SCORE MORE $\frac{150}{150}$

+2 CHEMISTRY

1 Mark	***Unitwise*** **Govt. Examination Q & A** (2006 to 2013)
3 Mark	
5 Mark	

&

Q -70 Compulsory problems (Solved)

CONTENTS

Rankers Education
Trichy ***9843 113 114***

1 MARK

1. ATOMIC STRUCTURE – II

1. $E_n = -\frac{313.6}{n^2}$, If the value of $E_n = -34.84$ to which value 'n' corresponds *[June-2008]*

a) 4 **b) 3** c) 2 d) 1

2. Dual character of an electron was explained by *[Mar-2006, Sep-2007, Sep-2008, June-2009, June-2010]*

a) Bohr b) Heisenberg **c) de-Broglie** d) Pauli

3. de-Broglie équation is *[June-2006, Sep-2009, Mar-2012, Sep-2012]*

a) $\lambda = \frac{mv}{h}$ b) $\lambda = hmv$ c) $\lambda = \frac{hv}{m}$ **d)** $\boldsymbol{\lambda = \frac{h}{mv}}$

4. Which of the following particle having same kinetic energy, would have the maximum de-Broglie wave length? *[Mar-2007]*

a) α-particle b) proton **c) β-particle** d) neutron

5. If the energy of an electron in the second Bohr orbit of H-atom is -E, what is the energy of the electron in the Bohr's first orbit? *[June-2011]*

a) 2E **b) – 4E** c) –2E d) 4E

6. The bond order of oxygen molecule is *[Sep-2010, Sep-2011]*

a) 2.5 b) 1 c) 3 **d) 2**

7. The hybridisation in SF_6 molecule is *[Mar-2008, Mar-2010, Sep-2013]*

a) sp^3 **b) sp^3d^2** c) sp^3d d) sp^3d^3

8. The intramolecular hydrogen bonding is present in *[June-2007, Mar-2009, Mar-2011, June-2010, June-2013]*

a) o-nitrophenol b) m-nitrophenol c) p-nitrophenol d) None

9. Which one of the following experiments confirmed the wave nature of electron? *[Mar-2010]*

a) G.P. Thomson's gold foil experiment b) Black body radiation
c) Photoelectric effect d) Milliken's oil drop experiment

10. The momentum of a particle which has de-Broglie wave length of 1Å is *[Mar-2006, Mar-2011]*

a) 6.6×10^{-23} kg ms^{-1} **b) $\boldsymbol{6.6 \times 10^{-24}}$** kg ms^{-1} c) 6.6×10^{-34} kg ms^{-1} d) 6.6×10^{34}kg ms^{-1}

11. The circumference of the circular orbit of the electron must be an integral multiple of --------- *[Sep-2006]*

a) Frequency b) Momentum c) Mass **d) Wavelength**

12. Number of spherical nodes in 2s- orbital is *[June-2009]*

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

13. The bond order of nitrogen molecule is *[June-2006, June-2012, June-2013]*
a) 0 b) 1 c) 2 **d) 3**

14. In a molecule eight electrons are present in bonding molecular orbitals and four electrons are present in antibonding molecular orbitals. Its bond order is *[Mar-2008]*
a) 3 b) 4 c) 2.5 **d) 2**

15. Energy levels of molecular orbitals have been determined experimentally by *[Sep-2007]*
a) spectroscopic studies b) x-ray diffraction c) crystallographic studies d) none

16. Molecular orbital with the least energy is ---------- *[Sep-2011]*
a) σ_{1s} b) σ^*_{1s} c) π_{2py} d) π^*_{2py}

17. The type of hybridization of I in ICl_4^- is *[Sep-2012]*
a) sp^3 **b) sp^3d^2** c)dsp^2 d) sp^3d

18. The nature of hybridization in IF_7 molecule is *[Sep-2006, Sep-2010]*
a) sp^3d^2 b) sp^3d^4 **c) sp^3d^3** d) sp^3d^4

19. The hybridization involved in XeF_6 is *[June-2007, June-2011]*
a) sp^3d^3 **b) sp^3d^2** c) sp^3d d) sp^3

20. The type of hybridization of S in SO_4^{2-} is *[Mar-2009]*
a) sp^3 b) sp^3d c) sp d) sp^2

21. The hybridization in CO_3^{2-} ion is *[Sep-2009]*
a) sp^2 b) sp^3 c) sp d) sp^3d

22. The hybridization in PCl_5 molecule is *[June-2012]*
a) sp^3d b) sp^3d c) sp^3 d) sp^2

23. The type of hybridization of N in NH_4^+ ion is *[Mar-2012]*
a) sp^3 b) sp^3d c) sp d) sp^2

24. Inter-molecular hydrogen bonding is present in *[Mar-2007]*
a) HF b) H_2O c) ethanol **d) all the above**

25. Water exists in liquid state. This is due to *[June-2008]*
a) high boiling point b) low boiling point c) freezing point is zero **d)hydrogen bond**

26. Intermolecular hydrogen bonding is present in *[Sep-2008]*
a) orthonitrophenol b)salicylic acid c) orthohydroxybenzaldehyde **d) HF**

27. The molecular orbitals are fi1led according to *[Sep-2013]*
a) Pauli's exclusion principle b) Hund’s rule c) Aulbau principle **d) all the above**

7. NUCLEAR CHEMISTRY

1. The most penetrating radiations are *[Sep-2009]*
a) α rays b) β rays **c) γ rays** d) all are equally penetrating

2. Which one of the following particles is used to bombard $_{13}Al^{27}$ to give $_{15}P^{30}$ and a neutron *[June-2006, Sep-2007, Mar-2009, Sep-2010]*
a) α particle b) deuteron c) proton d) neutron

3. The reaction $_5B^8 \longrightarrow {}_4Be^8$ takes place due to *[June-2008]*
a) α decay b) β decay c) electron capture **d) positron decay**

4. Radioactivity is due to *[Mar-2007, June-2010]*
a) Stable electronic configuration b) Stable nucleus
c) Unstable nucleus d) Unstable electronic configuration

5. In the following radioactive decay, $_{92}x^{232} \longrightarrow {}_{89}y^{220}$, how many α and β particles are ejected? *[Sep-2013]*
a) 3α and 3β b) 5α and 3β c) 3α and 5β d) 5α and 5β

6. $_{92}U^{235}$ nucleus absorbs a neutron and disintegrates into $_{54}Xe^{139}$, $_{38}Sr^{94}$ and *x*. What will be the product *x*? *[Mar-2011, Mar-2013]*
a) 3 neutrons b) 2 neutrons c) α particle d) β particle

7. Loss of a β-particle is equivalent to *[Sep-2006, June-2009, Sep-2011]*
a) Increase of one proton only b) Decrease of one neutron only
c) Both (a) and (b) d) None of these

8. After 24 hours 0.125 g of the initial quantity of 1 g of a radioactive isotope is left out. The half-life period is *[Mar-2006, June-2012, Sep-2012]*
a) 24 hours b) 12 hours **c) 8 hours** d) 16 hours

9. When $_7N^{15}$ is bombarded with a proton it gives $_6C^{12}$ and --------- *[June-2007]*
a) α-particle b) β-particle c) neutron d) proton

10. In a nuclear reaction -------- is/are balanced on both sides *[Mar-2008]*
a) mass b) number of atoms c) mass number **d) atomic number and mass number**

11. Half-life period of a radioactive element is 1500 years. The value of disintegration constant in terms of seconds is *[Sep-2008]*
a) $0.1465 \times 10^{-10}\ s^{-1}$ b) $0.2465 \times 10^{-10}\ s^{-1}$ c) $0.1465 \times 10^{-8}\ s^{-1}$ d) $0.3645 \times 10^{-10}\ s^{-1}$

12. Half-life period of a radioactive element is 100 seconds. Its average life period is *[Mar-2010]*
a) 100 seconds b) 50 seconds c) 200 seconds **d) 144 seconds**

13. Half-life of $_{79}Au^{198}$ nucleus s 150 days. The average life is *[Mar-2012]*
a) 216 days b) 21.6 days c) 261 days d) 26.1 days

14. In a reaction $_5B^8 \longrightarrow {}_4Be^8 + ?$ *[June-2011]*
a) α-particle b) β-particle c) electron capture **d) positron**

15. β-particle is represented as *[June-2013]*
a) $_{+1}e^0$ **b) $_{-1}e^0$** c) $_1H^1$ d) $_2He^4$

8. SOLID STATE – II

1. The Bragg's equation is *[Mar-2011]*
a) $\lambda = 2d \sin\theta$ b) $nd = 2\lambda \sin\theta$ c) $2\lambda = nd \sin\theta$ **d) $n\lambda = 2d \sin\theta$**

2. The crystal structure of CsCl is *[Sep-2006]*
a) Simple cubic b) face-centred cubic c) Tetragonal **d) Body centred cubic**

3. An example for Frenkel defect is *[June - 2012]*
a) NaCl **b) AgBr** c) CsCl d) FeS

4. Semiconductors which exhibit conductivity due to the flow of excess negative electrons are called *[June- 2006, June-2013]*
a) Superconductors **b) n-type semiconductors** c) p-type semiconductors d) Insulators

5. In the Bragg's equation for diffraction of X-rays,'n' represents *[June-2008]*
a) number of moles b) Avogadro number c) quantum number **d) Order of reflection**

6. The number of close neighbours in a body centred cubic lattice of identical spheres is *[Mar-2009, Mar - 2012]*
a) 6 b) 4 c) 12 **d) 8**

7. In a simple cubic cell, each point on a corner is shared by *[Mar -2006, June-2007, Sep-2010]*
a) One unit cell b) Two unit cell **c) 8 unit cell** d) 4 unit cell

8. The total number of atoms per unit cell in bcc is *[Sep-2007,Sep-2009,June-2010,Sep-2011]*
a) 1 **b) 2** c) 3 d) 4

9. Rutile is *[June - 2011]*
a) TiO_2 b) Cu_2O c) MoS_2 d) Ru

10. An example of metal deficiency defect *[Mar-2008, Sep-2008]*
a) NaCl b) AgCl c) CsCl **d) FeS**

11. The coordination number of ZnS is *[Mar-2010]*
a) 3 **b) 4** c) 6 d) 8

12. The crystal lattice with coordination number four is *[Sep-2012]*
a) CsCl **b) ZnO** c) BN d) NaCl

13. An ion leaves its regular site and occupies a position in the space between the lattice sites. This defect is called as *[March-2007]*
a) Schottky defect **b) Frenkel defect** c) Impurity defect d) Vacancy defect

