/Hg\text{-}HCl} CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2CH_3$

(c) $CH_3COCH_2 \cdot CO \cdot CH_3 \xrightarrow{I_2+NaOH} CHI_3 + CH_3COONa$

(d) $C_6H_5CHO + HCHO \xrightarrow{NaOH} C_6H_5CH_2OH + HCOONa$

Section C : Comprehension-1 **[3×2 = 6]**

The sums of first and second ionization energies and those of third and fourth ionization energies (in kJ mol^{-1}) of nickel and platinum are;

	$(IE)_1 + (IE)_2$	$(IE)_3 + (IE)_4$
Ni	2.49	8.80
Pt	2.66	6.70

Also both Ni and Pt have co-ordination number = 4

14. Which is most stable complex of Ni?

(a) $[Ni(CN)_4]^{2-}$ (b) $[Ni(CN)_6]^{2-}$

(c) $[Ni(CN)_3]^-$ (d) $[Ni(CO)_6]$

15. Which is least stable complex of Pt?

(a) $K_2[PtCl_6]$ (b) $[Pt(en)_3]Cl_4$

(c) $K_2[Pt(Cl_4)]$ (d) $K_2[Pt(C_2O_4)_3]$

Comprehension-2 **[2×3 = 6]**

A molecular formula having H-atom may represent an equilibrium mixture of two compounds due to migration of mobile H-atom between two polyvalent gps. These two molecules show interconversion of one into other so quickly that their isolation in independent state can not be made. However at equilibrium the ratio of their concentration depends on the characteristic value of their equilibrium constant *e.g.*

$$CH_3\overset{O}{\overset{\|}{C}}-CH_2 \cdot COOCH_3 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CHCOOCH_3$$

16. The solubility of methyl acetoacetate in dilute NaOH is due to the formation of :

(a) $Na \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOCH_2Na$

(b) $CH_3COCH_2COOCH_2Na$

(c) $CH_3-\overset{ONa}{\overset{|}{C}}=CHCOOCH_3$

(d) $CH_3 \cdot CO \cdot CH_2 \cdot COONa$

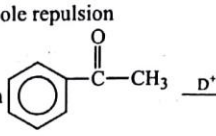
17. Enolic form of acetyl acetone is stabilized by :

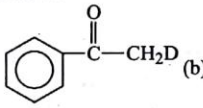
(a) van der Waals' forces

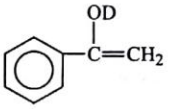
(b) Intermolecular H-bonding

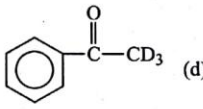
(c) Intramolecular H-bonding

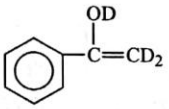
(d) dipole-dipole repulsion

18. In the reaction  the product formed is :

(a) 

(b) 

(c) 

(d) 

Section D: Single Integer Answer Problems **[3×8 = 24]**

19. Number of acidic hydrogen atoms in pentan-2,4-diene is .....

20. Number of atoms in upper layer of hexagonal close pack type arrangement is.....

21. On monochlorination of 2-methylbutane, the total number of chiral carbon atoms formed in the product molecule is.....

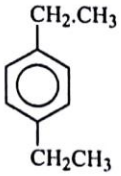
22. The uncertainty in location of an electron in an orbit is equal to its de Broglie wavelength. The minimum per cent error in its velocity measurement would be.....

23. A gas is present in a piston fitted vessel at 3 atm. How much pressure should be increased so that its volume is reduced to 25% of initial volume.....

24. Molarity of 10% mass/volume $CaCO_3$ solution is.....

25. A mixture having 100 mL of 0.5 *M*HCl and 12.5 mL of 0.2 *M* H_2SO_4 requires 50 mL of baryta water solution. What is molarity of baryta water solution ?

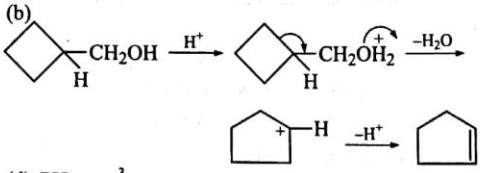
26. How many kinds of non equivalent H-atoms are there in



SOLUTION OF MODEL PAPER 2-B

Section A

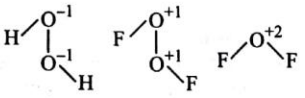
1. (b)



2. (d) PH_3 : sp^3
NCl_3 : sp^3
NH_3 : sp^3
N_3^- : sp^2

3. (c) Atomic radius decreases along the period;

4. (d)



The facts are based upon their geometry. Size of O^- > size of O^+ > Size of O^{2+}.

5. (c) Iodine in presence of CCl_4 gives chloro-iododerivative (mixed halides)

6. (c) $M_{H_2O_2} = \dfrac{\text{Volume strength}}{11.2} = \dfrac{33.6}{11.2} = 3M \quad \therefore N_{H_2O_2} = 6N$

i.e. 3 mol H_2O_2 in 1 litre solution or $1000 \times d$ g solution

$\therefore$ mass of water = $(1000d - 34 \times 3)$ g

$\therefore \quad m_{H_2O_2} = \dfrac{3 \times 1000}{(1000d - 34 \times 3)}$ g

mole fraction of $H_2O_2 = \dfrac{3}{3 + \dfrac{(1000d - 102)}{18}}$

$= \dfrac{54}{54 + (1000d - 102)} = \dfrac{54}{(1000d - 48)}$

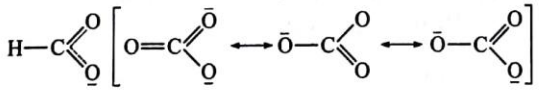
7. (b) These are facts about truncated tetrahedron.

8. (a) At Boyle's temperature, $PV = RT\,(B, C \ldots = 0)$

$\therefore \quad \dfrac{B}{Z} = 0$

Section B

9. (b, c, d)



Resonance Canonical forms

10. (a,d) I_3^- is linear (sp^3d) $\underset{\text{Lewis acid}}{I_2} + \underset{\text{Lewis base}}{I^-} \longrightarrow I_3^-$

11. (a,d) Due to different orientation of attached gps.

12. (a,c) Entropy of C_G and C_D are different. Average bond enthalpy and bond dissociation energy are different.

13. (d) This is crossed cannizzaro reaction. In clemmensen reduction (Zn–Hg/HCl), only $>C=O$ gp. are reduced to $-CH_2$. Pent-2,3-dione will not give iodoform reaction.

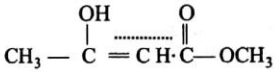
Section C

14. (a) Ni forms Ni^{2+} more readily than Pt^{2+} due to lower values of $(IE_1 + IE_2)$

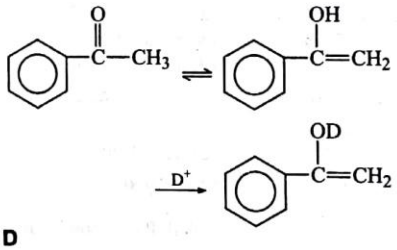
15. (c) Pt forms Pt^{4+} more readily than Ni^{4+} due to lower values of $(IE_1 + IE_2 + IE_3 + IE_4)$

16. (c) –OH gp is attacked by Na.

17. (c) intramolecular H–bonding



18. (b)



Section D

19. Two

20. Three

21. Two

22. Eight

23. Nine

24. One

25. One

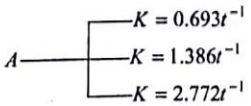
26. Three (1°, 2° sp^3 and 2° sp^2)

IIT-JEE MODEL PAPER CHEMISTRY 3-A

Time : 60 minutes **M.M. : 80**

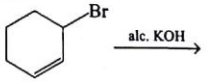
Section A : Single Correct Answer [2×9 = 18]

1. Which of the following statement is correct ?
   (a) The dipole moment of CH_3F is greater than CH_3Cl
   (b) Photobromination of 2-methyl propane gives a mixture of 1-bromo-2-methyl propane and 2-bromo-2-methyl propane in the ratio 9 : 1
   (c) Acetate ion is stronger base than methoxide ion
   (d) Sulphanilic acid is dipolar in nature
2. Which of the following is incorrect ?
   (a) Molar mass of NaCl determined experimentally is 58.5
   (b) SF_4 possess the bond angles 90°, 102° and 173°
   (c) Band gap in germanium is small
   (d) CuI_2 is less stable compound in aqueous medium
3. Select the incorrect statement :
   (a) Carbon nanotube has 20 hexagon and 5 pentagon.
   (b) Molar mass of Buckminster fullerene isotope of carbon is 720.
   (c) Liquid O_2 is pink in colour.
   (d) H_3PO_2 is stronger acid than H_3PO_4.
4. The volume in dm^3 of given mass of an ideal gas at 760 mm of Hg pressure and 298 K divided by 24.47 dm^3 gives :
   (a) Avogadro no. (b) mole of gas
   (c) mass of gas (d) pressure of gas
5. The specific volume of water is 1.003 cm^3g^{-1}. The density of water in g/cm^3 is :
   (a) 1.003 (b) 18×1.003
   (c) $\frac{1.003}{18}$ (d) 0.9970
6. Number of P—O, P = O and P—P bonds in P_4O_{10} are respectively :
   (a) 12, 4, 0 (b) 12, 4, 3
   (c) 6, 6, 3 (d) 6, 6, 0
7. u_{AV}, u_{rms} and u_{MP} are respectively average, root mean square and most probable speed of the molecule of an ideal monoatomic gas at absolute temperature T. The molecule mass of gas is M, then :
   (a) no molecule can have a speed greater than u_{rms}
   (b) no molecule can have a speed greater than u_{MP}
   (c) no molecule can have a speed greater than u_{AV}
   (d) average kinetic energy of a molecule is $\frac{3M}{4N}(u_{MP})^2$
8. The nuclear fusion which is not correct :
   (a) $4{}_1^1H \longrightarrow {}_2^4He + 2{}_{-1}^0e + 2$ neutrino + energy
   (b) ${}_6^{12}C + {}_1^1H \longrightarrow {}_7^{13}N$ + energy
   (c) ${}_7^{14}N + {}_1^1H \longrightarrow {}_8^{15}O$ + energy
   (d) ${}_5^{13}C + {}_1^1H \longrightarrow {}_6^{14}C$ + energy
9. Rate constants for a parallel path I order reactions are given as :



