UNIT1:SolidState

1. What are anisotropic substances.
2. In ancient building glass window pans become thicker in the bottom.
3. In ancient buildings old window pans become milky on long standing.
4. ZnO is white but turn yellow on heating.
5. Excess of Na in NaCl make it yellow (kin KCl make it violet, Li in LiCl make it pink).
6. Which defect lower the density of ionic crystal.
7. Which defect does not affect the density of the crystal.
8. Which defect increases the density of crystal.
9. Which group element be added to Si to make it p-type semi-conductor.
10. Which group element be added to Si to make it N-type semi conductor.
11. Name the type of crystal.

    $a \neq b \neq c \quad \alpha = \gamma = 90^\circ \quad \beta \neq 90^\circ$

12. Examine the defective crystal.

    $A^+ \quad B^- \quad A^+ \quad B^- \quad A^-$

    $B^- \quad O \quad B^- \quad A^+ \quad B^-$

    $A^+ \quad B^- \quad A^+ \quad O \quad A^-$

    (i) What type of stoichiometric defect is shown by the crystal.

    (ii) How is the density of crystal affected.

    (iii) What type of ionic substance show such defect.

13. How many atoms constitute one unit cell in a FCC.
14. What type of magnetism is shown by alignment of magnetic moment$\uparrow\uparrow\uparrow\uparrow$.
15. What type of point defect in produced, when AgCl is dopped with $CdCl_2$?
16. What is meant by doping in a semiconductor.

17. Fe_3O_4 is ferrimagnetic but turn paramagnetic when heated at 850 k. Why?

18. Define ferromagnetic substances. Give one example.

19. Define ferrimagnetic substance. Give one example.

20. How many atoms are in contact with one atom in hexagonal close packing structure.

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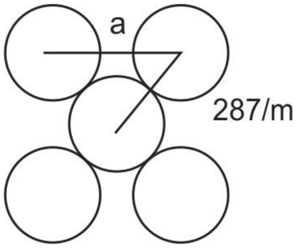
1. Iron is BCC with dimension of 286.65 pm. The density of iron is 7.874 g cm-3. Calculate Avogadro's number (Atomic mass of iron = 55.845 u).

2. KF is FCC having density 2.48 gcm^{-3}. Calculate edge length of the crystal. Given k = 39, F = 19 N_A = 6.02×10^{23}.

3. Silver crystallizes as FCC. The distance between two nearest silver atom is 287 pm. Calculate density of crystal. Given mass of silver 107.79 $gmol^{-1}$, NA = 6.02×10^{23}.

In FCC $r=\frac{\sqrt{2}a}{4}$



$2r = \frac{2\sqrt{2}a}{4}$ $\quad$ $d = \frac{z \times M}{a^3 \times N_A}$

$d = \frac{\cancel{2}\sqrt{2}a}{\cancel{4}_2}$ $\quad$ $d = \frac{4 \times 107.79}{(4.05 \times 10^{-10})^3 \times 6.02 \times 10^{23}}$

$a = \sqrt{2}d$ $\quad$ $= 10.5 \text{ g cm}^{-3}$

a = 1.414 × 287 = 405.8 m

4. Molybdenum atomic mass 96, has density 10.3 gcm-3 and edge length 314 pm. Determine lattice structure whether simple, BCC or FCC. ($N_A = 6.02 \times 10^{23}$ per mole.

5. Copper crystallize FCC, and radius of copper atom is 127.8 pm. Calculate density of crystal given: mass of copper = 63.5 $gmol^{-1}$ $N_A = 6.02 \times 10^{23}$ mol^{-1}.

6. Density of Lithium is 0.53 gcm^{-3}. The edge length of lithium is 3.5 Å. Find the number of atoms in a unit cell. Mass of Li = 6.94 $gmol^{-1}$, $N_A = 6.023 \times 10^{23}$ mol^{-1}.

7. An element with density 11.2 gcm^{-3} form FCC lattice with edge length 4×10^{-8} cm. Calculate atomic mass of element $N_A = 6.02 \times 10^{23}$ per mole.