14. The size of the anion in Frenkel defect crystal is *[June-2009]*
a) larger than the cation b) smaller than the cation
c) equal in size with cation d) both are larger in size

15. The total number of atoms per unit cell in fcc is *[Mar-2013]*
a) 1 b) 2 c) 3 **d) 4**

16. Which one of the following crystal has 8 : 8 structure? *[Sep-2013]*
a) MgF_2 **b) CsCl** c) KCl d) NaCl

20. ORGANIC NITROGEN COMPOUNDS

1. The isomerism exhibited by $CH_3CH_2NO_2$ and $CH_3\ CH_2 – O – N = O$ is *[Mar-2006, Sep-2011]*
a) position b) chain **c) functional** d) tautomerism

2. In nitro alkanes $–NO_2$ group is converted to $–NH_2$ group by the reaction with *[Sep-2006, Mar-2008, June-2009, Mar-2013]*
a) Sn/HCl b) Zn dust c) Zn/NH_4Cl d) Zn/NaOH

3. When nitromethane is reduced with Zn dust + NH_4Cl in neutral medium, we get *[Sep-2011, June-2012]*
a) CH_3NH_2 b) $C_2H_5NH_2$ **c) CH_3NHOH** d) C_2H_5COOH

4. The compound that is most reactive towards electrophilic nitration is *[Mar-2007]*
a) Toluene b) benzene c) benzoic acid d) nitrobenzene

5. Nitromethane condenses with acetaldehyde to give *[June-2007, Mar-2011]*
a) nitro propane **b) 1-nitro-2-propanol** c) 2-nitro-1-propanol d) 3-nitro propanol

6. Which of the following compounds has the smell of bitter almonds? *[June-2007, Sep-2009, June-2011]*
a) aniline b) nitro methane c) benzene sulphonic acid **d) nitrobenzene**

7. Nitrobenzene on electrolytic reduction in con. sulphuric acid, the intermediate formed is *[June-2006, Sep-2012]*
a) $C_6H_5NH – NHC_6H_5$ **b) $C_6H_5 – NHOH$** c) $C_6H_5 – N = N – C_6H_5$ d) $C_6H_5.HSO_4$

8. Electrophile used in the nitration of benzene is *[June-2010, Sep-2011, Sep-2013]*
a) hydronium ion b) sulphonic acid **c) nitronium ion** $[NO_2^+]$ d) bromide ion

9. The basic character of amines is due to the *[June-2007, Mar-2010]*
a) tetrahedral structure b) presence of nitrogen atom
c) lone pair of electrons on nitrogen atom d) high electronegativity of nitrogen

10. The organic compound that undergoes carbylamine reaction is *[Sep-2006, Sep-2007, Mar-2008, June-2012, Mar-2013, June-2013]*
a) $(C_2H_5)_2\ NH$ **b) $C_2H_5NH_2$** c) $(C_2H_5)_3\ N$ d) $(C_2H_5)_4\ N^+\ I^-$

11. Primary amine acts as *[June-2008, Sep-2008, June-2010]*
a) Electrophile **b) Lewis base** c) Lewis acid d) Free radical

12. Oxidation of aniline with acidified potassium dichromate gives *[Mar-2009]*
a) p-benzo quinone b) benzoic acid c) benzaldehyde d) benzyl alcohol

13. Which one of the following is a secondary amine? *[Mar-2011]*
a) aniline **b) diphenyl amine** c) sec.butylamine d) tert.butylamine

14. $C_6H_5NH_2 \xrightarrow{NaNO_2/\ HCl} X$. Identify X. *[June-2008, Sep-2008, June-2013, Sep-2013]*
a) C_6H_5Cl b) C_6H_5NHOH **c) $C_6H_5N_2Cl$** d) C_6H_5OH

15. Which of the following will not undergo diazotisation? *[June-2006, Sep-2009, Sep-2010, Mar-2012, Sep-2012]*
a) m-toluidine b) aniline c) p-amino phenol **d) benzyl amine**

16. Aniline differs from ethylamine by the reaction with *[Mar-2007]*
a) metallic sodium b) an alkyl halide c) chloroform and caustic potash **d) nitrous acid**

17. When aqueous solution of benzene diazonium chloride is boiled the product formed is *[Mar-2009, Mar-2011, June-2012]*
a) benzyl alcohol b) benzene + N_2 **c) phenol** d) phenyl hydroxylamine

18. Conversion of benzene diazonium chloride to chloro benzene is called [*Mar-2006, Mar-2013*]
a) Sand Meyer's reaction b) Stephen's reaction
c) Gomberg reaction d) Schotten-Baumann reaction

19. The compound used in the preparation of sulpha drugs is *[Sep-2006]*
a) methyl amine b) nitro methane **c) amino benzene** d) nitro benzene

20. The compound that does not show tautomerism is *[June-2006, Sep-2013]*
a) nitro benzene b) nitro methane c) nitro ethane d) 2-nitropropane

21. Nitro-acinitro tautomerism is exhibited by *[Mar-2007, June-2011]*
a) nitro methane b) nitro benzene c) CCl_3NO_2 d) o-toluidene

22. Chloropicrin is *[June-2013]*
a) CCl_3CHO **b) CCl_3NO_2** c) $CHCl_3$ d) CH_3NO_2

23. Chloropicrin (CCl_3NO_2) is used as *[Sep-2007, Mar-2008, June-2010, June-2011]*
a) soil sterilizing agent b) organic synthesis c) good solvent d) antioxidant

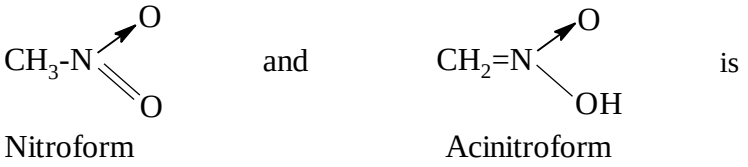
24. Oil of mirbane is *[June-2008, Mar-2012]*
a) nitro benzene b) benzaldehyde c) methyl salicylate d) Aspirin

25. The reaction between benzene diazonium chloride and benzene in the presence of NaOH is *[Sep-2007]*
a) Perkins reaction b) Gatterman's reaction
c) Sand Meyer's reaction **d) Gomberg Bachmann reaction**

26. Which one of the following will not undergo Hoffman's bromamide reaction? [*Sep-2008*]
a) ethanamide b) propanamide **c) methanamide** d) phenyl methanamide

27. Which among the following is a tertiary amine? *[Mar-2009]*
a) $(CH_3)_3CNH_2$ b) $(CH_3)_2CHNHCH_3$ **c) $(CH_3)_2$-N-C_2H_5** d) $(C_2H_5)_2C(CH_3)NH_2$

28. The isomerism exhibited by *[Sep-2010]*



Nitroform and Acinitroform is

a) Position b) Chain c) Functional **d) Tautomerism**

29. Which of the following nitro compounds behaves as an acid in the presence of strong alkali *[Mar-2006]*

a) primary b) secondary c) tertiary **d) both a and b**

30. The product obtained when nitrobenzene is treated with Zn / NaOH is *[Sep-2010]*

a) aniline b) azoxybenzene c) azobenzene **d) hydrozobenzene**

31. The correct order of basic strength is *[Sep-2009]*

a) $NH_3 < CH_3NH_2 < (CH_3)_2NH$ b) $NH_3 > CH_3NH_2 > (CH_3)_2NH$

c) $CH_3NH_2 < NH_3 < (CH_3)_2NH$ d) $CH_3NH_2 > NH_3 > (CH_3)_2NH$

32. Which one of the following is the most basic? *[Sep-2012]*

a) Ammonia b) Methylamine **c) Dimetylamine** d) Aniline

33. The tertiary nitro compound is *[June-2009]*

a) 2-nitropropane b) 1-nitropropane

c) 1-nitro-2,2-dimethylpropane **d) 2-nitro-2-methylpropane**

34. The intermediate formed in the nitration of benzene is *[June-2009]*

a) Arrenium ion b) Carbanion c) Oxonium ion d) Nitrite ion

35. Aniline reacts with benzoyl chloride in the presence of sodium hydroxide and gives benzanilide. This reaction is known as *[Mar-2010]*

a) Gattermann reaction b) Sandmeyer's reaction

c) Schotten-Baumann reaction d) Gomberg-Bachmann reaction

36. $C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2 / HCl} X$. The compound X is *[Mar-2010]*

a) $C_6H_5NH_2$ b) $C_6H_5NHNH_2$ c) $C_6H_5\text{-}C_6H_5$ **d) C_6H_5Cl**

37. $C_6H_5N_2Cl \xrightarrow{H_3PO_2 / Cu^+} X + N_2 + HCl$. The compound X is *[Mar-2012]*

a) C_6H_5Cl b) $C_6H_5NHNH_2$ **c) C_6H_6** d) $C_6H_5NO_2$

3 MARK

3. *p* -BLOCK ELEMENTS

1. What is potash alum and how is it prepared? *[March-2008]*

Potash Alum is K_2SO_4. $Al_2(SO_4)_3$. 24 H_2O

It is manufactured from alunite or alum stone.

Alunite or alum stone is K_2SO_4. $Al_2(SO_4)_3$. $4Al(OH)_3$. It is finely powdered and boiled with dilute sulphuric acid, the aluminium hydroxide part changes into aluminium sulphate. When a little more potassium sulphate in calculated amount is added, the alum is crystallised.

2. Write the uses of potash alum *[Jue-2012]*

1. It is used in purification of water, water proofing of textiles and in dyeing and paper industry.
2. It is used to arrest bleeding
3. It is used in water proofing of textiles and in dyeing and paper industry.

3. What is inert pair effect? *[Mar-2009]*

The tendency of being less availability of ns electron in bonding is known as inert pair effect. The inert pair effect increases down the group with the increase in atomic number.