   The average half life of A is :
   (a) 0.693 t (b) 0.406 t
   (c) 0.306 t (d) 0.206 t

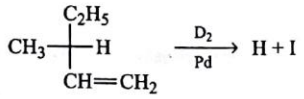
Section B : More Than One Correct Answers [3×5 = 15]

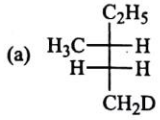
10. Disproportionation of Cu^+ ion into Cu^{2+} ion and Cu in aqueous solution can be prevented by the addition of :
    (a) Cu + HCl (b) thiourea
    (c) NaCl (d) benzene
11. Pick up the correct statements :
    (a) The magnitude of the potential energy of the electron in any orbit is greater than its kinetic energy.
    (b) Even when the metal surface is fainlly illuminated with suitable frequency of radiations, the photo electrons leave the surface immediately.
    (c) The time required for revolution of an electron in 4th Bohr's orbit is 8 times of the time required for revolution in 2nd Bohr's orbit.
    (d) Transition of electron from 4d orbital to 2s orbital is not possible.
12. Which of the following reaction produces conjugated dienes ?
    (a)  $\xrightarrow{\text{alc. KOH}}$
    (b) $CH_3CH(Br)\cdot CH = CH_2 \xrightarrow{\text{alc. KOH}}$
    (c) $Br\cdot CH_2\cdot CH = CH_2 \xrightarrow{\text{alc. KOH}}$
    (d) $Br\cdot CH_2\cdot CH_2\cdot CH = CH_2 \xrightarrow{\text{alc. KOH}}$
13. Which statement is correct about the following reaction ?

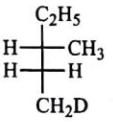
$$^{14}CH_2 = CH—CH_3 + Cl_2 \xrightarrow[\text{low conc. of } Cl_2]{\Delta} P + Q$$

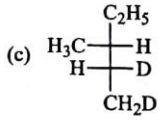
    (a) P and Q are $^{14}CH_2 = CH—CH_2Cl$ and $^{14}CH_2—CH = CH_2$ (Cl)
    (b) The reaction obeys free radical allylic substitution.
    (c) P and Q formed are in 1 : 1 ratio.
    (d) Rearrangement of free radical takes place.

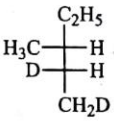
14. Which are the correct products of the reaction ?



(a) 

(b) 

(c) 

(d) 

Section C : Statement-Explanation Type Problems

Read the information given below and select the correct choice in terms of (a), (b), (c) and (d) for each question. **[4 × 3 = 12]**

(a) **S** is correct but **E** is wrong.
(b) **S** is wrong but **E** is correct.
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**.
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**.

15. **S:** $Cl_3C{\cdot}CH = CH_2 \xrightarrow{HCl} Cl_3{\cdot}C{\cdot}CHClCH_3$

E: $Cl_3C{\cdot}\overset{+}{C}H_2\,CH_2$ (1°) is more stable than $Cl_3C{\cdot}\overset{+}{C}H{\cdot}CH_3$ (2°).

16. **S:** Conversion of $CH{\equiv}CH \longrightarrow CH_3CHO$ is a redox change.

E: Hydration is never redox reaction.

17. **S:** All the detergents are surfactants but all the surfactants are not detergents.

E: Detergents possess surface activity as well as cleansing action.

Section D : Matching Type Problems [1 × 4 = 4]

18. **More than one match are possible :**

List A	List B
A. $2KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl + 3O_2(g)$	1. Homogeneous catalysis
B. $2H_2O_2(l) \xrightarrow{Hg(l)} 2H_2O(g) + O_2(g)$	2. Heterogeneous catalysis
C. $2H_2O_2(l) \xrightarrow{Pt} 2H_2O + O_2(g)$	3. $\Delta n_{reaction} \geq 1$
D. $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$	4. $\Delta n_{reaction} \leq 1$

19. **More than one match are possible** **[1 × 4 = 4]**

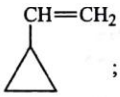
List A	List B
A. Work	1. Boundary phenomenon
B. Heat	2. Path function
C. Temperature	3. Intensive property
D. $q + w$	4. Extensive property

Section E : Comprehension [3 × 3 = 9]

Organic compounds may be saturated or unsaturated. The degree of unsaturation or sometimes called as index of hydrogen deficiency represents the number of pairs of H's a molecular formula lacks to be an alkane (C_nH_{2n+2}). Presence of ring and multiple bonds always brings in the index of hydrogen deficiency in molecule. More the number of multiple bonds more is hydrogen deficiency.

20. Which of the following possess degree of unsaturation as reported ?

(a) ; 1° (b) ; 3°

(c)  ; 3° (d) ; 4°

21. C_4H_5N has degree of unsaturation equal to :

(a) 1° (b) 2°
(c) 3° (d) 4°

22. A hydrocarbon (A) has 2° unsaturation. It is treated with 1 mole of H_2 catalytic hydrogenation. Experiment shows that there is no reaction. The hydrocarbon has :

(a) two double bond (b) one triple bond
(c) one ring (d) two rings

Section F : Single Integer Answer [3 × 6 = 18]

23. The number of cells which can be produced involving the redox change :

$Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}$ are :

24. Number of mole of As_2S_3 required to reduce 56 mole of HNO_3 according to reaction.

$As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$

25. The '*n*' factor of O_3 in the redox change, $2O_3 \longrightarrow 3O_2$ is :

26. The vapour pressure of a mixture of two volatile liquids is given by $P_m = 4.0X_A + 3.0$. The vapour pressure of pure *B* is:

27. The resistance of mercury becomes almost zero at ... K.

28. The relative strength of two weak acids $HA(K_a = 8\times10^{-5})$ and $HB(K_b = 2\times10^{-5})$ is :

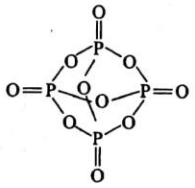
SOLUTION OF MODEL PAPER 3-A

Section A

1. (d) Sulphanilic acid is H_3N—C$_6$H$_4$—SO_3H

possess Zwitter ion structure as H_3^+N—C$_6$H$_4$—SO_3^-

2. (a) Exp. molar mass of electrolytes > cal. molar mass of electrolyte.
3. (c) Liquid O_2 is blue in colour.
4. (b) At 1 atm and 298 K volume of 1 mole of gas is 24.47 dm^3
   ∴No. of mole × volume of 1 mole = volume of n mole
5. (d) $\text{density} = \frac{1}{\text{specific volume}} = \frac{1}{1.003} = 0.9970$
6. (a)



7. (d) $\text{Av. K.E.} = \frac{3}{2}\frac{RT}{N} = \frac{3\times 2RTM}{4N\cdot M} = \frac{3M(U_{MP})^2}{4N}$
8. (d) Carbon has atomic no. 6.
9. (d) Av. $K = 0.693 + 1.386 + 2.772 = 4.851$

   $\therefore \quad T = \frac{1}{K} = 0.206$

Section B

10. (a,b) Due to complex formation, *e.g.*, $[CuCl_2]^-$ and $[Cu\{SC(NH_2)_2\}_3]^+$.
11. (a, b, c, d) For transition $\Delta l = \pm 1$
12. (a, b, d) In (c) cumulitive diene $CH_2 = C = CH_2$ is formed.
13. (a, b, c, d) $^{14}CH_2 = CH—CH_3 \longrightarrow {}^{14}CH_2 = CH—\dot{C}H_2$

$$\longrightarrow {}^{14}\dot{C}H_2—CH = CH_2$$

$$^{14}CH_2 = CH—\dot{C}H_2 \xrightarrow{Cl_2} {}^{14}CH_2 = CH—CH_2Cl$$

$$^{14}\dot{C}H_2—CH = CH_2 \xrightarrow{Cl_2} {}^{14}CH_2Cl—CH = CH_2$$

Thus, 1 : 1 mixture of two is obtained.

14. (c, d) This is addition of D_2 on C = C.

Section C

15. (b) The stability of 1° is more due to –ve *IE* of 3Cl than 2° and thus product formed is $Cl_3\cdot CH_2\cdot CH_2Cl$.
16. (b) S is wrong, the average oxidation number in CH ≡ CH and CH_3CHO is –1. Also hydration is never a redox reaction.
17. (c) Surfactants possess surface activity only whereas detergents possess surface activity and detergency, *i.e.*, cleansing action.

Section D

18. A—2, 3; B—2, 3; C—2, 3; D—1,4
19. A—1, 2, 4; B—1, 2, 4; C—3; D—4

Section E

20. (d) (a) is C_4H_6 having 2°, (b) is C_4H_8 having 1°, (c) C_5H_8 having 2°, (d) C_6H_8 having 4°.
21. (c) Disregard N but remove one H for each N.
22. (d) Two rings has 2° unsaturation and do not react with H_2.