8. What is the formula of a compound in which the element Y forms ccp lattice and atoms of X occupy 1/3rd of tetrahedral voids? ***2015***

9. An element with molar mass 27 g mol^{-1} forms a cubic unit cell with edge length 4.05×10^{-8} cm,. If its density is 2.7 g cm^{-3}, what is the nature of the cubic unit cell? ***2015***

UNIT2:Solution

1. Define molarity and molality. Which of the two is preferred in handling solution in chemistry.
2. Define vapour pressure and osmotic pressure.
3. What is reverse osmosis. Give its one use.
4. Why osmotic pressure is preferred over another colligative property to determine molecular mass of the organic compound.
5. What happens when a blood cell is placed in hypotonic solution and hypertonic solution.
6. Explain with example positive and negative deviation from Rasult's law.
7. State Henry's law. Write its two application.
8. State Raoult's law (i) for volatile liquids.

   (ii) when solvent alone is volatile.
9. Define the terms: (i) mole fraction (ii) isotonic solution (iii) Vant Hoff factor (iv) Ideal solution
10. A 1.0 molar solution of trichlero acetic acid boil at 100.18°C. Determine Vant Hoff factor Kb = 0.512 K $kgmol^{-1}$.
11. 18 g of glucose is dissolved in 1 kg of water. At what temperature the solution will boil.

    Kb = 0.52 k $kgmol^{-1}$, BP of pure water = 373.15 k.
12. (i) $\frac{P_A^\circ - P_A}{P_A^\circ} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$

    (ii) $\Delta Tb = iKbm$

    (iii) $\Delta Tf = ikfm$

    (iv) $\pi = i \times \frac{W_B}{M_B} \times \frac{RT}{V}$
13. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its FP by 0.48 K, Kf = 5.12 k kg mol^{-1}.
14. Determine the osmotic pressure a solution prepared by dissolving 2.5×10^{-2} g of K_2SO_4 in one L of water at 25°C assuming that K_2SO_4 is completely dissociated R = 0.0821 L atm K^{-1} mol^{-1} molar mass of K_2SO_4 = 174 g mol^{-1}.
15. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2k. (kf = 1.86 kg mol^{-1}.

16. 3.24 g of Sulphur is dissolved in 40.0 g of benzene. The Boiling point is raised by 0.81. Calculate molecular formula of sulphur. Given: atomic mass of sulphur = 32 u. Kb = 2.53 K kg mol^{-1}.

$$\Delta Tb = Kbm$$

$$\Delta Tb = \frac{2.53 \times 3.24 \times 1000}{0.81 \times 40} = 253$$

$$n = \frac{\text{Mol. mass}}{\text{Atomic mass}} = \frac{253}{32} = 7.99 \approx 8$$

$$\text{Mol. formula of Sulphur} = S_8$$

17. 3.26 g of Selenium is dissolved in 226 g of benzene. The freezing point in lowered by 0.112 K. Deduce the value of x in Se_x. Given: Kf for benzene = 4.90 K kgmol^{-1}, Atomic mass of Selenium is 78.8 g mol^{-1}. $\Delta\tau f = Kfm$

18. The solubility of $Ba(OH)_2.8H_2O$ in water at 298 K is 5.6 g per 100 g of water. Calculate the molality of hydroxide ion in a saturated solution of Barium hydroxide (Ba – 137, O = 16, H = 1) molar mass of $Ba(OH)_2.8H_2O$ = 315 g mol^{-1}.

$$m = \frac{W_B}{M_B} = \frac{100}{W_A}$$

$$= \frac{5.6}{315} \times \frac{1000}{100} = 0.178 \text{ mol/kg.}$$

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2\bar{O}H$$

$$\text{Molality of } \bar{O}H = 0.178 \times 2 = 0.356 \text{ mol}^{-1}.$$

19. Concentrated H_2SO_4 has a density of 1.84 g cm^{-3} and is 95% by mass. Calculated the volume of water is required to prepare 100 mL H_2SO_4 of 15% mass having density 1.10 gcm^{-3}.

$$M_1V_1 = M_2V_2 \qquad \boxed{M = \frac{\% \times d \times 10}{M_B}}$$

$$95 \times 1.84 \times V_1 = 15 \times 1.10 \times 10$$

20. Calculate the molality of 1 M KCl solution of density 1.0745 gcm^{-3} (Given K = 39, Cl = 35.5)

$$M = \frac{M}{d - \frac{\text{strength}}{1000}} \qquad \text{Strength} = \text{Molarity} \times \text{Mol. mass}$$

$$M = \frac{1}{1.0745 - \frac{1 \times 74.5}{1000}}$$

21. 3.9 g of benzoic acid dissolved in 49g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the natur of solute (associated or dissociated). ***2015***

22. Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law?Give an example. ***2015***

23. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation? ***2015***

UNIT3:Electro-Chemistry

1. Alkaline medium decrease the rate of corrosion why.
2. Saline medium increases the rate of corrosion why.
3. Write anodic and cathodic reaction of rusting of iron.
4. Write anodic andcathodic reaction in

   (i) dry cell (ii) mercury cell (iii) lead storage cell (iv) Ni-Cd cell, (v) Fuel cell
5. Define molar conductivity. Write its unit what is limiting molar conductivity.
6. State kohlrausch law.
7. State Faraday's laws of electrolysis.
8. Explain graphically, the variation of molar conductivity against concentration. Why the curve of weak electrolyte cannot be extrapolated.
9. The potential of mercury cell does not change during its life time.
10. How much charge is required for reduction of one mole of Cu^{2+} to Cu.
11. Resistance of a conductivity cell filled with 0.1 M, KCl solution is 100 ohm. If the resistance of the same cell when filled with 0.02 M KCl is 520 ohm. Calculate conductivity and molar conductivity of 0.02 M KCl solution. The conductivity of 0.1 KCl solution is $1.29 \times 10^{-2} \Omega^{-1} cm^{-1}$.

    Cell constant = Conductivity × resistance

    $1.29 \times 10^{-2} \times 100 = 1.29\ cm^{-1}$

    $$\text{Conductivity of 0.02 M} = \frac{\text{Cell constant}}{\text{R}} = \frac{1.29\ \text{m}^{-1}}{520} = 0.248 \times 10^{-2}\ \text{gcm}^{-1}$$

    Concentration = 0.02 M

    $$\Lambda_m^{\circ} = \frac{1000k}{M} = \frac{1000 \times 0.248 \times 10^{-2}}{0.02} = 124.5\ \text{cm}^{-1}$$

Nernst Equation

1. $$E = E° - \frac{0.0591}{n} \log \frac{\text{oxidised conc}}{\text{reduced conc.}}$$

   1 calculate the emf of the cell at 298 k

   $Fe(s)\ Fe^{2+}\ (0.001\ M)\ ||\ H^{+}\ (1\ m)\ |\ H_2(g)\ |\ pt(1\ Br)$

$E^\circ Fe^{2+}/Fe = –0.440\ E^\circ H+/r = \infty$

$$E = 0 – (–0.44) – \frac{0.0591}{2} \log \frac{(Fe^{2+})}{(H^+)^2}$$

2. $Zn(s) + Sn^{4+}$ (1.5 m) → Sn^{2+} (0.5m) + Zn^{2+} (2m)

   $E°Zn^{2+}/Zn = –0.76$ V $E°Sn^{4+}/Sn^{2+} = 0.13$V

$$E = E°_{Cell} – \frac{0.0591}{n} \log \frac{|Sn^{2+}||Zn^{2+}|}{|Sn^{4+}|}$$

3. For what concentration of $|Ag^+|$ the concentration of $|Cu^{2+}|$ will be 0.1 M at equilibrium. $E°_{Cu}{}^{2+}/_{Cu}$ = 0.34 V, $E°_{Ag}{}^{+}/_{Ag}$ = 0.80 V.

$$E = E°_{cell} – \frac{0.0591}{n} \log \frac{|Cu^{2+}|}{|Ag^+|^2}$$

$$0 = (0.80 – 0.34) – \frac{0.0591}{2} \log \frac{0.1}{|Ag^+|^2}$$

$$0.46 = 0.0295 \log \frac{1}{(Ag^+)^2}$$

$$\log \frac{1}{(Ag^+)^2} = \frac{0.46}{0.0295} = 15.53$$

$$\frac{1}{(Ag^+)^2} = \text{Antilog } 15.53$$

$$\frac{1}{(Ag^+)^2} = 4.43 \times 10^{15}$$

$$(Ag^+)^2 = \frac{1}{4.43 \times 10^{15}}$$

$$(Ag^+)^2 = \frac{1}{4.43} \times 10^{15}$$

$$(Ag^+)^2 = \frac{10}{4.43} \times 10^{16}$$

$(Ag^+)^2 = 2.25 \times 10^{-16}$ $(Ag^+) = 1.5 \times 10^{-8}$ M.