4. Write a note on plumbo solvency

[June-2006, Sep-2006, June-2007, June-2009, Mar-2010, Sep-2010, June-2011, Mar-2013]

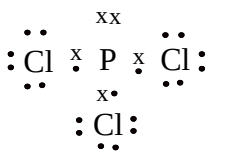
Lead is not attacked by pure water in the absence of air, but water containing dissolved air has a solvent action on it due to the formation of lead hydroxide (a poisonous substance). This phenomenon is called **Plumbo solvency**.

$$2Pb + O_2 + 2H_2O \longrightarrow 2Pb(OH)_2$$

5. Draw the electronic structure [electron dot formula] of a) PCl_3 b) PCl_5 c) H_3PO_3 d) H_3PO_4 e) $H_4P_2O_7$ *(Any 2)* *[Sep-2008, Mar-2008, June-2011]*

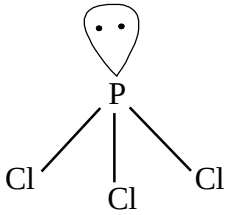
a) PCl_3

PCl_3 molecule has a pyramidal shape, which arises from sp^3 hybridisation of phosphorus atom. One of the tetrahedral positions is occupied by a lone pair of electrons.



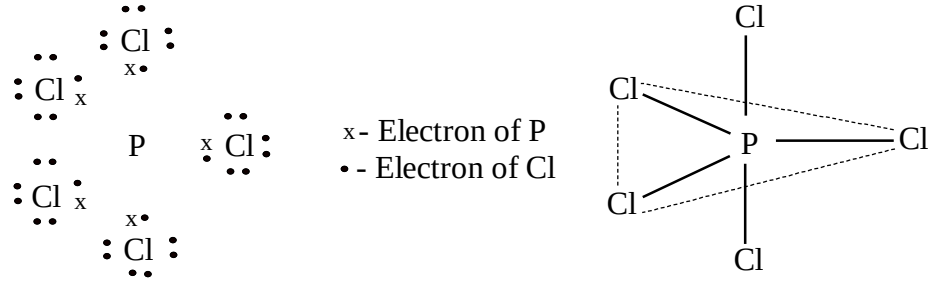
x - Electron of P

• - Electron of Cl

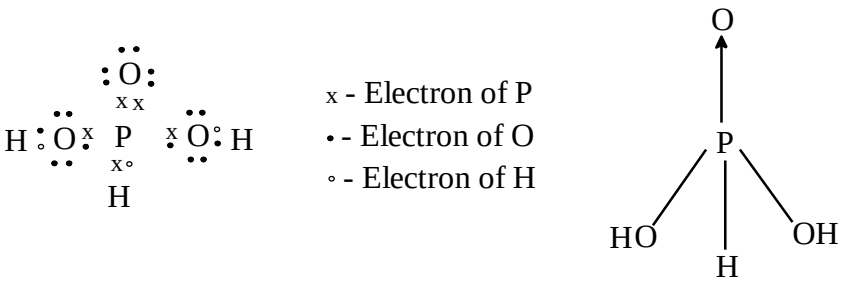


b) PCl_5

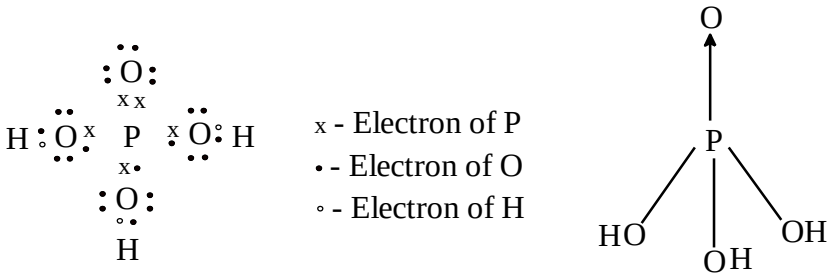
PCl_5 molecule has trigonal bipyramidal shape in vapour state which arises from sp^3d hybridisation of phosphorus atom.



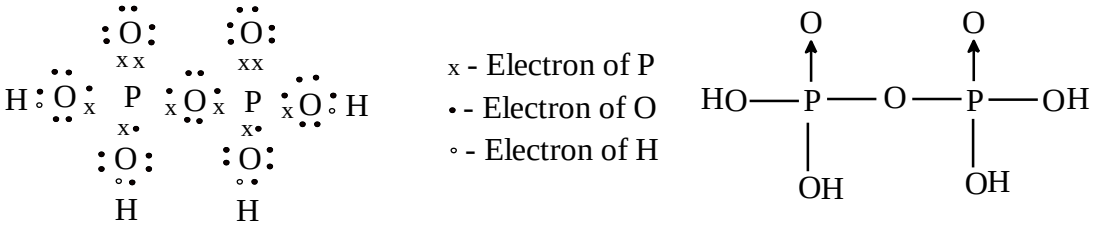
c) H_3PO_3



d) H_3PO_4



e) $H_4P_2O_7$



6. H_3PO_3 is diprotic *or* dibasic acid. Why? *[Sep-2009, Mar-2010, June-2013]*

H_3PO_3 is a dibasic acid and gives salts of two types.

$$H_3PO_3 + NaOH \longrightarrow NaH_2PO_3 + H_2O$$

Sodium dihydrogen Phosphite

$$H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_3 + 2H_2O$$

Disodium hydrogen Phosphite

7. Prove that H_3PO_4 is a tribasic acid (triprotic acid)

[March-2006, March-2013][June-2007 – 5Mark]

It is a tribasic acid. It combines with alkalies like NaOH to form three series of salts.

$$H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$$

Sodium dihydrogen phosphate

$$H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4 + 2H_2O$$

Disodium hydrogen phosphate

$$H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + 3H_2O$$

Sodium phosphate

8. Prove that P_2O_5 is a powerful dehydrating agent.

[Sep-2006, March-2007, Mar-2009, June-2010, Mar-2012, Sep-2012] [Sep-2008 – 5Mark]

Phosphorus pentoxide extracts water from many inorganic compound including sulphuric acid, nitric acid and several organic compounds. It is therefore, used as a powerful dehydrating agent.

$$H_2SO_4 \xrightarrow{P_4O_{10}} SO_3 + H_2O$$

$$2HNO_3 \xrightarrow{P_4O_{10}} N_2O_5 + H_2O$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow{P_4O_{10}} \underset{\text{Nitrile}}{RCN} + H_2O$$

9. How will you prove that H_3PO_3 is a powerful reducing agent?

[June-2006] [June-2007 – 5Mark]

H_3PO_3 is a powerful reducing agent because it has P-H bond. It reduces silver nitrate solution into silver.

$$2AgNO_3 + H_2O + H_3PO_3 \longrightarrow 2Ag + H_3PO_4 + 2HNO_3$$

10. How is orthophosphoric acid prepared in laboratory? *[June-2008]*

In the laboratory orthophosphoric acid can be prepared by boiling a mixture of red phosphorus with 50% nitric acid in a flask fitted with a reflux condenser on a water bath till no more oxides of nitrogen are liberated.

Iodine acts as a catalyst. The product is evaporated below 453 K and then cooled in a vacuum desiccators surrounded by freezing mixture when crystals of orthophosphoric acid are deposited.

$$P + 5HNO_3 \rightarrow H_3PO_4 + 5NO_2 + H_2O$$

11. Write note on Holme's signal *[Sep-2007, Sep-2009]*

Containers which have a perforated bottom and a hole at the top are filled with calcium phosphide and calcium carbide. These are thrown into the sea. Water enters the container through the bottom and reacts with calcium carbide and calcium phosphide to give acetylene and phosphine. Phosphine gets ignited spontaneously as it comes in contact with air and also ignites acetylene. Thus a bright red flame is produced which is accompanied by huge smoke due to the burning of phosphine. This serves as a signal to the approaching ships.

$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3\uparrow + 3Ca(OH)_2$$

$$CaC_2 + 2H_2O \longrightarrow C_2H_2\uparrow + Ca(OH)_2$$

12. What is the action of heat on phosphorus acid? *[June-2009]*

When H_3PO_3 is heated it undergoes auto-oxidation and reduction to form phosphoric acid and phosphine.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

13. What is the action of heat on ortho phosphoric acid? *[Mar-2011]*

On heating it gives pyrophosphoric acid at 523 K and at 589 K gives metaphosphoric acid

$$2H_3PO_4 \xrightarrow{523\,K} H_4P_2O_7 + H_2O$$

$$H_4P_2O_7 \xrightarrow{589\,K} 2HPO_3 + H_2O$$

14. Discuss the oxidising power of fluorine *[June-2007, Sep-2011, June-2013] [Sep-2008 – 5Mark]*

Oxidizing property of the halogen is due to high electron affinity of halogen atoms. The oxidizing power decreases from fluorine to iodine. Fluorine is the strongest oxidising agent. It oxidises other halide ions to halogens in solution or when dry.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 \quad (X^- = Cl^-, Br^-, I^-)$$

Halogen of low atomic number oxidises the halide ion of higher atomic number.

15. Why is HF not stored in glass bottles? *[March-2007, Mar-2011, Sep-2013]*

HF cannot be stored in glass or silica bottles as it attacks silicates and silica.

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

So, HF is stored in wax bottles.

16. Write the uses of fluorine *[Sep-2012]*

1. Fluorine is used in the manufacture of freons (dichlorodifluoro methane $CF_2\ Cl_2$.). These non-toxic, non-combustible and volatile liquids are used as refrigerants in refrigerators, deep freezers and air conditioners.
2. CaF_2 is used as flux in metallurgy.
3. NaF is used as a preservative to prevent fermentation and also for preventing dental cavities.
4. Teflon is used as container to store hydrofluoric acid.