Section F

23. **Three :** Electrode : $PtFe^{2+}|Fe^{3+}$ $Fe^{2+} \longrightarrow Fe^{3+} + e$

    Electrode : $Fe|Fe^{2+}$ $Fe \longrightarrow Fe^{2+} + 2e$

    Electrode : $Fe|Fe^{3+}$ $Fe \longrightarrow Fe^{3+} + 3e$

    use any two at one time and get three cells with same redox change.
24. **Six :** $(As^{3+})_2 \longrightarrow 2As^{5+} + 4e; 3e + N^{5+} \longrightarrow N^{2+}]\times 28$ ...(i)

    $(S^{2-})_3 \longrightarrow 3S^{6+} + 24e$

    $As_2S_3 \longrightarrow 2H_2AsO_4 + 3H_2SO_4 + 28e]\times 3$ ...(ii)

    By (i) and (ii)

    $3As_2S_3 + 28HNO_3 \longrightarrow 6H_3AsO_4 + 9H_2SO_4 + 28NO$

    $\therefore 3As_2S_3 \equiv 28HNO_3$
25. **Six :** $2O_3 \longrightarrow 3O_2$

    2 mol $O_3 \equiv 3$ mol $O_2 \equiv 4\times 3$ eq. O_2

    $\equiv 12$ eq. O_3

    1 mol $O_3 \equiv 6$ eq. O_3
26. **Three :** $P_M = 4.0X_A + 3.0$

    if $X_A = 0$, $P_M = P_B^\circ$

    $\therefore \quad P_B^\circ = 3.0$
27. **Four :** It is a fact.
28. **Two :** Relative strength of two weak acids $= \frac{\sqrt{K_{a_1}\cdot C_1}}{\sqrt{K_{a_1}\cdot C}}$

    if $C_1 = C_2$

    $\text{R.S.} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \sqrt{\frac{8\times 10^{-5}}{2\times 10^{-5}}} = 2$

IIT-JEE MODEL PAPER CHEMISTRY 3-B

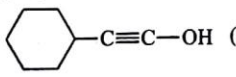
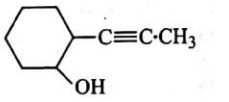
Time : 60 minutes **M.M. : 80**

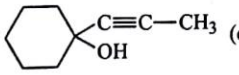
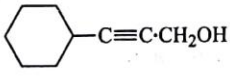
Section A : Single Correct Answer [2×9 = 18]

1. Which of the following is incorrect ?
   (a) Enthalpy is an extensive property
   (b) Zeroth law suggest for thermal equilibrium
   (c) First law of thermodynamics fails to explain systems away from equilibrium
   (d) First law of thermodynamics predicts the feasibility of change and rate of reaction.
2. The no. of neutrons (n) and no. of protons (p) in a nucleus can be depicted as :
   (a) n is always greater than p
   (b) n is always equal to p
   (c) $n \gtrless p$ or $n = p$
   (d) The ratio of n and p is always 1.5
3. At very high pressure helium (He) crystallises as :
   (a) bcc (b) ccp
   (c) fcc (d) can not be crystallised
4. Analysis shows that a non stoichiometric compound exists as $Ni_{0.98}O_{1.0}$. The ratio of fraction Ni^{2+} and Ni^{3+} present in $Ni_{0.98}O_{1.0}$ is :
   (a) 98.04 (b) 23.51
   (c) 49.02 (d) 24.01
5. The temperature of a bomb calorimeter was found to rise by 1.617 K, when a current of 3.2 ampere was passed for 27.0 second from a source of 12.0 volt. Assuming heat is taken only by bomb calorimeter, the calorimeter constant is :
   (a) 19.155 JK^{-1} (b) 191.5 JK^{-1}
   (c) 641.18 JK^{-1} (d) 1.915 JK^{-1}
6. Which of the following metal does not give the following reaction ?

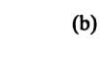
$$M \xrightarrow{\text{Dissolved in } NH_3} M^{2+} + 2[e(NH_3)_X]^{-1}$$

   (a) Be (b) Mg
   (c) Ca (d) Ba
7. The product formed during action of cyclohexanone with propenyl ion followed by hydrolysis is :

(a)  (b) 

(c)  (d) 

8. Glyoxal on reaction with dil. NaOH gives :

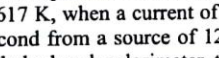
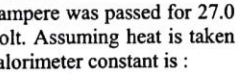
(a) (b) 

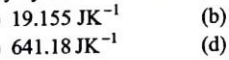
(c) (d)

9. Select the incorrect statement :
   (a) Central C—C bond in buta-1, 3-diene is shorter than n-butane.
   (b) $CH_2 = CH^-$ is more basic than $^-C \equiv CH$.
   (c) Diphenyl bromoethene on reaction with KNH_2 gives diphenyl ethane.
   (d) Vinyl chloride on reaction with dimethyl copper gives an alkene.

Section B : More Than One Correct Answers [4×3 = 12]

10. Select the correct statements :
    (a) Dipole moment of NH_3 is greater than dipole moment of NF_3.
    (b) Solvents with high dielectric constants tend to be more polar.
    (c) Wave functions are used to calculate the quantised energy of orbit.
    (d) In MO theory conservation of orbitals takes place.
11. Contributing canonical forms of diazomethane CH_2N_2, towards its resonance structure are :

(a)  (b) 

(c)  (d)

12. Select the correct statements :
    (a) E_a is small and ΔH_r is negative, reaction is fast and exothermic.
    (b) E_a is large and ΔH_r is negative, reaction is slow and exothermic.
    (c) Catalyst can increase rate by increasing entropy of activation.
    (d) For an exothermic reaction $\Delta H < E_a$.

Section C : Comprehension Type Problems [2×5 = 10]

Indicators are the substances used to detect the end point or completion point of a reaction. Acid-base indicators are themselves weak acid or weak base. Phenolphthalein is not a good indicator for weak acid titrations, whereas methyl orange is not a good indicator for weak alkali titrations.

13. Methyl organge on dissociation gives :
    (a) coloured cation
    (b) coloured anion
    (c) both coloured ions
    (d) both colourless ions

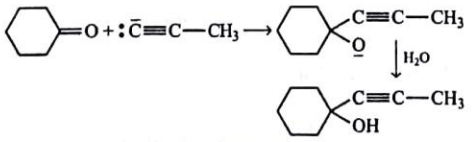
14. Select the incorrect statement about quantitative estimation by volumetric analysis :
    (a) Equivalence point is theoretical value.
    (b) End point is experimental value.
    (c) Both these point are exactly same.
    (d) Both these points are almost same.
15. For which titration phenolphthalein can not be used :
    (a) $CH_3COOH + NaOH$ (b) $H_2C_2O_4 + KOH$
    (c) $HCl + NH_4OH$ (d) $H_2SO_4 + KOH$
16. For which titration methyl orange can not be used ?
    (a) HCl *vs* NH_4OH (b) HCl *vs* NaOH
    (c) $FeSO_4$ *vs* $KMnO_4$ (d) H_2SO_4 *vs* KOH
17. Select the correct statement :
    (a) Phenolphthalein is more dissociated in NH_4OH than in NaOH.
    (b) The degree of dissociation of phenolphthalein is more in HCl than in KOH.
    (c) Phenolphthalein gives coloured cation on dissociation.
    (d) The degree of dissociation of phenolphthalein is more is strong base than in weak base.

Section D : Single Integer Answer [4×10 = 40]

18. Number of possible isomers of the complex ion $[Cr(NH_3)(OH)_2Cl_3]^{2-}$ are ...
19. Number of phases of a substance (*e.g.*, S_R, S_M, S_l, S_V) can exist together in equilibrium for one component system.
20. Disproportionation of P_4 in alkaline medium produces how much mole of HPO_3^{2-}?
21. '*n*' factor for Fe_2O_3 in its reaction with HCl (*aq.*) to produce $FeCl_3$ and H_2O is ...
22. Number of nearest neighbours NH_3 molecules to each molecule of NH_3 in solid ammonia.
23. At what pH a $1.0\times10^{-3}\,M$ solution of a basic indicator ($K_{ind} = 1.0\times10^{-10}$) change colour ?
24. Following electrodes are coupled to from a cell. The standard E° for the given cell is ...
    $A^{3+} + 3e \longrightarrow A;\ E^\circ = 1.50$ V
    $B^{2+} + 2e \longrightarrow B;\ E^\circ = -2.50$ V
25. Ionisation constants for acids HA and BH^+ are 10^{-7} and 10^{-3} respectively. The $pK_{eq.}$ for the reaction $HA + B \rightleftharpoons BH^+ + A^-$ is ...
26. Specific rotation of a pure enantiomer is +10°. If the isomer is isolated from a reaction showing 80% retention and 20% recemisation, the observed rotation will be plus.
27. How many kinds of H's are there in $CH_3—CH=CH_2$?