4. (a) Following reactions occur at cathode during the eletrolysis of aqueous silver chloride solution.

$$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s) \qquad E° = +0.80\ V$$

$$H^{+}(aq) + e^{-} \longrightarrow \frac{1}{2}H_2(g) \qquad E° = +0.00\ V$$

On the basis of their standard reduction electrode potential(E°) values, which reaction isfeasible at the cathode and why?

(b) Define limiting molar conductivity. Whyconductivity of an electrolyte solution decreases with the decrease in concentration? ***2015***

5. Calculate emf of the following cell at 25°C.

$Fe\ |\ Fe^{2+}\ (0.001\ M)\ ||\ H^{+}(0.01\ M)\ |\ H_2(g)\ (1\ bar)\ |\ Pt(s)$

$E^{o}\ (Fe^{2+}\ |\ Fe) = -0.44\ V$ $E°\ (H^{+}\ |\ H_2) = 0.00\ V$.

UNIT 4:Chemical Kinetics

1. Give two difference between order and molecularly.
2. Define collision frequency.
3. Give one example of zero order reaction.
4. What one pseudo first order reaction. Give one example.
5. Numerical: K = $\frac{2.303}{t}\log\frac{(R_o)}{(R)}$ including $t_{1/2}$
6. For the reaction:

   $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

   Following data were collected. All measurements one taken at 263 k.

Expt. Number	**Initial (No) (M)**	**Initial (Cl2) (M)**	**Rate of disappearance of Cl_2 (m/min)**
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

rate $\propto [No]^x\,[Cl_2]^y$

Reading $\frac{2}{1} = \frac{(0.15)^x(0.30)^y}{(0.15)^x(0.15)^y} = \frac{1.20}{0.60}$

$2^y = 2$

$y = 1$

Reading $\frac{3}{1} = \frac{(0.30)^x(0.15)^y}{(0.15)^x(0.15)^y} = \frac{2.40}{0.60}$

$2^x = 4$

$x = 2$

order n = x + y (1 + 2 = 3)

rate = $k[No]^2\,[Cl_2]$

(ii) $K = \dfrac{\text{rate}}{[NO]^2[Cl_2]} = \dfrac{0.60}{0.15\times0.15\times0.15} = 177.77$

(iii) rate = $K[NO]^2\,[Cl_2]$

$= 177.77 \times 0.25 \times 0.25 \times 0.25$

$= 177.77 \times 15625 \times 10^{-6} = 2.77\ \text{mL}^{-1}\ \text{sec}^{-1}$.

7. Following data were obtained during first order thermal decomposition of SO_2Cl_2 at constant volume.

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

Experiment	Time/sec^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

$$K = \frac{2.303}{t}\log\frac{p^\circ}{p^\circ - p}$$

$$K = \frac{2.303}{100}\log\frac{0.4}{0.4\times 2 - 0.7}$$

$$K = \frac{2.303}{100}\log 4$$

$$K = \frac{2.303}{100}\times 0.602 = 0.0131\ \text{min}^{-1} = 1.39\times10^{-2}\ \text{min}^{-1}$$

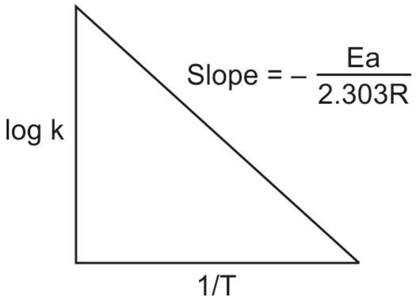
8. Rate constant K of a reaction varies with temperature T according to equation.

$$\log K = \log A - \frac{Ea}{2.303}\cdot\frac{1}{T}$$

when a graph is plotted for log k vs $\frac{1}{T}$, a straight line with a slope of -4250 k is obtained. Calculate Ea for the reaction given R = 8.314 $JK^{-1}\ mol^{-1}$.

$$\text{Slope} = -\frac{Ea}{2.303R}$$

$$-4250 = -\frac{Ea}{2.303\times 8.314}$$



$\text{Ea} = 4250 \times 2.303 \times 8.314 = 81375 \text{ J mol}^{-1}$.