17. What are interhalogen compounds? How are they formed? *[Sep-2008, June-2012]*

Each halogen combines with another halogen to form several compounds known as interhalogen compounds. They can all be prepared by direct combination or by the action of a halogen on a lower interhalogen

$$Cl_2 + F_2 \xrightarrow{473\,K} 2ClF$$

$$Cl_2 + 3F_2 \xrightarrow{573\,K} 2ClF_3$$

$$IF_5 + F_2 \xrightarrow{573\,K} IF_7$$

18. How are xenon fluorides prepared? *[Sep-2011]*

Xenon forms three binary fluorides XeF_2 , XeF_4 and XeF_6 by the direct union of elements under appropriate experimental conditions.

$$Xe + F_2 \xrightarrow{673\,K} XeF_2$$

$$Xe + 2F_2 \xrightarrow{673\,K} XeF_4$$

$$Xe + 3F_2 \xrightarrow{573\,K} XeF_6$$

19. Give any three uses of helium. *[Sep-2007]*

1. Because of its lightness and non-inflammability helium is used to filling balloons for meteorological observations
2. Because of its lightness it is used in inflating aeroplane tyres.
3. A mixture of oxygen and helium is used in the treatment of asthma.

20. Write the uses of Neon? *[June-2008, June-2010, Sep-2010, Mar-2012, Sep-2013]*

1. Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
2. Mixed with helium it is used to protect electrical instruments from high Voltages.
3. It is also used in beacon lights for safety of air navigation as the light possesses fog and storm-penetrating power.
4. Neon light is used in botanical gardens as it stimulates growth and helps the formation of chlorophyll.

9. THERMODYNAMICS – II

1. What is entropy? What are the units of entropy? *[March-2006]*

Entropy is a measure of randomness or disorder of the molecules of a system. It is a state function.

$$S = \frac{q}{T}$$

S = entropy, q = heat involved, T = temperature of the process

Units of entropy:

cgs unit of entropy is cal K^{-1} (or) eu

SI unit of entropy is J K^{-1} (or) EU (1 eu = 4.184 EU)

2. State Trouton's rule *[June-2009]*

According to Trouton's rule, the heat of vaporisation (ΔH_{vap}) in calories per mole divided by the boiling point of the liquid in Kelvin is a constant equal to 21 cal deg^{-1} $mole^{-1}$ and is known as the entropy of vapourisaiton.

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = 21 \text{ Cal deg}^{-1} \text{ mol}^{-1}$$

ΔH_{vap} = Enthalpy change of vapourisation = Latent heat of vapourisation.

This equation is useful for estimating the molar heat of vaporisation of a liquid of known boiling point.

3. What type of liquids or substances deviate from Trouton's rule? *[Sep-2006, June-2011]*

1. Low boiling liquids such as hydrogen and Helium which boil only a little above 0 K
2. Polar substances like water, alcohol which form hydrogen bonded liquids and exhibit very high boiling points as well as high ΔH_{vap}
3. Liquids such as acetic acid whose molecules are partially associated in the vapor phase and possess very low entropy vaporization which is very much less than 21 cal deg^{-1} mol^{-1}

4. What is Gibb's free energy? *[June-2006]*

Gibb's free energy **G** is defined as,

$$\mathbf{G = H - TS}$$

where H = enthalpy or heat content of the system,
T = Temperature in Kelvin
S = entropy

In an isothermal process, if ΔH and ΔS are the changes in enthalpy and entropy of the system, then free energy change ΔG is given by,

$$\Delta G = \Delta H - T\Delta S$$

5. How ΔG is related to ΔH and ΔS? What is the meaning of $\Delta G = 0$? *[Sep-2010]*

$$\Delta G = \Delta H - T\Delta S$$

Where, ΔG = free energy change
ΔH = changes in enthalpy
ΔS = changes in entropy
T = Temperature in Kelvin

If $\Delta G = 0$ then the process is in equilibrium (reversible)

6. What is the nature of reaction when $\Delta G > 0$, $\Delta G < 0$, $\Delta G = 0$? *[Sep-2011]*

$\Delta G > 0$: Non spontaneous
$\Delta G < 0$: Spontaneous
$\Delta G = 0$: Equilibrium

7. Give Kelvin – Planck statement of second law of thermodynamics

[Mar-2007, Sep-2012, June-2013]

"It is impossible to construct an engine operating in a complete cycle which will absorb heat from a single body and convert it completely to work without leaving some changes in the working system".

8. Give Clausius statement of second law of thermodynamics *[June-2007]*

"It is impossible to transfer heat from a cold body to a hot body by a machine without doing some work".

9. Give Entropy statement of second law of thermodynamics *[Sep-2008]*

'A process accompanied by increase in entropy tends to be spontaneous".
Entropy is a measure of randomness or disorder of the molecules of a system
A system always spontaneously changes from ordered to a disordered state. Therefore entropy of a spontaneous process is constantly increasing.

10. What is the entropy change of an engine that operates at 100°C when 453.6 k.cal of heat is supplied to it? *[Sep-2007, Sep-2009, June-2012]*

$$\Delta S_{rev} = \frac{\Delta q_{rev}}{T} = \frac{453.6}{373} = 1.216 \text{ k Cal } K^{-1} = 1216 \text{ Cal } K^{-1}$$

11. For a chemical reaction the values of ΔH and ΔS at 300 K are –10 k Cal mol^{-1} and 20 Cal $deg^{-1}mol^{-1}$ respectively. What is the value of ΔG of the reaction? *[June-2008, June-2010]*

$\Delta H = -10$ k Cal $mol^{-1} = -10{,}000$ Cal mol^{-1}
$\Delta S = 20$ Cal.deg^{-1} mol^{-1}

$\Delta G = \Delta H - T\Delta S$
$= -10{,}000 - (300 \times 20)$
$= -16000$ Cal mol^{-1}

12. Calculate the molar heat of vapourisation of the ideal liquid CCl_4 (B.Pt 76.7°C and ΔS =87.864 J K^{-1} mol^{-1}) *[March-2008]*

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

$\Delta S = 87.864$ J K^{-1} mol^{-1} & $T_b = 76.7 + 273 = 349.7$ K

$\therefore \Delta H_{vap} = 87.864 \times 349.7 = 30726$ J $mol^{-1} = 30.726$ kJ mol^{-1}

13. Calculate the molar heat of vapourisation of the ideal liquid $CHCl_3$ (B.Pt 61.5°C) *[March-2012]*

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

$\therefore \Delta H_{vap} = (21$ cal mol^{-1} $K^{-1} \times 4.184)(273 + 61.5)$K
$= 29390$ J mol^{-1}

$= 29.390$ kJ mol^{-1}

14. Calculate the change of entropy for the process, water (liq) to water (vapour, 373 K) involving ΔH_{vap} = 40850 J mol^{-1} at 373 K *[Mar-2010, Sep-2013]*

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{40850}{373} = 109.517 \text{ J } K^{-1} mol^{-1}$$

15. Calculate the entropy change involved in the conversion of 1 mole of ice at 0°C and 1 atm to liquid at 0°C and 1 atm. The enthalpy of fusion per mole of ice is 6008 J mol^{-1} *[Mar-2009]*

$$H_2O_{(s)} \xrightarrow{0^\circ C} H_2O_{(l)}$$
Ice → water

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_m}$$

$\Delta H_{fusion} = 6008$ J mol^{-1} & $T_m = 0^oC + 273 = 273$ K

$\therefore \Delta S_{fusion} = \frac{6008}{273} = 22.007$ J K^{-1} mol^{-1}

16. Calculate the maximum % efficiency possible from a thermal engine operating between 110°C and 25°C *[Mar-2011]*

$$\% \text{ efficiency} = \left(1 - \frac{T_2}{T_1}\right) \times 100$$

$T_1 = 110°C + 273 = 383\ K$

$T_2 = 25°C + 273 = 298\ K$

$$= \left(1 - \frac{298}{383}\right) \times 100$$

$$= 22.2\ \%$$

17. Calculate the entropy change for the following process possessing $\Delta H_{(transition)}$ =2090 Jmol^{-1}

1 mole Sn (α, 13ºC) ⇌ 1 mole Sn (β, 13ºC) *[Mar-2013]*

$T_{(transition)} = 13°C + 273 = 286\ K$

$$\Delta S_{(transition)} = \frac{\Delta H_{transition}}{T_{transition}} = \frac{2090}{286} = 7.307\ J\ K^{-1}\ mol^{-1}$$

19. CARBOXYLIC ACIDS

1. Give the source and trivial names of i) HCOOH ii) CH_3COOH iii) C_3H_7COOH iv) C_4H_9COOH v) $C_{11}H_{23}COOH$ *[June-2007]*

Formula	Source	Trivial name
HCOOH	Red ant	Formic acid
CH_3COOH	vinegar	Acetic acid
C_3H_7COOH	Butter	Butyric acid
C_4H_9COOH	Root of valarion plant	Valeric acid
$C_{11}H_{23}COOH$	Laurel oil	Lauric acid

2. Write a note on esterification reaction with an example *[June-2006]*

Carboxylic acids react with alcohols in the presence of mineral acid as catalyst and form esters. This reaction is called esterification.

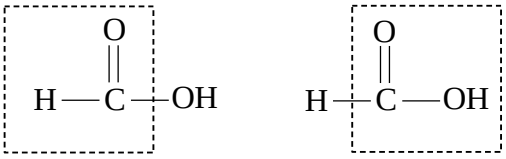
$$CH_3{-}CO\boxed{OH} + H\boxed{OC_2H_5} \xrightarrow{H^+} CH_3{-}COOC_2H_5 + H_2O$$

acetic acid ethyl alcohol ethyl acetate

3. Formic acid reduces Tollen's reagent, but acetic acid does not-Give reason

[Sep-2007, Sep-2008, Sep-2009, Sep-2010, June-2012]

Formic acid is unique because it contains both an aldehyde group and carboxyl group. Hence it can act as a reducing agent. It reduces Tollens reagent and Fehling's solution.



a) Formic acid reduces ammoniacal silver nitrate solution (Tollen's reagent) to metallic silver.

$$H\text{-}COOH + Ag_2O \longrightarrow CO_2 + H_2O + 2Ag \downarrow \text{(Metallic silver)}$$

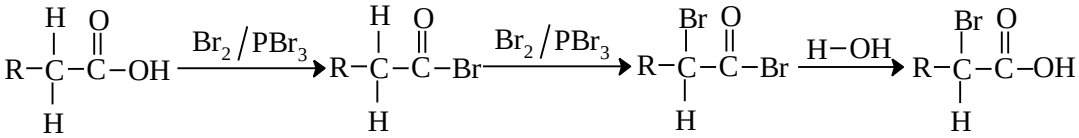
b) Formic acid reduces Fehling's solution. It reduces blue coloured cupric ions to red coloured cuprous ions.

$$\underset{\text{Blue}}{H\text{-}COOH + 2CuO} \longrightarrow CO_2 + H_2O + \underset{\text{Red}}{Cu_2O}$$

Since acetic acid does not contain aldehyde group, it does not reduce Tollen's reagent.