SOLUTION OF MODEL PAPER 3-B

Section A

1. (d) Ist law of thermodynamics does not suggest about rate of reaction.
2. (c) $\frac{n}{p} = 1$ for ${}_1^1H$ and $\frac{n}{p} = 2$ maximum for ${}_1^3H$.
3. (c) It is a fact.
4. (b) Oxidation no. of Ni in $Ni_{0.98}O_{1.0} = \frac{200}{98}$
   Let, % of Ni^{2+} and Ni^{3+} be a and b respectively. Thus,
   $a + b = 100$.
   Thus, $a\times2 + (100-a)\times3 = \frac{200}{98}\times100$
   $\therefore \quad a = 95.92$
   $\therefore \quad b = 4.08$
   $\therefore \quad \frac{a}{b} = 23.51$
5. (c) Energy given = $3.2\times27\times12.0 = 1036.8$
   Heat taken by calorimeter = $mS\times1.617$
   $\therefore mS$ of calorimeter = $\frac{1036.8}{1.617} = 641.18$ J
6. (a) Be does not show this property.
7. (c) 
8. (c) This is intramolecular Cannizzaro reaction.
9. (c) $(C_6H_5)_2C=C(H)Br \xrightarrow{KNH_2} C_6H_5—C\equiv C—C_6H_5$

Section B

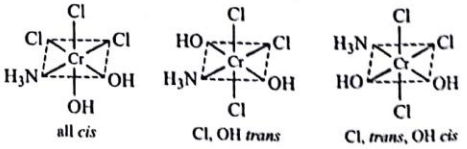
10. (a,b, d) $\mu_{NH_3} = 1.46D; \mu_{NF_3} = 0.24$ D No. of orbitals mixed = No. of MO formed; wave functions are used to calculate quantised energy of an electron in an orbital.
11. (a,b) Rest all are unstable forms and do not contributes significantly.
12. (a, b, c) For an exothermic reaction $\Delta H \gtrless E_a$.

Section C

13. (a) $MeOH \rightleftharpoons Me^+ + OH^-$
14. (c) Equivalence point ≃ Experimental value of end point.
15. (c) Phenolphthalein is not a good indicator for weak acid titration.
16. (c) Methyl orange is an acid-base indicator. This is redox change.
17. (d) Phenolphthalein is weak acid and thus dissociates more in base.
    $HPh \rightleftharpoons H^+ + Ph^-$

Section D

18. **Three**



19. Three : F + P = C + 2; F = 0 (minimum); C = 1

$\therefore$ P = 3

20. Two : $P_4 + 4OH^- + 2H_2O \longrightarrow 2PH_3 + 2HPO_3^{-2}$

21. Six : $Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$

$$E = \frac{M}{6}$$ [Fe_2O_3 is base]

22. Six : It is a fact.

23. Four : $K_b = \frac{[B^+][OH^-]}{[BOH]}$; At 50% $[OH^-] = 1 \times 10^{-10}$

$\therefore$ pOH = 10 and pH = 4

24. Four : $3B + 2A^{3+} \longrightarrow 3B^{2+} + 2A$

$E^\circ = 2.50 + 1.50 = 4.0$ volt

25. Four : $K_{a_{HA}} = \frac{[H^+][A^-]}{[HA]} = 10^{-7}$ ...(1)

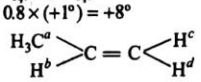
$$K_{BH^+} = \frac{[B][H^+]}{[BH^+]} = 10^{-3}$$

$$\therefore \quad \frac{K_{a_{HA}}}{K_{a_{BH^+}}} = \frac{[A^-][BH^+]}{[HA][B]} = K_{eq.} = \frac{10^{-7}}{10^{-3}} = 10^{-4}$$

or $-\log K_{eq.} = pK_{eq.} = 4$.

26. Eight : $0.8 \times (+1^\circ) = +8^\circ$

27. Four :

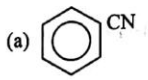
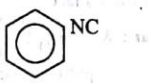
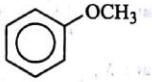


The H atoms on right of double bond are not equivalent since, one is *cis* to CH_3 and other is *trans*. Replacement of H^c by *X* gives the *cis*-diastereomer. Replacement of H^d gives *trans*-diastereomer.

IIT-JEE MODEL PAPER CHEMISTRY 4-A

Time : 60 minutes **M.M. : 82**

Section A : Single Correct Answer [2×9 = 18]

1. Which of the following does not show Lewis acid-base reaction ?
   (a) $BrF_3 + F^-$ (b) $AlCl_3 + BF_3$
   (c) $I_2 + I^-$ (d) $KH + H_2O$
2. Which of the following is finger print of an atom ?
   (a) Molecular spectrum (b) X-ray spectrum
   (c) IR spectrum (d) Line spectrum
3. Ziegler-Natta catalyst used in polymerisation of ethylene is :
   (a) $TiCl_4(C_2H_5)_3B$ (b) $TiCl_4(C_2H_5)_3Na$
   (c) $TiCl_4(C_2H_5)_3Zn$ (d) $TiCl_4(C_2H_5)_3Al$
4. If X is the mole fraction of solute when dissolved in water. The molality of a solution can be given by :
   (a) $\frac{500X}{9(1-X)}$ (b) $\frac{500(1-X)}{9\cdot X}$
   (c) $\frac{1000(1-X)}{9\cdot X}$ (d) $\frac{1000X}{9(1-X)}$
5. Which one is not correct about N_2Cl_4?
   (a) It is a non-planar molecule
   (b) Both the N atoms are sp^3-hybridized
   (c) Both are pyramidal N atoms
   (d) One N is sp^3 and the other is sp^2 hybridized
6. Pure PCl_5 is introduced into an evacuated chamber and attains the equilibrium at 250°C and 2 atm pressure. The equilibrium mixture contains 40% chlorine by volume. K_p of reaction at 250°C is :
   (a) 0.133 (b) 1.6
   (c) 1.78 (d) 0.266
7. The pH of solution by mixing 50 mL of 0.6 M NH_4OH and 50 mL of 0.1 M H_2SO_4 is : (Given K_a for $NH_4^+ = 10^{-9}$)
   (a) 4.39 (b) 6.61
   (c) 9.30 (d) 7.39
8. Select the wrong statement about Cannizzaro reactions :
   (a) It is a disproportionation reaction.
   (b) Addition of OH^- occurs in I step on the carbonyl gp. to form complex anion.
   (c) The complex anion formed acts as H^- donor to other molecule of aldehyde reducing it to methoxide ion while the anion is itself oxidised to formic acid.
   (d) The resulting methoxide ion and formic acid acts as Lewis base-Lewis acid to form methyl formate ion.
9. Phenols on treatment with diazomethane in presence of ether gives :
   (a)  (b) 
   (c) (d) 

Section B : More Than One Correct Answers [3×4 = 12]

10. Point out the correct reactions :
    (a) $BrCCl_3 + ROOR \longrightarrow ROBr + {:}CCl_3$
    (b) $BrC\cdot Cl_3 + ROOR \longrightarrow ROCl + {:}CBrCl_2$
    (c) $HCCl_3 + ROOR \longrightarrow ROH + {:}CCl_3$
    (d) $HCCl_3 + ROOR \longrightarrow ROCl + {:}CHCl_2$
11. The nature of H's in $CH_3\cdot CH = CHCH_2CH_2CH(CH_3)_2$ can be correctly represented as :
    (a) it has two types of allylic and one type of vinylic H-atoms, along with 3°, 2° and 1° H-atoms
    (b) both the vinylic H-atoms are equivalent
    (c) the reactivity order of H's is allylic 2° > allylic 1° > 3° > 2° > 1° > vinylic
    (d) both the allylic H's are equivalent
12. IUPAC name of $[Ni(NH_3)_6]_3[Co(NO_3)_6]_2$ is :
    (a) Hexaamine nickel (III) hexanitrocobaltate (II)
    (b) Hexaamine nickellette (III) hexanitrocobalt (II)
    (c) Hexaamine nickel (II) hexanitrocobaltate (III)
    (d) Hexaamine nickellete (II) hexanitrocobalt (III)
13. Select the correct statements :
    (a) K-electron capture always leads to γ-rays emission.
    (b) K-electron capture shows a decrease in atomic number.
    (c) K-electron capture shows an increase in mass number.
    (d) K-electron capture shows an increases in $\frac{n}{p}$ ratio.

Section C : Statement-Explanation Type Problems

Choose the correct choice from the codes (a), (b), (c) and (d) given below for each question :

(a) **S** is correct but **E** is wrong.
(b) **S** is wrong but **E** is correct.

(c) Both **S** and **E** are correct and **E** is correct explanation of **S**.

(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**. [3×4 = 12]

14. **S:** Activation energy for nuclear fusion is very high.
E: Nuclear fusion are made at high temperature to overcome electrostatic repulsion between two nuclei.

15. **S:** VIBGYOR is a continuous spectrum.
E: In continuous spectrum each colour fades into next colour.

16. **S:** Ionisation energy of Li is higher than that of sodium.
E: It is easier to oxidise Li(s) to $Li^+(aq)$ as compared to Na(s) to $Na^+(aq)$.

17. **S:** A nucleophile Nu^- : adds to $C=C$ of $-\overset{|}{C}=C-\overset{|}{C}=O$ but not to ordinary alkenes.
E: Nu^-: adds to the α-carbon leaving a resonance stabilized carbaion enolate.