9. $\text{Ea} = 2.\,2.303R\left(\dfrac{T_1T_2}{T_2 - T_1}\right)\log\dfrac{k_2}{k_1}$

10. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained.

t/s	0	30	60
$[CH_3COOCH_3]$/mol L^{-1}	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(Given log 2 = 0.3010, log 4 = 0.6021)

OR

(a) For a reaction $A + B \longrightarrow P$, the rate is given by
Rate = k [A] $[B]^2$
(i) How is the rate of reaction affected if the concentration of B is doubled?
(ii) What is the overall order of reaction if A is present in large excess?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.
(log 2 = 0.3010). **2015**

UNIT 5: Surface Chemistry

1. In reference to freundlich adsorption isotherm write the expression for adsorption of gases on solids in the form of equation.

Ans. $\frac{x}{m} = kp^{1/n}$ or $\log\frac{x}{m} = \log k + \frac{1}{n}\log p$

2. Write one important characteristic of lyophilic sol.

Ans. Reversible, stable, strong aflinety for solvent.

3. Based on type of particles of dispersed phase, give one example each of associated colloid & multi-molecular colloid.

Ans. Associated colloid: soap/micelle

multi-molecular colloid – S_8 and gold sol.

4. Write dispersed phase and dispersion medium of the following colloid. (i) smoke (ii) milk.
5. What are lyophilic and lyophobic colloids. Which can be easily coagulated on addition of small amount of electrolyte.
6. Why sky appears blue.
7. Why delta's are formed.
8. Why fog and mist are formed.
9. What is meant by coagulation of a colloid. Describe any three methods by which coagulation of lyophobic sol can be carried out.
10. What is the difference between oil/water and water/oil emulsions. Give one example of each.
11. What happens when:

    (i) An electrolyte is added to a hydrated ferric oxide sol in water

    (ii) A beam of light is passed through a colloidal solution.

    (iii) An electric current is passed through a colloidal solution.
12. Mention differences between physisorption and chemisorption in terms of specificity, enthalpy of adsorption, Reversilibility, Temperature.
13. What aremultimolecular, macromolecular and associated colloids. Give examples of each type.
14. Explain (i) Brownian movement (ii) Tyndall effect (iii) Electropheresis.

15. Give one chemical method to prepare each of sulphur and gold sol in water.

16. How will you prepare sol by (i) Bredig’s are method (ii) Peptization.

17. Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal Sol? Give reason. **2015**

18. Give reasons for the following observations:

    (i) Leather gets hardened after tanning.

    (ii) Lyophilic sol is more stable than lyophobic sol.

    (iii) It is necessary to remove CO when ammonia is prepared by Haber's process. **2015**

UNIT 6: Extraction of Metals

1. What is the composition of copper matte.
2. Describe the principle involved in each of the following processes.

   (i) mond process of refining of Nickel (ii) column chromatography for purification of rare earth element
3. What is the role of graphite in the electrometallurgy of aluminium.
4. Name the method used for refining of nickel metal.
5. Which of the following ores can be concentrated by froth floatation method Fe_2O_3.ZnS Al_2O_3.
6. What is the role of silica in the metallurgy of copper.
7. Which solution is used for leading of silver metal in presence of air in the metallurgy of silver – NaCN.
8. Out of C and CO which is a better reducing agent at the lower temperature range in the blast furnace to extract iron from oxide ore CO
9. Write the principles of the following method.

   (i) froth floatation method (ii) Electrolytic refining.
10. What is the role of cryolite in the metallurgy of aluminium.
11. Which reducing agent is employed to get copper from leached low grade copper are H_2 or Fe
12. Explain principle and process of zone refining.
13. Write the reactions involved in the metallurgy of copper.
14. Write the reactions occurring in blast furnace in the extraction of iron.
15. What are depressants give one example.
16. (i) Indicate the principle behind the method used for the refining of zinc.

    (ii) What is the role of silica in the extraction of copper?

    (iii)Which form of the iron is the purest form of commercial iron? **2015**

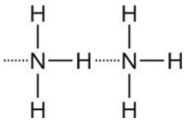
UNIT 7: p-Block

1. Ammonia is a stronger base than phosphine.

Ans. The lone pair of electron on N-atom in NH_3 is directed, due to dipole H⟶N and can be donated easily. In PH_3 lone pair of e- on p remain diffused over larger surface area and cannot be denoted effectively vacant d in p increases surfaces area.

2. Boiling point of PH_3 is lower than NH_3.

Ans. BP of PH_3 is lower than NH_3 due to intermolecular H-bonding in NH_3.