4. Write a note on HVZ reaction *[Sep-2006]*

Carboxylic acids having α-hydrogen atoms can be converted to α-halo acids by halogen and phosphorus trihalide. This reaction is known as Hell-Volhard Zelinsky reaction.

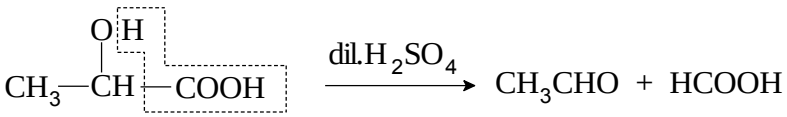


5. Write the tests for carboxylic acid *[June-2009, Sep-2012, Mar-2013]*

1. Aqueous solution of carboxylic acids turn blue litmus into red colour
2. Carboxylic acids give *brisk effervescence* with sodium bi-carbonate due to the evolution of carbon-di-oxide
3. On warming carboxylic acids with alcohol and concentrated sulphuric acid it forms ester which is identified from its fruity odour

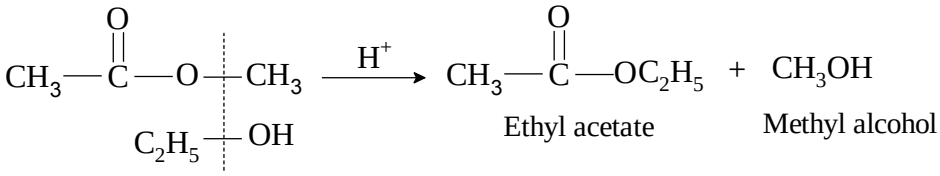
6. What is the action of dilute sulphuric acid with lactic acid? *[Mar-2008]*

With dil. H_2SO_4 acid it dissociates to acetaldehyde and formic acid



7. Write a note on trans esterification *[Mar-2006]*

In presence of a little acid, methyl acetate is cleaved by ethyl alcohol to form ethyl acetate. This is called **'trans esterification'.**

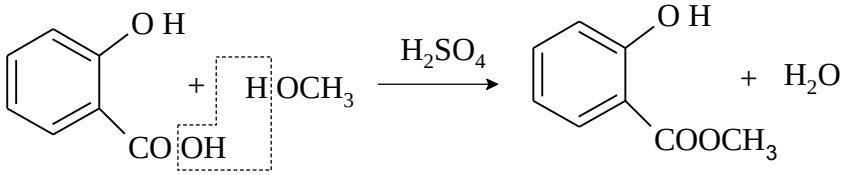


8. Write the tests for salicylic acid *[Mar-2010]*

1. An aqueous solution of salicylic acid gives violet colour with neutral ferric chloride.
2. It gives effervescence with sodium bicarbonate.
3. It is soluble in sodium hydroxide and reprecipitated on acidification.
4. With Bromine water the colour is discharged with the formation of white precipitate.

9. How is methyl salicylate prepared? *[June-2008]*

On heating salicylic acid with methyl alcohol in presence of con.H_2SO_4 a pleasant smelling liquid-**methyl salicylate is formed.**



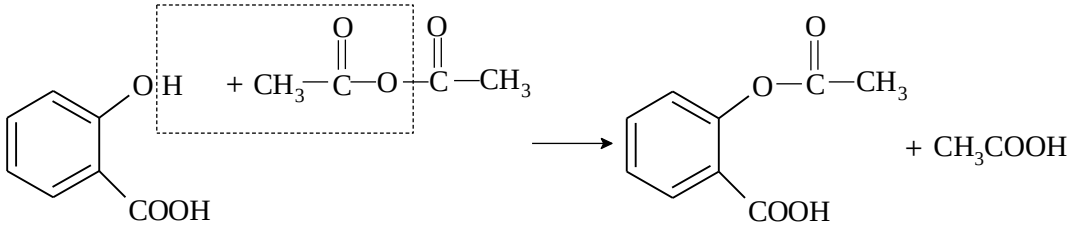
Methyl salicylate

Methyl salicylate is present in the **oil of winter green**.

10. What is aspirin? Write its preparation and use *[Mar-2011]*

Acetyl salicylic acid is known as aspirin

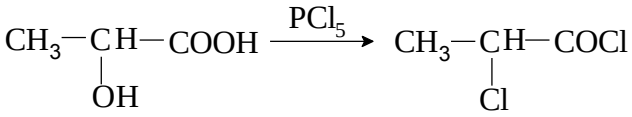
Salicylic acid undergoes acetylation by heating with acetic anhydride to form aspirin which is used as an analgesic and antipyretic.



Acetyl salicylic acid or Aspirin

11. What happens when lactic acid is treated with PCl_5? Write the equation *[Mar-2012]*

With PCl_5 lactic acid forms lactyl chloride.



Lactyl chloride

12. Compare the strength of mono, di, trichloro acetic acid *[Sep-2013]*

Cl is electron withdrawing group (–I effect). So, it decreases the strength of the –O–H bond and hence the release of hydrogen becomes easy. Three chlorine atoms in trichloro acetic acid withdraw the electrons more powerfully making the acid very strong. Thus the strength of mono, di, trichloro acetic acid varies in the order,

$$CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$$

13. Write the uses of benzoic acid *[June-2010]*

1. Benzoic acid is used as an urinary antiseptic
2. Sodium benzoate is used as food preservative
3. Benzoic acid vapours are used to disinfect bronchial tube.
4. It is used for the manufacture of dyes.

14. Mention the uses of oxalic acid *[Mar-2007, Mar-2009, June-2011, Sep-2011]*

1. for removing ink stains and iron stains.
2. as mordant in dyeing and calico printing.
3. in manufacture of ink and metal polishes.
4. Redox titration

15. Write the uses of lactic acid *[June-2013]*

1. In tanning industry.
2. In soft drinks.
3. In the treatment of digestive disorder in children.
4. Silver lactate as an antiseptic and astringent.

5 MARK

2. PERIODIC CLASSIFICATION – II

1. Explain Pauling's Method to determine ionic radii

[Mar-2006, Sep-2009, Mar-2010, June-2010, Sep-2010, Sep-2011, Mar-2012]

1. Pauling has calculated the radii of the ions on the basis of the observed internuclear distances in four crystals namely NaF, KCl, RbBr and CsI.

2. In each ionic crystal the cations and anions are isoelectronic with inert gas configuration.

   NaF crystal : Na^+ - 2, 8 } Ne type configuration
   F^- - 2, 8 }

   KCl crystal : K^+ - 2, 8, 8 } Ar type configuration
   Cl^- - 2, 8, 8 }

3. The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the inter nuclear distance between them.

   $$r(C^+) + r(A^-) = d(C^+–A^-) \quad \text{..... (1)}$$

   where
   $r(C^+)$ - radius of cation, C^+
   $r(A^-)$ - radius of anion, A^-
   $d(C^+–A^-)$ - internuclear distance between C^+ and A^- ions in C^+A^- ionic crystal

4. For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge. i.e.

   $$r(C^+) \propto \frac{1}{Z^*(C^+)} \quad \text{..... (2)}$$

   $$r(A^-) \propto \frac{1}{Z^*(A^-)} \quad \text{..... (3)}$$

   where,
   $Z^*(C^+)$ & $Z^*(A^-)$ are the effective nuclear charges of cation (C^+) and anion (A^-) respectively.

   On combining (2) & (3)

   $$\frac{r(C^+)}{r(A^-)} = \frac{Z^*(A^-)}{Z^*(C^+)} \quad \text{..... (4)}$$

5. Hence the above two equations (1) & (4) can be used to evaluate the values of $r(C^+)$ and $r(A^-)$ provided that the values of $d(C^+–A^-)$, $Z^*(C^+)$ and $Z^*(A^-)$ are known.

2. Explain the factors which affect ionization energy. *[June-2008, June-2013]*

The ionization energy depends upon the following factors:

a) Size of atom

The ionization energy decreases with the increasing size of atom. The larger the size of atom, lesser is the ionization energy. This is due to the fact that electrons are tightly held in smaller atoms whereas in large atoms, electrons are held quite loose, i.e., lesser energy is required for removal of electrons from larger atoms than the smaller one. Hence ionization energy is lower for larger atoms and higher for smaller atoms.

b) Magnitude of nuclear charge

The higher the nuclear charge of protons in the nucleus, the higher is the ionization energy. Because of the higher nuclear charge, the electrons are bound with more force and hence higher energy will be required for their removal.

c) Effect of number of electrons in the inner shells (Screening or shielding effect)

The attractive force exerted by the nucleus on the most loosely bound electron is atleast partially counterbalanced by the repulsive forces exerted by the electrons present in the inner shells. The electron to be removed is thus shielded from the nucleus by the electrons in the inner shell. Thus, the electron in the valence shell experiences less attraction from the nucleus. Hence the ionisation energy will be low.

d) Effect of shape of orbital

The shape of orbital also influences the ionization potential. As s-electrons remain closer to the nucleus than p-,d-, and f-electrons of the same valence shell, the ionization energy decreases in the order : s > p > d > f

e) Effect of arrangement of electrons

The more stable the electronic arrangement, the greater is the ionization energy. As the noble gases have completely filled, stable electronic arrangements, they show maximum ionization energy.

3. Explain the factors which affect electron affinity

[June-2006, Sep-2006, Mar-2007, June-2007, Mar-2009, June-2011, June-2012, Sep-2013]

1) Atomic size

$$\text{Electron affinity} \propto \frac{1}{\text{Size of atom}}$$

Smaller the size of an atom, greater is its electron affinity. As the size of atom increases, the nuclear attraction for adding electron decreases. Consequently, atom will have less tendency to attract additional electron towards itself.