Section D : Single Integer Answer [4 × 10 = 40]

18. The basicity of $K_XH_Y(PO_4)_Z$ in the reaction is :
$K_XH_Y(PO_4)_Z + KOH \longrightarrow K_{X+1}H_{Y-1}(PO_4)_Z + H_2O$

19. The acidity of $K_2H_Y(PO_4)_2$ is :

20. The ratio of mole of H^+ furnished to 90 g $H_2C_2O_4$ and 126 g $H_2C_2O_4 \cdot 2H_2O$ is :

21. A bottle is labelled 122.5% oleum. 22.7 mL of $Ca(OH)_2$ of unknown molarity are used to completely neutralise 1 g oleum. The normality of $Ca(OH)_2$ is :

22. No. of electrons in the redox change :
$NO_2^- + H^+ + ne \longrightarrow NO + H_2O$

23. Most probable speed of butane at 348 K is same as root mean square speed of H_2 at T K. The value of T is :

24. 8 g of CH_4 diffuses through a pin hole in 2 sec. At the same temperature and pressure mass of He diffuses through same pin hole is 4 sec is :

25. For the given reaction : $RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$; the pOH value for 10^{-2} N RNH_2 solution is : (Given pK_a for RNH_3^+ is 10)

26. van't Hoff's factor for very dilute solution of $NaHSO_4$ is :

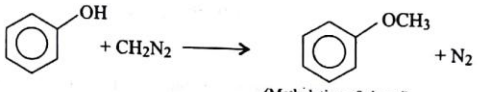
27. Total number of aromatic isomers of the formula C_7H_8O are :

SOLUTION OF MODEL PAPER 4-A

Section A

1. (b) Both are Lewis acid.
2. (d) Each atom shows a characteristic line spectrum.
3. (d) It is a fact.
4. (a)
$$\frac{n}{n+N} = X$$
$$\frac{N}{n+N} = 1 - X$$
$$\therefore \quad \frac{n}{N} = \frac{X}{1-X}$$
$$\frac{n \times M \times 1000}{w \times 1000} = \frac{X}{1-X}$$
$$\therefore \quad \text{Molality} = \frac{X}{1-X} \times \frac{1000}{18} = \frac{500X}{9(1-X)}$$
5. (d) Others are facts about N_2Cl_4.
6. (a) $\underset{20}{PCl_5} \rightleftharpoons \underset{40}{PCl_3} + \underset{40}{Cl_2}$
Total mole or volume = 100 ($\because V \propto n$ at constant P, T)
$$\therefore K_p = \frac{n_{PCl_3} \times n_{Cl_2}}{n_{PCl_5}} \times \left[\frac{P}{\Sigma n}\right]^1$$
$$K_p = \frac{40 \times 40}{20} \times \frac{2}{100} = \frac{16}{10} = 1.6 \text{ atm}$$
7. (c) $2NH_4OH + H_2SO_4 \rightleftharpoons (NH_4)_2SO_4 + 2H_2O$

Meq. at $t = 0$	30	10	0	0
Meq. after reaction	20	0	10	10

$$\therefore [(NH_4)_2SO_4] = \frac{10}{2 \times 100} M$$
$$\therefore \quad [NH_4^+] = \frac{10 \times 2}{2 \times 100} M = 0.1\ M$$
$$[NH_4OH] = \frac{20}{100} = 0.2\ M$$
$$pOH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]} = 10^{-5} + \log\frac{0.1}{0.2}$$
$$= 5 - 0.3010 = 4.6989$$
$$\therefore \quad pH = 9.3010$$
8. (d) The process of step (d) involves exchange of proton, *i.e.*, Bronsted acid-base reaction.
9. (d) 

(Methylation of phenol)

Section B

10. (a,c) The $ROOR$ dissociates to $^\bullet OR + {}^\bullet OR$
11. (a, b, c) $\overset{a}{CH_3}-\overset{b}{CH}=\overset{b}{CH}-\overset{c}{CH_2}-\overset{d}{CH_2}-\overset{e}{CH}(\overset{f}{CH_3})_2$

a—Allylic 1°	d—2°
b—Vinyl	e—3°
c—Allylic 2°	f—1°

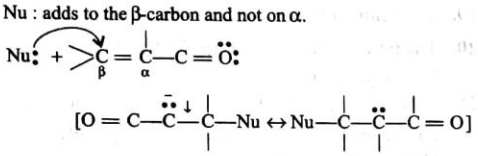
The reactivity order is : $c > a > e > d > f > b$
12. (c) It is a fact.
13. (b, d) $^1_1p + {}^0_{-1}e \longrightarrow {}^1_0n$ + X - rays
e.g., $^{133}_{56}Ba + {}^0_{-1}e \longrightarrow {}^{133}_{55}Cs$ + X - rays
Mass no. remains same; at. no. decrease, $\frac{n}{p}$ increases.

Section C

14. (c) Explanation is correct reason for statement.
15. (c) –do–

16. (d) Due to more hydration energy of Li^+; Thus $E^\circ_{RP}Li > E^\circ_{RP}Na$.

17. (a) Nu : adds to the β-carbon and not on α.



Section D

18. **One :** No. of replaced H atom = 1

19. **Two :** Total charge on cation (other than H)

20. **One :** Both gives 2 mole H^+

21. **Two :** (100 + 22.5)% oleum means 222.5 g H_2SO_4

$$H_2O + SO_3 \longrightarrow H_2SO_4$$

$\because$ 18 g H_2O gives = 98 g H_2SO_4

$\therefore$ 22.5 g H_2O gives $= \frac{98 \times 22.5}{18} = 122.5$ g H_2SO_4 in 100 g oleum

$\therefore$ Total $H_2SO_4 = 100 + 122.5 = 222.5$ g

1 g oleum $\equiv 2.225$ g $H_2SO_4 = \frac{2.225}{49} \times 1000 = 45.41$ meq.

$\therefore$ Meq. of $H_2SO_4 = 45.41$

$\therefore$ $22.7 \times N = 45.41$

$N = 2$

22. **Three :** $NO_2^- + 4H^+ + 3e \longrightarrow NO + 2H_2O$

23. **Eight :** $\frac{2R \times 348}{58} = \frac{3RT}{2}$

$\therefore$ $T = \frac{4 \times 348}{58 \times 3} = 8$ K

24. **Eight :** $\frac{8}{2} \times \frac{4}{w} = \sqrt{\frac{16}{4}} = 2$

$w = 8$ g

25. **Three :** $RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$

$$[OH^-] = C\alpha = \sqrt{\frac{K_b}{C}} \cdot C = \sqrt{K_b \cdot C}$$

$$= \sqrt{\frac{K_w}{K_a} \cdot C} = \sqrt{\frac{10^{-14}}{10^{-10}} \times 10^{-2}}$$

$$= \sqrt{10^{-6}} = 10^{-3}$$

$\therefore$ pOH = 3

26. **Three :** $\underset{1}{NaHSO_4} \rightleftharpoons \underset{1}{Na^+} + \underset{1}{H^+} + \underset{1}{SO_4^{2-}}$

27. **Four :** *o*-, *m*-, *p*-cresol and anisole and benzyl alcohol.

IIT-JEE MODEL PAPER CHEMISTRY 4-B

Time : 60 minutes **M.M. : 82**

Section A : Only One Answer Correct **[2×9 = 18]**

1. Which of the following statement about chemical equilibrium are correct ?
   (I) For gaseous reaction, the equilibrium can be established in open container
   (II) The state of equilibrium is dynamic and not static
   (III) If temperature is kept constant, the colour of the reacting system changes with time
   (IV) For gaseous reaction, the equilibrium can be attained at constant volume or constant pressure
   (a) I, II and IV (b) II and III
   (c) II and IV (d) I, II and III
2. At 1 atm b.pt. of aqueous solution is greater than 100°C because :
   (I) non volatile solute on dissolution in water lowers the vapour pressure of solvent
   (II) non electrolyte solute on dissolution in water lowers the vapour pressure of solvent
   (III) electrolyte solute on dissolution in water lowers the vapour pressure of solvent
   (IV) chemical potential of water in solution is more than the chemical potential of water in pure state
   (a) I, II and III (b) I, II and IV
   (c) I, II, III and IV (d) I, III and IV
3. According to Lewis concept, which of the following is correct acidic order ?
   (a) $Fe^{3+} < Fe^{2+}$ (b) $Na^+ < K^+$
   (c) $Be^{2+} < B^{3+}$ (d) None of these
4. Which of the aqueous solution will act as buffer ?
   (I) $CH_3COOH + CH_3COONH_4$
   (II) $NH_4OH + CH_3COONH_4$
   (III) $NaH_2PO_4 + Na_2HPO_4$
   (IV) $H_3BO_3 + Na_2B_4O_7$
   (a) III only (b) III and IV
   (c) I and II (d) I, II, III and IV
5. Which of the following statement are correct about H atom ?
   (I) It can form a covalent bond with other atoms
   (II) It can form an ionic bond with other atoms, it self changing to H^+
   (III) It can form an ionic bond with other atoms, it self changing to H^-
   (IV) It can form co-ordinate bond with other molecule
   (a) I and II (b) I, II and III
   (c) I, II, III and IV (d) I and III
6. Which of the following statements are correctly reported ?
   (I) α-D(+)-glucose and β-D(+)-glucose are anomers
   (II) Fructose is reducing sugar and sucrose is not reducing sugar
   (III) Glucose is non reducing sugar
   (IV) Maltose shows mutarotation
   (a) I, II and III (b) I, II and IV
   (c) I, III and IV (d) II, III and IV
7. The correct order of stability of the given carbanions is :
   1. $CH_3—\overset{-}{C}H_2$ 2. $CH_2=\overset{-}{C}H$
   3. $CH\equiv\overset{-}{C}$ 4. $C_6H_5—\overset{-}{C}H_2$
   (a) 1 > 2 > 3 > 4 (b) 4 > 3 > 1 > 2
   (c) 4 > 3 > 2 > 1 (d) 1 > 2 > 4 > 3
8. I_2 can be obtained from chili salt peter as :
   $$2X + 6HSO_3^- \longrightarrow 2Y + 6SO_4^{2-} + 6H^+$$
   $$5Y + X \longrightarrow 2Z + 3H_2O$$
   In these reactions *X*, *Y* and *Z* respectively are :
   (a) I^-, IO_4^- and I_2 (b) I^-, IO_3^- and I_2
   (c) IO_3^-, I^- and I_2 (d) IO_4^-, I^- and I_2
9. Which of the following gives NH_3 on heating to decomposition ?
   (I) $(NH_4)_2Cr_2O_7$ (II) $(NH_4)_2SO_4$
   (III) NH_4NO_3 (IV) NH_4NO_2
   (a) II, III and IV (b) III and IV
   (c) II only (d) IV only