3. NH_3isaliquid while PH_3 is gas – some as above

4. Bond dissociation enthalpy of F_2 is lower than Cl_2.

Ans. Because of smaller size of F-atom, shorter bond length and the electron-electron repulsion among the lone pair is greater than Cl_2.

5. Helium is used in diving apparatus.

Ans. Helium is less soluble in blood.

6. Fluorine does not exhibit positive oxidation state.

Ans. Due to highest electronegatively of fluorine.

7. Oxygen show catenation less than sulphur.

Ans. O—O bond is weaker than S—S bond.

8. Sulphur in vapour state exhibit paramagnetic behavior.

Ans. There are two unpaired electron in antibonding molecular orbital π *33Px1 π&3Py1 of sulphur. So paramagneticsulphur existasS_2 at 1000K.

9. $SnCl_4$ is more covalent than $SnCl_2$.

Ans. Higher oxidation state, more covalency.

10. H_3PO_2 is a stronger reducing agent than H_3PO_3.

Ans. Due to presence of 2H-atoms directly attached to P, cannot be donated as proton and involved in reduction.

11. Bi(V) is a stronger oxidizing agent than Sb(V).

Ans. Bi tends to attain the oxidation state of +3 and more stable than Sb+3 due to inert pair effect.

12. N—N based is weaker than P—P single bond.

Ans. Because of interelectronic repulsion owing to small bond length of N—N and smaller size of Nitrogen atom.

13. Noblegases have very low boiling point.

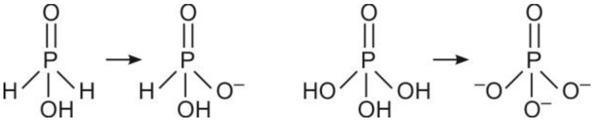
Ans. Because of weak dispersion forces (vander waal forces).

14. Molecular nitrogen N_2 is particularly unreactive.

Ans. Due to high bond dissociation enthalpy of N≡N (941.6 $kJmol^{-1}$)

15. H_3PO_4 is triprotic while H_3PO_3 is diprotic.

Ans. In H_3PO_3 are H-atoms is directly attached to P with a covalent bond and cannot be denoted as proton.



16. Phosphinic acid (hypophosphous acid) is monoprotic.

Ans. Due to presence of P(OH) group, two H-atoms are directly attached to P with covalent bond and cannot be denoted as proton.

17. Maximum covalent bond formed by nitrogen is 4.

Ans. There is no d-orbital in nitrogen so it cannot expand it valence shell.

18. NCl_5 is not formed.

Ans. There is no d-orbital in N.

19. Inter halogens are move reactive than halogens.

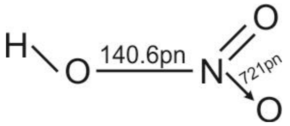
Ans. Due to low bond dissociation enthalpy of inter halogen than halogens.

20. SF_4 can be hydrolysed while SF_6 does not.

Ans. SF_6 is inert due to sterically protected S-atom by 6F-atoms.

21. In HNO_3 NOH bond length is longer (140.6 pm) than NO bond length (121 pm).

Ans. In NOH, N—O bond is sp^3 hybridised and single bond character white in NO, sp^2 hybridisation and partial double bond character.



22. Electrong gain enthalpy of fluorine is less negative than Cl.

Ans. Due to high inter electronic repulsion among three lone pairs of electron in small size F atom than Cl.

23. Electron gain enthalpy of oxygen is less negative than sulphur.

Ans. Due to high interelectronic repulsion in small size oxygen atom than sulphur.

24. All PCl_5 bond length are not equal. Give one evidence.

Ans. Phosphorus consists of two different sets of hybridization sp^2 and P_2dz^2 so axial bond suffer repulsion from equatorial bond and are longer than equatorial bond. $PCl_5 \rightarrow PCl_3 + Cl_2$.

25. How PCl_5 exist in solid state, write its structure.

Ans. PCl_5 exist as ionic solid

$[PCl_4^+]$ $[PCl_6^-]$

Tetrahedral Octahedral

26. Why only Xe and F form compounds.

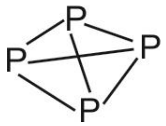
Ans. (i) Highest electro-negativity of F

(ii) Lowest ionization enthalpy of among noble gases.

(iii) Vacant d in xenon.

27. White phosphorous is more reactive than red phosphorus.

Ans. Due to high strained bonds in white phosphorus in P_4 molecule.