2) Effective nuclear charge

$$\text{Electron affinity} \propto \text{Effective nuclear charge.}$$

As the effective nuclear charge of atom increases, nuclear attraction for adding electron increases.

3) Shielding or Screening Effect

$$\text{Electron affinity} \propto \frac{1}{\text{Shielding effect}}$$

Electronic energy state, lying between nucleus and outermost state hinder the nuclear attraction for incoming electron. Therefore, greater the number of inner lying state, less will be the electron affinity.

4) Electronic Configuration

The electronic configurations of elements influence their electron affinities to a considerable extent. Electron affinities of inert gases are zero. This is because their atoms have stable $ns^2\ np^6$ configuration in their valence shell and there is no possibility for addition of an extra electron.

4. Explain the Pauling's scale for the determination of electronegativity *[Mar-2008, Sep-2012]*

This scale is based on an empirical relation between the energy of a bond and the electronegativities of bonded atoms.

Consider a bond A-B between two dissimilar atoms A and B of a molecule AB. Let the bond energies of A-A, B-B and A-B bonds be represented as $E_{A\text{-}A}$, $E_{B\text{-}B}$ and $E_{A\text{-}B}$ respectively. It may be seen that the bond dissociation energy of A-B is almost higher than the geometric mean of the bond dissociation energies of A-A and B-B bonds i.e.,

$$E_{A\text{-}B} > \sqrt{E_{A-A} \times E_{B-B}}$$

$$\Delta = E_{A\text{-}B} - \sqrt{E_{A-A} \times E_{B-B}}$$

The difference (Δ) is related to the difference in the electronegativities of A and B according to the following equation

$$\Delta = (X_A - X_B)^2$$

$$\sqrt{\Delta} = (X_A - X_B)$$

$$0.208\sqrt{\Delta} = (X_A - X_B)$$

Here, X_A and X_B are the electronegativities of A and B respectively. The factor 0.208 arises from the conversion of Kcals to electron volt.

Considering arbitarily the electronegativity of hydrogen to be 2.1, Pauling calculated electronegativities of other elements with the help of this equation.

Disadvantage of Pauling scale

The disadvantage of Pauling's scale is that bond energies are not known with any degree of accuracy for many solid elements.

Disadvantage of Mulliken scale:

Electron affinities with the exception of a few elements are not reliably known.

5. Write the applications of electronegativity

1) Nature of bond *[Sep-2007, June-2009, Mar-2011]*

The concept of electronegativity can be used to predict whether the bond between similar or dissimilar atoms is non-polar covalent bond, polar covalent bond (or) ionic bond.

Electronegativity	Nature of A-B bond	Representation	Example
$X_A = X_B$, i.e. $X_A - X_B = 0$	Non polar covalent bond	A–B	H –H
$X_A > X_B$ i.e. $X_A - X_B$ is small	Polar covalent bond	$A^{\delta-}$–$B^{\delta+}$	$O^{\delta-}$-$H^{\delta+}$ in H_2O
$X_A >> X_B$ i.e. $X_A - X_B$ is very large	Ionic bond	$A^- B^+$	Na^+Cl^-

2) Percentage of ionic character in a polar covalent bond *[Sep-2008]*

Pauling estimated the percentage of ionic character in various $A^{\delta-}$-$B^{\delta+}$ polar covalent bonds from known (X_A–X_B) values and has derived the following conclusions:

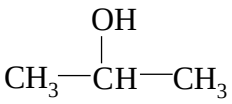
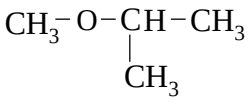
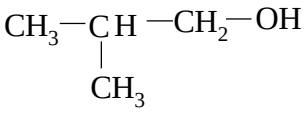
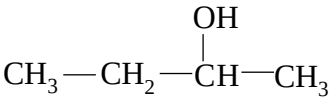
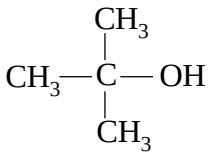
Electronegativity difference	Bond character	Bond type	Representation
(X_A–X_B) = 1.7	ionic character = 50% covalent character =50%	50% ionic and 50% covalent	$A^{\delta-}$–$B^{\delta+}$
(X_A–X_B) < 1.7	ionic character < 50% covalent character >50%	Predominantly covalent	A–B
(X_A–X_B) > 1.7	ionic character > 50% covalent character <50%	Predominantly ionic	$A^- B^+$

17. ETHERS

1. Write a note on the type of isomerism exhibited by ethers *[June-2006, Sep-2007]*

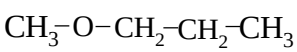
i) Functional Isomerism

Ethers are functional isomers of alcohols as both have the same general formula $C_nH_{2n+2}O$.

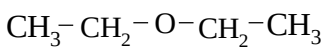
Molecular formula	Ethers	Alcohols
C_2H_6O	$CH_3–O–CH_3$ dimethyl ether	CH_3CH_2OH ethyl alcohol
C_3H_8O	$CH_3–O–CH_2–CH_3$ Ethyl methyl ether	$CH_3–CH_2–CH_2–OH$ n-propyl alcohol  isopropyl alcohol
$C_4H_{10}O$	$CH_3–CH_2–O–CH_2–CH_3$ Diethyl ether $CH_3–O–CH_2–CH_2–CH_3$ Methyl n-propyl ether  Methyl isopropyl ether	$CH_3–CH_2–CH_2–CH_2–OH$ n-butyl alcohol  Isobutyl alcohol  sec.butyl alcohol  tert.butyl alcohol

ii) Metamerism

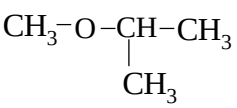
It is a special isomerism in which molecules with same formula, same functional group, differing only in the nature of the alkyl group attached to oxygen.



methyl n-propylether



diethylether



methyl isopropylether

2. Give the methods of preparing diethyl ether

[June-2007, Mar-2008, Mar-2010, Mar-2012, Mar-2013]

a. Intermolecular dehydration of alcohol

When excess of alcohol is heated with con. H_2SO_4 two molecules condense losing a molecule of water forming ether.

$$C_2H_5 - O - H + H - O - C_2H_5 \xrightarrow{\text{con. } H_2SO_4} C_2H_5 - O - C_2H_5 + H_2O$$

b. Williamson's synthesis

Ethers are prepared by heating alkyl halides with sodium or potassium alkoxide.

$$C_2H_5Br + NaOC_2H_5 \longrightarrow C_2H_5 - O - C_2H_5 + NaBr$$

This method is suitable to prepare all kinds of ethers - simple and mixed ethers.

c. From alkyl halides

Ethers may be prepared by heating alkyl halides with dry silver oxide.

$$C_2H_5 - I + Ag_2O + I - C_2H_5 \xrightarrow{\Delta} C_2H_5 - O - C_2H_5 + 2AgI$$

3. How does ether react with the following?

a) Air or O_2 / long contact b) dil.H_2SO_4 c) PCl_5 *[Mar-2007, June-2011]*

a) Air or O_2 / long contact

$$C_2H_5–O–C_2H_5 \xrightarrow{(O)} (C_2H_5)_2O_2$$

Diethyl peroxide

Diethyl peroxide is unstable and decomposes violently with explosion on heating. Hence ether should not be evaporated to dryness.

b) dil.H_2SO_4

Ethers on boiling with water in presence dilute acids are hydrolysed to form alcohols.

$$C_2H_5–O–C_2H_5 + H–O–H \xrightarrow{H_2SO_4} 2\ C_2H_5OH$$

Ethyl alcohol

c) PCl_5

$$C_2H_5–O–C_2H_5 + PCl_5 \longrightarrow 2C_2H_5\ Cl + POCl_3$$

Ethyl chloride

4. How does diethyl ether react with PCl_5, one equivalent of HI and excess of HI? *[Sep-2010]*

a) PCl_5

$$C_2H_5–O–C_2H_5 + PCl_5 \longrightarrow 2C_2H_5\ Cl + POCl_3$$

Ethyl chloride

b) With one equivalent of HI

$$C_2H_5 - O - C_2H_5 + HI \longrightarrow C_2H_5OH + C_2H_5I$$

Ethyl alcohol Ethyl iodide

c) With excess of HI

$$C_2H_5 - O - C_2H_5 + 2HI \longrightarrow 2C_2H_5I + H_2O$$

Ethyl iodide

5. How do ethers react with HI? Give the significance of the reaction *[Mar-2006]*

With one equivalent of HI

$$C_2H_5 - O - CH_3 + HI \longrightarrow C_2H_5OH + CH_3I$$

Halogen **(I)** prefers to attack the carbon atom of **the smaller alkyl group.**

With excess hot concentrated hydroidic acid

$$CH_3 - O - C_2H_5 + 2HI \longrightarrow CH_3I + C_2H_5I + H_2O$$

This reaction is used in the **Zeisel's method of detection and estimation of alkoxy (especially methoxy) group** in natural products like alkaloids.