Section B : More Than One Correct Answers **[3 × 4 = 12]**

10. Select the correct choices :
    (a) Cu_2O is added to glass to give ruby red colour
    (b) Normal domestic glass for windows is calcium alkali silicate
    (c) Glass is categorised amorphous solid on cooling its solution
    (d) Composition of glass may vary
11. Select the correct answers :
    (a) *p*-hydroxy phenol has higher b.pt. than *o*-hydroxy phenol
    (b) *o*-hydroxy phenol has higher b.pt. than phenol
    (c) *p*-hydroxy phenol has higher b.pt. than phenol
    (d) The order of m.pt. of cresols is *p*-cresol > *o*-cresol > *m*-cresol
12. Which of the following cells do not need liquid junction potential ?
    (a) $Fe(s) \mid FeO(s) \mid KOH(aq) \mid + Ni_2O_3(s) \mid Ni$
    (b) $Cd \mid CdO(s) \mid KOH\ (aq) \mid NiO_2(s) \mid Ni$
    (c) $Pb \mid PbSO_4(s) \mid H_2SO_4 \mid PbO_2(s) \mid Pb$
    (d) H_2 | Porous carbon road (with Pt or Pd in finely divide state) | NaOH | Porous carbon rod with Co, Pt or Ag finely divided state | O_2

13. K_p for the reaction : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is given by $K_p = \frac{n^2}{1-n} \times \left[\frac{P}{1+n}\right]$ where P is the pressure at equilibrium and n is degree of dissociation of PCl_5. Select the incorrect statement about this reaction if N_2 is added at equilibrium :
(a) On adding N_2 at constant volume, 'n' decreases
(b) On adding N_2 at constant volume, 'n' increases
(c) On adding N_2 at constant pressure, 'n' increases
(d) On adding N_2 at constant pressure, the K_p changes

Section C : Matching Type Problems

14. **Match the following : Only one match is possible :** [1 × 4 = 4]

	List A Reaction		List B Product
(A)	Heating glycerol with conc. H_2SO_4	1.	Glyoxal as one of the products
(B)	Hydrogenation of carbon	2.	2-hydroxy ethanoic acid
(C)	Action of glyoxal with NaOH	3.	Synthetic petrol
(D)	Reductive ozonolysis of ethyne	4.	Acrolein

15. **Match the following : Only one match is possible :** [1 × 4 = 4]

	List A		List B
(A)	Amatol	1.	Explosive
(B)	Bronsted acid	2.	$B(OH)_3$
(C)	Hypo	3.	H_3PO_4
(D)	Lewis acid	4.	Photography

Section D : Statement-Explanation Type Problems [3 × 4 = 12]

Acid salt are the substances which possess one or more replaceable H-atom. The acid salts possess acidity as well as basicity. The basicity of acid salts depends on the nature of reaction whereas acidity refers for the total charge on metal cation.

16. The acidity of $Ba_X H_Y (PO_4)_2$ is :
(a) 2 (b) 3
(c) 4 (d) 6

17. Which of the following is not acid salt ?
(a) KH_2PO_3 (b) $Ba(HPO_3)$
(c) $Ba(H_2PO_4)_2$ (d) KHC_2O_4

18. Which one is correct about $Al_X H_Y (PO_4)_Z$:
(a) $Y = 3(Z - X)$ (b) $Y = Z - 2X$
(c) $Y = X - Z$ (d) $Y = 3Z - 2X$

19. The basicity of $Ba_X H_Y (PO_4)_2$ in the reaction is

$$Ba_X H_Y (PO_4)_2 + \frac{Y}{2} Ba(OH)_2 \longrightarrow Ba_{\left(X+\frac{Y}{2}\right)}(PO_4)_2 + H_2O$$

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

Section E : Single Integer Answer [4 × 8 = 32]

20. Number of anti bonding electrons in CO^+ according to molecular orbital theory are :

21. The heat of reaction of a redox change is 9.65×10^5 J. If the same redox change is made in the working of cell showing cell efficiency 60% and e.m.f. of 1.2 volt. What was the number of electrons involved in cell reaction ?

22. Mole fraction of a solute (in a solvent of molar mass 250) is 0.02. If elevation constant of solvent is 24.5 K molality^{-1}, the elevation in b.pt. will be :

23. A drop of solution (volume 0.05 mL) contains 3×10^{-2} mole of H^+. If the rate constant of disappearance of H^+ is 1.0×10^2 mol litre^{-1} minute^{-1}. How long (in minute) will it take to disappear all the H^+ ions ?

24. If $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$; $K_1 = 2 \times 10^{-13}$
and $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$; $K_2 = 7.2 \times 10^{-12}$
The equilibrium constant for :
$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$ is :

25. Number of optical isomers for 1,3-dimethylalene $(CH_3CH = C = CHCH_3)$ are :

26. C_4H_5N has degree of unsaturation a^0. The value of a is :

27. How many H atoms are bonded to a chiral methyl gp. ?

SOLUTION OF MODEL PAPER 4-B

Section A

1. (c) These are facts.
2. (c) –do–
3. (d) Smaller in size of cation more is Lewis acid nature.
4. (d) All these acts as buffer (An acid + its conjugate base – acidic buffer) and (A base + its conjugate acid – basic buffer)
5. (b) H—H; H^+Cl^-, Na^+H^-; H^+ can form co-ordinate bond and not H.
6. (b) Glucose is reducing sugar.
7. (c) Benzylic carbanion is most stable due to resonance stabilization. Also stable structures of carbanions possess –ve charge on more electronegative atom. Order of electronegativity of C in $\bar{C} \equiv CH$, $H\bar{C}=CH_2$, $H_2\bar{C}-CH_3$

   $sp > sp^2 > sp^3$
8. (c) $\underset{Y}{5I^-} + \underset{X}{IO_3^-} \longrightarrow \underset{Z}{3I_2} + 3H_2O$
9. (c) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

   $NH_4NO_3 \longrightarrow N_2O + 2H_2O$

   $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

   $(NH_4)_2SO_4 \longrightarrow NH_3 + NH_4HSO_4$

Section B

10. (b, c, d) Cu_2O is added to impart blue colour to glass.
11. (a,c,d) *o*-hydroxy phenol shows intramolecular H-bonding, *p*-hydroxy phenol shows and phenol inter molecular H-bonding (more stronger). The given order to m.pt. of cresol is experimental value.

    $\underset{35°C}{p\text{-cresol}}$ $\underset{31°C}{o\text{-cresol}}$ $\underset{11°C}{m\text{-cresol}}$
12. (a, b, c, d) First three shows redox reaction and do not involve any solution state in it. The fourth is a fuel cell. Thus junction of two liquids is not present in any cell.
13. (a, b, d) If $\Delta n \neq 0$ and addition is made at constant V, then no effect. No doubt P increases but Σn (total mole) also increase. K_p remains constant in both cases either constant P or constt. V. If addition of inert gas is made at constant P, Σn *i.e.*, $(1 + n)$ increases and to have K_p constant n increases.

Section C

14. A—4; B—3; C—2; D—1
15. A—1; B—3; C—4; D—2

Section D

16. (c) Ba, H and PO_4 are bivalent monovalent and trivalent respectively.

    $2X + 1\times Y - (3\times 2) = 0$

    $2X + Y = 6$

    X and Y are positive integers.

    if $Y = 1$ then $X = 5/2$

    $Y = 2$ then $X = 2$

    $Y = 3$ then $X = 3/2$
17. (b) H_3PO_3 is dibasic acid.
18. (a) $3\cdot X + Y\cdot 1 - 3\cdot Y = 0$

    $\therefore\ Y = 3Z - 3X$
19. (b) For $Ba_XH_Y(PO_4)_2$: $2X + Y = 6$

    For $Ba_{\left(X+\frac{Y}{2}\right)}\cdot(PO_4)_2$: $2X + Y = 6$

    Also the salt obtained is derivative of H_3PO_4. Ba is bivalent and thus, $2X$ should be even number thus, Y should be 2.

    or $2X + 2 = 6$

    $X = 2$

Section E

20. **Three :** CO^+ is $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma 2p_x^2 \begin{bmatrix}\pi 2p_y^2 \\ \pi 2p_z^2\end{bmatrix} \sigma^* 2s^1$

    Bond order of CO^+ is 3.5.
21. **Five :** $\eta = \dfrac{\Delta G}{\Delta H} = \dfrac{nEF}{\Delta H}$

    $0.6 = \dfrac{n\times 1.2\times 9.65\times 10^4}{9.65\times 10^5}$

    $\therefore\quad n = \dfrac{6}{1.2} = 5$
22. **Two :** $\dfrac{n}{n+N} = 0.02$

    $\dfrac{N}{n+N} = 0.98$

    $\dfrac{n}{N} = \dfrac{1}{49}$

    $\dfrac{w\times M\times 1000}{m\times W\times 1000} = \dfrac{1}{49}$

    $\text{Molality} = \dfrac{1}{49}\times\dfrac{1000}{M} = \dfrac{1000}{49\times M}$

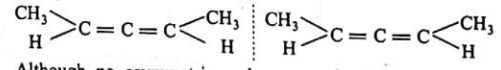
    $\Delta T_b = K_b' \times \text{molality}$

    $\Delta T_b = \dfrac{1000\times 24.5}{49\times 250} = 2$
23. **Six :** 0.05 mL has 3×10^{-2} mol of H^+

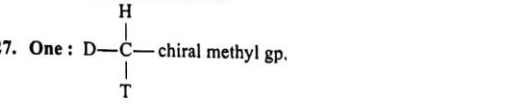
    1000 mL has $\dfrac{3\times 10^{-2}\times 1000}{0.05} = 600$ mol H^+

    $K = \dfrac{X}{t}$ (zero order, follow unit of K)

    $t = \dfrac{600}{1\times 10^2} = 6$ minute
24. **Six :** $K_c = \sqrt{\dfrac{K_2}{K_1}} = \sqrt{\dfrac{7.2\times 10^{-12}}{2\times 10^{-13}}} = \sqrt{36} = 6$
25. **Two :**

    Although no asymmetric carbon atom but it shows a pair of enantiomers. In other words chirality and not the presence of asymmetric carbon atom is the criteria for enantiomerism.
26. **Three :** Disregard N but remove an H for each N. Thus, C_4H_4 which has 3° unsaturation.

    
27. **One :** D—C(H)(T)— chiral methyl gp.

APPENDICES

Appendix-1

S. No.	Physical quantities	Symbol	SI units	Symbol of units
1.	Area	A	Square meter	m^2
2.	Volume	V	Cubic meter	m^3
3.	Density	d	kilogram meter^{-3}	$kg\ m^{-3}$
4.	Velocity	u	meter per sec	$m\ s^{-1}$
5.	Acceleration	g	meter per sec^2	$m\ s^{-2}$
6.	Energy	E	joule	$J(kg\ m^2\ s^{-2})$
7.	Force	F	newton	$N(kg\ m\ s^{-2})$
8.	Power	—	Watt	$W(kg\ m^2\ s^{-3}$ or $Js^{-1})$
9.	Pressure	P	Pascal	$Pa(N\ m^{-2})$
10.	Frequency	ν	Hertz	$Hz(s^{-1})$
11.	Electric charge	Q	Coulomb	C(Ampere second)
12.	Electrical potential difference	V	Volt	$V(kg\ m^2\ s^{-3}\ A^{-1})$
13.	Electrical resistance	R	Ohm	$\Omega(kg\ m^2\ s^{-3}\ A^{-2})$
14.	Electrical conductance	S	Siemens	$S(\Omega^{-1})$
15.	Amount	mole	mole	$mole\left(\frac{Mass}{Molar\ mass}\right)$

Appendix-2

Numerical Prefixes

S.No.	Prefixes	Value	S.No.	Prefixes	Value
1.	Hemi	$\frac{1}{2}$	12.	Deca	10
2.	Mono	1	13.	undeca	11
3.	Sesqui	$1\frac{1}{2}$	14.	Dodeca	12
4.	Di or Bi	2	15.	Trideca	13
5.	Tri	3	16.	Tetra deca	14
6.	Tetra	4	17.	Penta deca	15
7.	Penta	5	18.	Hexa deca	16
8.	Hexa	6	19.	Hepta deca	17
9.	Hepta	7	20.	Octa deca	18
10.	Octa	8	21.	Nona deca	19
11.	Nona	9	22.	Eicosa	20

Appendix-3

Fractions Prefixes, symbols and their multiples

S.No.	Prefix	Symbol	Multiples	S.No.	Prefix	Symbol	Multiples
1.	Atto	a	10^{-18}	9.	deca	da	10
2.	Femto	f	10^{-15}	10.	hecto	h	10^2
3.	Pico	p	10^{-12}	11.	kilo	k	10^3
4.	Nano	n	10^{-9}	12.	mega	M	10^6
5.	Micro	μ	10^{-6}	13.	giga	G	10^9
6.	Milli	m	10^{-3}	14.	tera	T	10^{12}
7.	Centi	C	10^{-2}	15.	peta	p	10^{15}
8.	Deci	d	10^{-1}	16.	exa	E	10^{18}

Appendix-4

Traditional Units with SI and CGS Values

S.No.	Quantity	Traditional Units	SI and CGS Value
1.	Mass	amu	1.6605×10^{-27} kg = 1.6605×10^{-24} g = 1 amu
2.	Length	Å	10^{-10} meter = 10^{-8} cm = 1Å
3.	Volume	litre	10^{-3} m^3 = 10^3 cm^3 = 1 litre
4.	Force	dyne	10^{-5} Newton = 1 dyne
5.	Energy	erg	10^{-7} joule =1 erg
		cal	4.184 joule = 1 cal
		electron volt	1.602×10^{-19} joule = 1 eV
		kilo watt hour	3.6×10^{6} joule = 1 kWh
		horse power	2.6845×10^{6} joule = 1 np
6.	Pressure	atmosphere	101325 N m^{-2} or pascal = 1 atm
		cm	1333.2237 N m^{-2} = 1 cm
		mm or torr	133.32237 N m^{-2} = 1 mm
		bar	101325 N m^{-2} = 1 bar
7.	Temperature	centigrade	273.15 K = 0°C
8.	Electric charge	esu	3.3356×10^{-10} C = 1 esu
9.	Work	litre atm	101.3 J = 1 litre atm
10	Radioactivity	curie or Ci	3.7×10^{10} dps or Bq = 1 curie
		Rutherford	10^{6} dps = 10^{6} Bq = 1 rd

Appendix-5

Greek Alphabets and their Symbols

Greek alphabets	Symbol	Greek alphabets	Symbol
Alpha	α	Nu	ν
Beta	β	Xi	ξ
Gamma	γ	Omioron	Θ
Delta	δ or Δ	Pi	π
Epsilon	ε	Rho	ρ
Zeta	ζ	Sigma	σ or Σ
Eta	η	Tau	τ
Theta	θ	Upsilon	υ
Iota	ι	Phi	ϕ
Kappa	κ	Chi	χ
Lambda	λ	Psi	ψ
Mu	μ	Omega	ω

Appendix-6

Wavelengths and Frequencies of Electromagnetic Radiations

S. No.	Radiations	Wavelength λ (in Å)	Frequency(γ) (in Hz or sec^{-1})
1.	Radio wave	3×10^{9} to 3×10^{13}	1×10^{5} to 1×10^{9}
2.	Micro wave	6×10^{6} to 3×10^{9}	1×10^{9} to 5×10^{11}
3.	Infra red	3×10^{9} to 7.6×10^{3}	1×10^{11} to 3.95×10^{14}
4.	Visible rays	3800 to 7600	3.95×10^{14} to 7.9×10^{14}
5.	Ultra violet rays	150 to 3800	7.9×10^{14} to $2\times2\times10^{16}$
6.	X-rays	0.1 to 150	2×10^{16} to 3×10^{19}
7.	Gamma rays (γ)	0.01 to 0.1	3×10^{19} to 3×10^{20}
8.	Cosmic rays	0.00 to 0.001	3×10^{21} to infinite

Appendix-7

Some Physical Constants

S. No.	Name	Symbol	CGS value	SI unit value
1.	Universal Gas constant	(R)	8.314×10^{7} erg K^{-1}	8.314 J K^{-1} mol^{-1}
2.	Boltzmann constant	(k)	1.380×10^{-16} erg K^{-1}	1.380×10^{-23} JK^{-1}
3.	Planck's constant	(h)	6.626×10^{-27} erg sec	6.626×10^{-34} J sec
4.	Speed of light	c	2.9979×10^{10} cm sec^{-1}	2.9979×10^{8} m sec^{-1}
5.	Molar volume at STP	$\bar{v}$	22414 cm^3	0.0224 m^3
6.	Avogadro's No.	N	6.022169×10^{23} mol^{-1}	6.022169×10^{23} mol^{-1}
7.	Charge on electron	e	4.80291×10^{-10} esu	1.60210×10^{19} C
8.	Atomic mass unit	amu	1.660531×10^{-24} g	1.660531×10^{-27} kg
9.	Mass of electron in rest	m_e	9.109558×10^{-28} g	9.109558×10^{-31} kg
10.	Mass of proton	m_p	1.67261×10^{-24} g	1.67261×10^{-27} kg
11.	Mass of neutron	m_n	1.67492×10^{-24} g	1.67492×10^{-27} kg
12.	Rydberg constant	R_H	1.097373×10^{5} cm^{-1}	1.097373×10^{7} m^{-1}
13.	Faraday	(F)	2.89461×10^{14}	9.6487×10^{7} C / kg
14.	Accelaration due to gravity	(g)	980.665 cm sec^{-2}	9.80665 m sec^{-2}
15.	I. Bohr's radius (for H)	r_{1H}	0.529×10^{-8} cm	0.529×10^{-10} m
16.	Atmospheric pressure	(P)	1.013250×10^{6} dyne cm^{-2}	1.013250×10^{5} N m^{-2}
17.	Specific charge of electron	(e/m)	5.2764×10^{17} esu / g	1.75880×10^{11} C kg^{-1}
18.	Ice point	(m.pt.)	273.150 K	273.150 K
19.	Triple point of H_2O		273.16 K	273.16 K

Appendix-8

Element	Symbol	Atomic number	Atomic mass	Known Isotopes
Actinium	Ac	89	(227)	—
Aluminium	Al	13	25.9815	1
Amercium	Am	95	(243)	—
Antimony	Sb	51	121.75	2
Argon	Ar	18	39.948	3
Arsenic	As	33	74.9216	1
Astatine	At	85	(210)	—
Barium	Ba	56	137.34	7
Berkelium	Bk	97	(247)	—
Beryllium	Be	4	9.0122	2
Bismuth	Bi	83	208.980	14
Boron	B	5	10.820	14
Bromine	Br	35	79.904	2
Cadmium	Cd	48	112.40	9
Calcium	Ca	20	40.08	6
Californium	Cf	98	(251)	—
Carbon	C	6	12.01	2
Cerium	Ce	58	140.12	4
Cesium	Cs	55	132.905	5
Chlorine	Cl	17	35.453	3
Chromium	Cr	24	51.996	4
Cobalt	Co	27	58.9332	2
Copper	Cu	29	63.546	2
Curium	Cm	96	(247)	—
Dysprosium	Dy	66	162.50	4
Einsteinium	Es	99	(294)	—
Erbium	Er	68	167.26	4
Europium	Eu	63	152.00	2
Fermium	Fm	100	(253)	—
Flurine	F	9	19.0	1
Francium	Fr	87	(223)	—
Gadolinium	Gd	64	157.25	5
Gallium	Ga	31	69.72	2

† Values in parentheses are mass numbers of the most stable or the best known isotopes.