6. How is anisole prepared? Write its chemical properties and uses

[June-2008, Mar-2009, June-2012, Sep-2012, June-2013]

a. Williamson's synthesis

$$\underset{\text{sodium phenoxide}}{C_6H_5ONa} + CH_3{-}I \longrightarrow \underset{\text{Anisole}}{C_6H_5{-}O{-}CH_3} + NaI$$

b. Using diazomethane

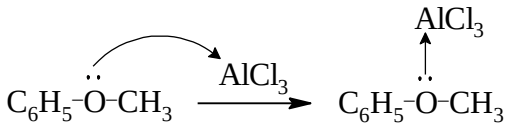
$$\underset{\text{phenol}}{C_6H_5{-}O{-}H} + \underset{\text{diazomethane}}{CH_2{-}N_2} \longrightarrow \underset{\text{Anisole}}{C_6H_5{-}O{-}CH_3} + N_2$$

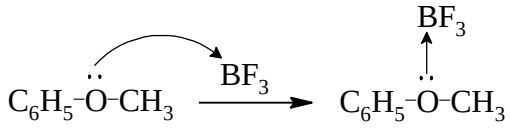
c. Using dimethyl sulphate

$$\underset{\text{phenol}}{C_6H_5{-}O{-}H} + \underset{\text{dimethyl sulphate}}{(CH_3)_2{-}SO_4} \xrightarrow{NaOH} \underset{\text{Anisole}}{C_6H_5{-}O{-}CH_3} + CH_3HSO_4$$

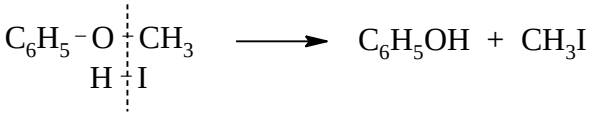
Chemical properties

1. Anisole forms oxonium compounds with Lewis acids



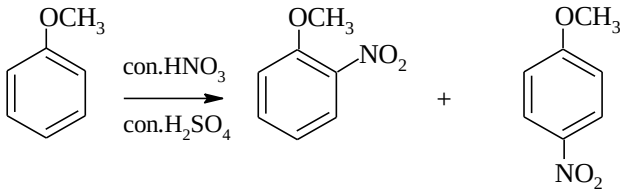


2. Anisole reacts with hydroiodic acid to give phenol and methyl iodide

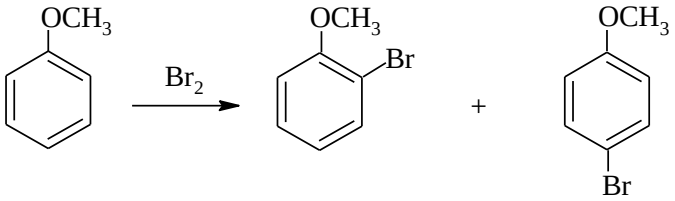


3. Reaction due to the benzene ring : ***Electrophilic substitution reactions***
$-OCH_3$, group increase the reactivity of the benzene ring with respect to electrophilic attack and is **ortho, para –directing.**

a) With a mixture of con.HNO_3 and con.H_2SO_4 it gives a mixture of ortho and para nitro anisole



b) Bromination yields ortho bromoanisole and para bromoanisole



Uses of anisole
1. It is used in perfumery.
2. It is used as a starting material in organic synthesis.

7. Give the differences between aromatic ether and aliphatic ether
[Sep-2006, Sep-2008, June-2009, Sep-2009, June-2010,Mar-2011, Sep-2011, Sep-2013]

No	Aromatic ether (Anisole)	Aliphatic ether (Diethyl ether)
1	Comparatively high boiling liquid	Volatile liquid
2	Used in perfumery	Used as anaesthetic
3	Not used as solvent	Used as a solvent
4	Can not be used as a substitute for petrol	Mixed with alcohol, used as a substitute for petrol
5	On heating with HI forms phenol and CH_3I only	It forms C_2H_5OH, and C_2H_5I
6	With nitrating mixture forms nitro anisoles	Nitration does not take place
7	Does not form peroxide easily	Forms peroxide in air.

(Q-70) d-BLOCK ELEMENTS

Hints:

	Group 3	4	5	6	7	8	9	10	11	12
Period 4	Sc	Ti	V	**Cr**	Mn	Fe	Co	Ni	**Cu**	**Zn**
5									**Ag**	
6									**Au**	

Element	Group	Period	Colour
Cr	6	4	Silvery white metal
Cu	11	4	Reddish brown metal
Ag	11	5	White lustrous metal
Au	11	6	Lustrous yellow metal
Zn	12	4	Bluish white metal

Metallic compound	Colour
Potassium dichromate $K_2Cr_2O_7$	Orange red crystal
Potassium chromate K_2CrO_4	Yellow
Coppersulphate pentahydrate $CuSO_4.5H_2O$ (Blue Vitriol)	Blue
Silver nitrate $AgNO_3$ (Lunar Caustic)	White
Zinc carbonate $ZnCO_3$ (Calamine)	White powder
Zinc oxide ZnO (Philosopher's wool)	White cloud
Purple of Cassius (Colloidal gold)	Purple or red

1. An element (A) belongs to group number 11 and period number 4. (A) is a reddish brown metal. (A) reacts with HCl in the presence of air and gives compound (B). (A) also reacts with conc. HNO_3 to give compound (C) with the liberation of NO_2. Identify (A),(B) and (C). Explain the reactions. *[Mar-2006, June-2011]*

a) Element (A) is copper: Group = 11 and period = 4. It is a reddish brown metal.

b) $2Cu + 4HCl + O_2 \longrightarrow 2CuCl_2 + 2H_2O$

Compound (B) is $CuCl_2$

c) $Cu + 4HNO_3\,(con) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Compound (C) is $Cu(NO_3)_2$

A	Cu	copper
B	$CuCl_2$	Cupric chloride
C	$Cu(NO_3)_2$	Cupric nitrate

2. Silver reacts with dil. HNO_3 to give compound (A) which on heating at 723K gives (B). (B) on further heating gives (C). Further compound (A) reacts with KBr and gives (D) which is highly useful in photography. Identify (A),(B),(C) and (D) and explain the reactions.
[June-2006 , Mar-2009]

a) $3Ag + 4HNO_3\,(dil) \longrightarrow 3AgNO_3 + NO + 2H_2O$

Compound (A) is $AgNO_3$

b) $2AgNO_3 \xrightarrow{723K} 2AgNO_2 + O_2$

Compound (B) is $AgNO_2$

c) $AgNO_2 \xrightarrow{980K} Ag + NO_2$

Element (C) is Ag

d) $AgNO_3 + KBr \longrightarrow AgBr + KNO_3$

Compound (D) is AgBr which is highly useful in photography.

A	$AgNO_3$	Silver nitrate
B	$AgNO_2$	Silver nitrite
C	Ag	Silver
D	AgBr	Silver bromide

Hints:

1. $pH = -\log_{10}[H^+]$

2. $pOH = -\log_{10}[OH^-]$

3. $pH + pOH = 14$

4. pH of acidic buffer, $pH = pK_a + \log \frac{[salt]}{[acid]}$

5. pOH of basic buffer, $pOH = pK_b + \log \frac{[salt]}{[base]}$

6. Ionic product of water $K_w = [H^+]\,[OH^-] = 1 \times 10^{-14}\ mol^2\ dm^{-6}$

7. Dissociation constant of the weak acid, $K_a = \frac{C\alpha^2}{1-\alpha}$

8. For weak acids, $[H^+] = C\alpha$

$$= \sqrt{K_a C}$$

9. Specific conductance, $\kappa = \frac{1}{R}\frac{l}{a}$

10. Specific conductance = Cell constant × Conductance

11. Specific conductance $= \frac{\text{Cell constant}}{\text{Resistance}}$

12. Equivalent conductance, $\lambda_C = \kappa \frac{10^3}{N}$ mho cm^2 (gm equiv)$^{-1}$

$$\lambda_C = \kappa \frac{10^{-3}}{N} \text{ mho } m^2 \text{ (gm equiv)}^{-1}$$

13. Molar conductance, $\mu_C = \frac{\kappa \times 10^{-3}}{M}$ mho m^2 mol^{-1}

1. What is the pH of a solution containing 0.5 M propionic acid and 0.5 M sodium propionate? The K_a of propionic acid is 1.34×10^{-5}. What happens to the pH of the solution when volume is doubled by adding water? *[Mar-2006, June-2010]*

$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log (1.34 \times 10^{-5}) + \log \frac{0.5}{0.5}$$

$$= 5 - \log 1.34 + \log 1$$

$$= 5 - 0.1271 + 0$$

$$= 4.8729$$

When volume is doubled by adding water, the concentrations of salt and acid are reduced to the same extent and therefore the ratio $\frac{[\text{salt}]}{[\text{acid}]}$ remains the same. So, there will be no change in pH of the solution.

2. Find the pH of a buffer solution containing 0.20 mole per litre sodium acetate and 0.15 mole per litre acetic acid. K_a for acetic acid is 1.8×10^{-5}.

[June-2006, Sep-2006, Sep-2007, June-2011, Sep-2011]

$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{0.20}{0.15}$$

$$= 5 - \log 1.8 + \log 20 - \log 15$$

$$= 5 - 0.2553 + 1.3010 - 1.1761$$

$$= 4.8696$$

3. Calculate the pH of a buffer solution containing 0.04 M NH_4Cl and 0.02 M NH_4OH. For NH_4OH K_b is 1.8×10^{-5}. *[Mar-2007]*

$$\text{pOH} = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{0.04}{0.02}$$

$$= 5 - \log 1.8 + \log 2$$

$$= 5 - 0.2553 + 0.3010$$

$$= 5.0457$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 5.0457$$

$$= 8.9543$$

(Q-70) ORGANIC CHEMISTRY

Hints:

1. General formula of aliphatic monohydric alcohols: $C_nH_{2n+2}O$

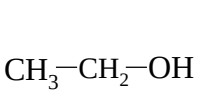
2. Alcohols liberate hydrogen gas with metallic sodium

3. Primary alcohols
   - ⇒ No turbidity with Lucas reagent at room temperature
   - ⇒ Give red colour in Victor Meyer's test
   - ⇒ Give aldehydes on oxidation and then carboxylic acid (same number of carbons)
   - ⇒ Give aldehydes with Cu at 573 K (dehydrogenation)

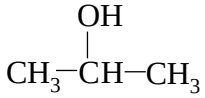
4. Secondary alcohols
   - ⇒ Give turbidity with Lucas reagent at room temperature after 5 – 10 minutes
   - ⇒ Give blue colour in Victor Meyer's test
   - ⇒ Give ketones on oxidation and then carboxylic acid
     (Carboxylic acid contains one carbon less than alcohol)
   - ⇒ Give ketones with Cu at 573 K (dehydrogenation)

5. Tertiary alcohols
   - ⇒ Give turbidity with Lucas reagent at room temperature immediately
   - ⇒ Give no colour in Victor Meyer's test
   - ⇒ Give ketones on oxidation and then carboxylic acid
     (Ketone contains one carbon less than alcohol & Carboxylic acid contains two carbons less than alcohol)
   - ⇒ Give alkene with Cu at 573 K (dehydration)