Element	Symbol	Atomic number	Atomic mass	Known Isotopes
Germanium	Ge	32	72.60	5
Gold	Au	79	196.67	—
Hafnium	Hf	72	178.49	5
Helium	He	2	4.0026	2
Holmium	Ho	67	164.930	1
Hydrogen	H	1	1.00797	3
Indium	In	49	114.81	2
Iodine	I	53	126.9044	1
Iridium	Ir	77	192.2	2
Iron	Fe	26	55.847	4
Krypton	Kr	36	83.80	6
Kurchatovium	Ku	104	(260)	—
Lanthanum	La	57	183.91	1
Lawrenchium	Lw	103	(257)	—
Lead	Pb	82	207.19	16
Lithium	Li	3	6.94	2
Lutetium	Lu	71	174.97	1
Magnesium	Mg	12	24.312	3
Manganese	Mn	25	54.9380	7
Mendelevium	Md	101	(256)	—
Mercury	Hg	80	200.59	8
Molybdenum	Mo	42	95.94	8
Neodymium	Nd	60	144.24	5
Neon	Ne	10	20.183	3
Neptunium	Np	93	(237)	—
Nickel	Ni	28	58.71	5
Niobium	Nb	41	92.906	1
Nitrogen	N	7	14.0067	2
Nobelium	No	102	(254)	—
Osmium	Os	76	190.2	6
Oxygen	O	8	15.9994	3
Palladium	Pd	46	106.4	6
Phosphorus	P	15	30.9738	1

Element	Symbol	Atomic number	Atomic mass	Known Isotopes
Platinum	Pt	78	195.09	5
Plutonium	Pu	94	(242)	–
Polonium	Po	84	(210)	–
Potassium	K	19	39.102	3
Praseodymium	Pr	59	140.007	1
Promethium	Pm	61	(147)	–
Protactinium	Pa	91	(231)	–
Radium	Ra	88	(226)	4
Radon	Rn	86	(222)	–
Rhenium	Re	75	186.2	2
Rhodium	Rh	45	102.905	2
Rubidium	Rb	37	85.47	2
Ruthenium	Ru	44	101.07	7
Samarium	Sm	62	150.35	7
Scandium	Sc	21	44.956	1
Selenium	Se	34	78.96	6
Silicon	Si	14	28.086	3
Silver	Ag	47	107.868	2
Sodium	Na	11	22.9898	3
Strontium	Sr	38	87.62	4
Sulphur	S	16	32.064	1
Tantalum	Ta	73	180.948	1
Technetium	Tc	43	(99)	–
Tellurium	Te	52	127.60	8
Terbium	Tb	65	158.924	1
Thallium	Tl	81	204.37	8
Thorium	Th	90	232.038	8
Thulium	Tm	69	168.934	1
Tin	Sn	50	118.69	10
Titanium	Ti	22	47.90	5
Tungusten	W	74	183.85	4
Uranium	U	92	238.03	8
Vanadium	V	23	50.942	1
Xenon	Xe	54	131.30	9
Ytterbium	Yb	70	173.04	5
Yttrium	Y	39	88.905	1
Zinc	Zn	30	65.37	5
Zirconium	Zr	40	91.22	5

Appendix-9

Some direct conversion factors

1 erg	$= 10^{-7}$ joule $= 2389 \times 10^{-8}$ cal $= 6.242 \times 10^{11}$ eV
1 calorie	$= 4.184 \times 10^{7}$ erg $= 4.184$ joule $= 2.613 \times 10^{19}$ eV
1 electron volt	$= 1.6021 \times 10^{-12}$ erg $= 1.6021 \times 10^{-19}$ joule $= 3.827 \times 10^{-20}$ calorie
1 litre	$= 1000$ mL or cm^3 $= 10^{-3} m^3$
1 angstrom	$= 10^{-8}$ cm $= 10^{-10}$ m
1 nanometer	$= 10^{-9}$ m $= 10^{-7}$ cm
1 coulomb	$= 2.9979 \times 10^{9}$ esu
1 faraday	$= 9.6487 \times 10^{4}$ coulomb
1 curie	$= 3.7 \times 10^{10}$ disintegration sec^{-1}
1 rutherford	$= 10^{6}$ dps

Appendix-10

Electrochemical Series

Half reactions	Standard reduction potential at 25°C(In volt)
$Li^+ + e \longrightarrow Li$	–3.04
$K^+ + e \longrightarrow K$	–2.92
$Ba^{2+} + 2e \longrightarrow Ba$	–2.90
$Sr^{2+} + 2e \longrightarrow Sr$	–2.89
$Ca^{2+} + 2e \longrightarrow Ca$	–2.87
$Na^+ + e \longrightarrow Na$	–2.71
$Mg^{2+} + 2e \longrightarrow Mg$	–2.37
$Al^{3+} + 3e \longrightarrow Al$	–1.66
$Mn^{2+} + 2e \longrightarrow Mn$	–1.18
$Zn^{2+} + 2e \longrightarrow Zn$	– 0.76
$Cr^{3+} + 3e \longrightarrow Cr$	– 0.74
$Fe^{2+} + 2e \longrightarrow Fe$	– 0.44
$Cd^{2+} + 2e \longrightarrow Cd$	– 0.40
$Co^{2+} + 2e \longrightarrow Co$	– 0.27
$Ni^{2+} + 2e \longrightarrow Ni$	– 0.25
$Sn^{2+} + 2e \longrightarrow Sn$	– 0.13
$Pb^{2+} + 2e \longrightarrow Pb$	– 0.12
$2H^+ + 2e \longrightarrow H_2$	0.00
$Sn^{4+} + 2e \longrightarrow Sn^{2+}$	+0.15
$Cu^{2+} + 2e \longrightarrow Cu$	+0.34
$Fe^{3+} + e \longrightarrow Fe^{2+}$	+0.77
$Hg_2^{2+} + 2e \longrightarrow 2Hg$	+0.79
$Ag^+ + e \longrightarrow Ag$	+0.80
$Hg^{2+} + 2e \longrightarrow Hg$	+0.85
$Pt^{2+} + 2e \longrightarrow Pt$	+1.20
$Cl_2 + 2e \longrightarrow 2Cl^-$	+1.36
$Au^{3+} + 3e \longrightarrow Au$	+1.50
$Co^{3+} + 1e \longrightarrow Co^{2+}$	+1.84
$F_2 + 2e \longrightarrow 2F^-$	+2.87

Appendix-11
Some Important discoveries

1.	Law of electrolysis	Faraday
2.	Law of conservation of mass	Lavoisier
3.	Law of constant proportion	Prout
4.	Law of multiple proportion	Dalton
5.	Law of reciprocal proportion	Ritcher
6.	Law of gases	Boyle, Charles, Gay Lussac
7.	Law of gaseous diffusion	Graham
8.	Law of partial pressure	Dalton
9.	Law of mass action	Guldward and Waage
10.	Electron	Thomson
11.	Proton	Gold Stein
12.	Neutron	Chadwick
13.	Neutrino	Pauli
14.	Mesons	Yukawa
15.	Nucleus	Rutherford
16.	Wave nature of electron	de Broglie
17.	Wave nature of light	Plancks
18.	Uncertainty principle	Heisenburg
19.	Multiplicity rule	Hund
20.	Exclusion principle	Pauli
21.	Radioactivity	Becquerrel
22.	Artificial radioactivity	Irene Curie and F. Joliot
23.	Radium	Marie Curie and P. Curie
24.	Radioactive dating	Libby W.F.
25.	Group displacement law	Soddy-Fajan
26.	Cyclotron	Lawrence E.O.
27.	Charge on electron	Millikan
28.	Periodic law	Mendeleeff (old); Mosley (new)
29.	Atomic number	Mosley
30.	X-rays	Roentzen
31.	Photoelectric effect	Thomson
32.	Electrovalence	Kossel and Lewis
33.	Covalence	Lewis
34.	Co-ordinate valence	Sugden
35.	Valence bond theory	Heitler and London
36.	Molecular orbital theory	Hund and Mulliken
37.	Deuterium	Urey
38.	Heavy water	Urey
39.	H_2O_2	Thenard
40.	N_2	Scheele
41.	Argon	Rayleigh and Ramsay
42.	Neon	Ramsay and Travers
43.	Krypton	Ramsay and Travers
44.	Xenon	Ramsay and Travers
45.	Radon	Dorn
46.	Helium	Lockyer and Frankland
47.	Compounds of xenon	Bartlett
48.	Theory of dissociation	Arthenius
49.	Theory of strong electrolytes	Debye and Huckel
50.	Theory of relativity	Einstein