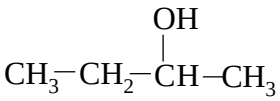
6. Alcohols containing CH_3CHOH- group answer haloform test (form iodoform with I_2 / NaOH)



Ethyl alcohol



iso propyl alcohol



sec.butyl alcohol

7. Benzyl acetate ($CH_3COO\ CH_2C_6H_5$) has fragrance of jasmine and it is used in perfumery

8. Phenol (C_6H_5OH) gives violet colour with neutral ferric chloride

9. Phenol decolourises Br_2 / H_2O and gives white precipitate

10. Phenol gives red orange dye with benzene diazonium chloride (Dye test)

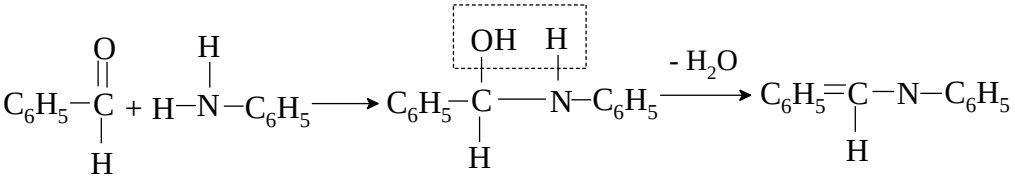
1. An organic compound (A) of molecular formula C_7H_6O is not reduced by Fehling's solution but will undergo Cannizaro reaction. Compound (A) reacts with aniline to give compound (B). Compound (A) also reacts with Cl_2 in the presence of catalyst to give compound (C). Identify (A), (B) and (C) and explain the reactions. *[Mar-2006]*

i) Aromatic aldehydes reduce Tollen's reagent but not Fehling's solution

ii) Since compound (A) undergoes Cannizzaro reaction, it is benzaldehyde

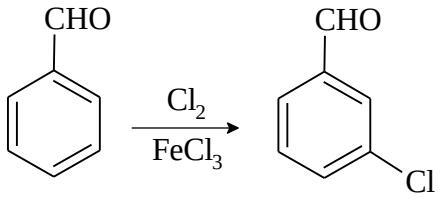
iii) $(A) \xrightarrow{\text{aniline}} (B)$

C_7H_6O

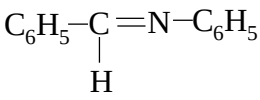
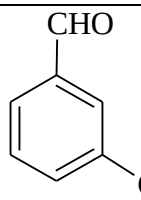


Benzaldehyde (A) Aniline Schiffs base (B)

iv) $(A) \xrightarrow{Cl_2 \,/\, \text{catalyst}} (C)$



Benzaldehyde (A) *m* - chloro benzaldehyde (C)

A	C_6H_5CHO	Benzaldehyde
B		Schiffs base
C		*m*-chlorobenzaldehyde

2. An organic compound (A) of molecular formula C_3H_8O gives turbidity within 5-10 minutes on reaction with anhydrous $ZnCl_2$/HCl. Compound (A) on treatment with sodium hypochlorite gives a carbonyl compound (B) which on further chlorination gives compound (C) of molecular formula $C_3H_3OCl_3$. Identify (A), (B) and (C) and explain the reactions.

[Mar-2006]

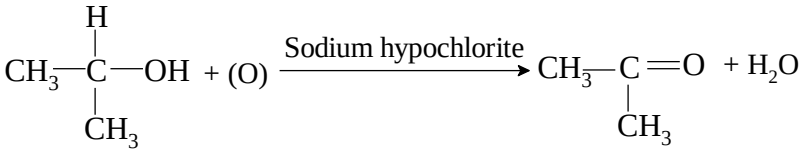
i) $(A) \xrightarrow{\text{anhydrous } ZnCl_2 / HCl}$ Turbidity within 5 - 10 minutes

C_3H_8O

(A) $\Rightarrow$ secondary alcohol $\Rightarrow$ isopropyl alcohol

ii) $(A) \xrightarrow{\text{sodium hypochlorite}} (B)$

C_3H_8O carbonyl compound



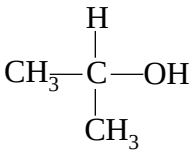
isopropyl alcohol (A) acetone (B)

iii) $(B) \xrightarrow{\text{chlorination}} (C)$

$C_3H_3OCl_3$

$CH_3\text{-}CO\text{-}CH_3 + 3Cl_2 \longrightarrow CCl_3\text{-}CO\text{-}CH_3 + 3HCl$

Acetone (B) Trichloro acetone (C)

A		Isopropyl alcohol
B	$CH_3–CO–CH_3$	Acetone
C	$CCl_3–CO–CH_3$	Trichloro acetone

7. An organic compound A of molecular formula C_3H_6O on reduction with $LiAlH_4$ gives B. Compound B gives blue colour in Victor Meyer's test and also forms a chloride C with $SOCl_2$. The chloride on treatment with alcoholic KOH gives D. Identify (A), (B), (C) and (D) and explain the reactions. *[Mar-2007]*

i) (A)

$C_3H_6O \Rightarrow C_nH_{2n}O \Rightarrow$ (A) is aliphatic aldehyde or ketone

ii) (A) $\xrightarrow[\text{Reduction}]{LiAlH_4}$ (B) $\xrightarrow{\text{Victor Meyer's test}}$ Blue colour

(B) $\Rightarrow$ Secondary alcohol (Isopropyl alcohol) & (A) $\Rightarrow$ Ketone (Acetone)

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 2[H] \xrightarrow{LiAlH_4} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3$$

Acetone (A) — Isopropyl alcohol (B)

iii) (B) $\xrightarrow{SOCl_2}$ (C) $\xrightarrow{\text{Alcoholic KOH}}$ (D)

$$CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 \xrightarrow{SOCl_2} CH_3-\overset{\overset{Cl}{|}}{C}H-CH_3 \xrightarrow{\text{Alcoholic KOH}} CH_3-CH=CH_2 + KCl + H_2O$$

Isopropyl alcohol (B) — Isopropyl chloride (C) — Propene (D)

A	CH_3COCH_3	Acetone
B	$CH_3-\overset{\overset{OH}{\|}}{C}H-CH_3$	Isopropyl alcohol
C	$CH_3-\overset{\overset{Cl}{\|}}{C}H-CH_3$	Isopropyl chloride
D	CH_3-CH=CH_2	Propene

40. Compound (A) with molecular formula C_2H_4O reduces Tollen's reagent. (A) on treatment with HCN gives compound (B). Compound (B) on hydrolysis with an acid gives compound (C) with molecular formula $C_3H_6O_3$ which is an optically active compound. Compound (A) on reduction with N_2H_4 / C_2H_5ONa gives a hydrocarbon (D) of molecular formula C_2H_6. Identify (A),(B),(C), (D) and explain the reactions. *[Mar-2013]*

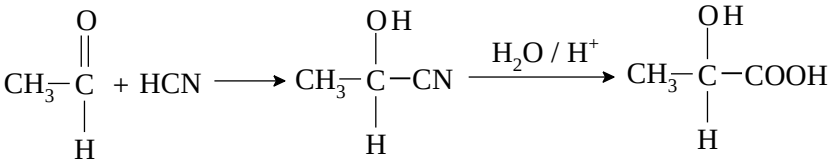
i) (A) $\Rightarrow$ Reduces Tollen's reagent $\Rightarrow$ Aldehyde $\Rightarrow$ Acetaldehyde

C_2H_4O

ii) $(A) \xrightarrow{HCN} (B) \xrightarrow{H_2O / H^+} (C)$

C_2H_4O $\qquad$ $C_3H_6O_3$

optically active

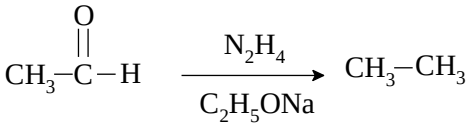


Acetaldehyde (A) $\qquad$ Acetaldehyde cyanohydrin (B) $\qquad$ Lactic acid (C)

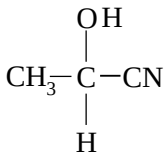
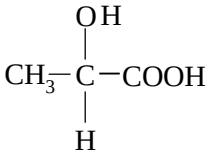
iii) $(A) \xrightarrow{N_2H_4 / C_2H_5ONa} (D)$

C_2H_4O $\qquad$ C_2H_6

Hydrocarbon



Acetaldehyde $\qquad$ Ethane

A	CH_3-CHO	Acetaldehyde
B		Acetaldehyde cyanohydrin
C		Lactic acid
D	CH_3-CH_3	Ethane

41. An organic compound (A) C_3H_8O with Lucas reagent gives turbidity after 5 – 10 minutes. (A) with P / I_2 gives (B). Compound (B) on treatment with silver nitrite gives (C) which gives blue colour with nitrous acid. Identify (A),(B) and (C) and explain the reactions. *[Sep-2013]*

i) $(A)\ C_3H_8O \xrightarrow{\text{Lucas reagent}}$ turbidity after 5-10 minutes

$\Rightarrow 2^o$ alcohol $\Rightarrow$ iso propyl alcohol

ii) $(A) \xrightarrow{P / I_2} (B) \xrightarrow{AgNO_2} (C) \xrightarrow{HNO_2}$ blue colour

$$CH_3—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow{P/I_2} CH_3—\underset{\underset{I}{|}}{CH}—CH_3 \xrightarrow{AgNO_2} CH_3—\underset{\underset{NO_2}{|}}{CH}—CH_3$$

iso propyl alcohol (A) — iso propyl iodide (B) — 2-nitropropane (C)

(C) $\xrightarrow{HO-N=O}$

$$CH_3—\overset{\overset{N=O}{|}}{\underset{\underset{NO_2}{|}}{C}}—CH_3$$

Pseudo nitrol

Blue colour

A	$CH_3—\underset{\underset{OH}{|}}{CH}—CH_3$	Isopropyl alcohol
B	$CH_3—\underset{\underset{I}{|}}{CH}—CH_3$	Isopropyl iodide
C	$CH_3—\underset{\underset{NO_2}{|}}{CH}—CH_3$	2-nitro propane

For complete Material

Contact