28. Explain the following giving an appropriate reason.

(i) O_2 and F_2 both stabilize higher oxidation stable of metals but O_2 exceeds F_2 in doing so.

(ii) Structure of xenon fluorides can not be explained by valence bond approach.

Ans. (i) Charge on O^{2-} and F^-, more repulsion in F^-, oxygen can form multiple bond.

(ii) Completely filled ns^2 and np^6.

29. HNO_3 does not oxidise Aluminium and chromium.

Ans. Due to formation of oxide film on their surface.

30. OF_2 is called oxygen difluoride not fluorine oxide.

Ans. Fluorine is more electronegative than oxygen and name of electropositive element is written first.

31. HF is weaker acid than HI.

Ans. Due to high bond dissociation entralpy of HF and also intermolecular H-bonding.

32. H_2O is liquid while has is gas

Ans. intermolecular H-bond in H_2O.

33. What inspired N. Barlett for carrying out reaction between Xe and F.

34. What happens when

(i) PCl_5 is heated

(ii) H_3PO_3 is heated

35. (a) Account for the following: **2015**

(i) Acidic character increases from HF to HI.

(ii) There is large difference between the melting and boiling points of oxygen and sulphur.

(iii) Nitrogen does not form pentahalide.

(b) Draw the structures of the following.

(i) ClF_3

(ii) XeF_4

OR

(i) Which allotrope of phosphorous is more reactive and why?

(ii) How the supersonic jet aero planes are responsible for the depletion of ozone layers?

(iii) F_2 has lower bond dissociation enthalpy than Cl_2. Why?

(iv) Which noble gas is used in filling balloons for meteorological observations?

(v) Complete the equation:

$XeF_2 + PF_5 \longrightarrow$ **2015**

36. What is the basicity of H_3PO_4? **2015**

Complete the following equation

1. $NH_3 + Cl_2$ (excess) ⟶
2. NH_3 (excess) + Cl_2 ⟶
3. NaOH (old and dil) + Cl_2 ⟶
4. NaOH (hot and conc) + Cl_2 ⟶
5. $P_4 + NaOH + H_2O \longrightarrow$
6. $Ca_3P_2 + H_2O \longrightarrow$
7. $KF + XeF_6 \longrightarrow$
8. $XeF_2 + PF_5 \longrightarrow$
9. $XeF_4 + O_2F_2 \longrightarrow$
10. $Cu + HNO_3$ (conc.) ⟶
11. $Cu + HNO_3$ (conc.) ⟶
12. $Al_2O_3 + NaOH + H_2O \longrightarrow$
13. $Al_2O_3 + HCl + H_2O \longrightarrow$
14. $P_4 + HNO_3 \longrightarrow$
15. $C_{12}H_{22}O_{11} \longrightarrow$
16. $C_{10}H_{16} + Cl_2 \longrightarrow$
17. $Cu^{2+} + NH_3 \longrightarrow$
18. $FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow$
19. $AgNO_3 + H_3PO_4 + K_2O \longrightarrow$
20. $P_2O_5 + H_2O \longrightarrow$
21. $P_4 + SO_2Cl_2 \longrightarrow$
22. $XeF_6 + H_2O \longrightarrow$

1. Draw the structures of the following BrF_3.$XeOF_4$ N_2O_5 $(HPO_3)_n$ XeF_6, XeF_4 XeF_2 $H_2S_2O_8$, H_4P_2O, H_3PO_2.

2. predict the shape and asked angle (90° or more or less) in each of the following (i) SO_3^{2-} and angle O—S—O (ii) ClF_3 and angle F—Cl—F (iii) XeF_2 and angle F—Xe—F.

UNIT 8: d-Block Elements

Given Reasons

1. Define transition metals.
2. Why Zn, Cd & Hg are not considered as transition metals.
3. Transition metals have high enthalpy of atomization.
4. Atomic and ionic radii of transition metals decreases from left to right in a period.
5. Density of transition metals increase along the period.
6. Transition metals exhibit variable and multiple oxidation state.
7. Transition metals form coordination complexes.
8. Transition metals form alloys.
9. Transition metal form coloured compounds.
10. Transition metal form interstitial compounds.
11. Ce^{4+} is strong oxidizing agent.
12. Actinoid exhibit greater range of oxidation states.
13. Most of transition metals are paramagnetic.
14. Atomic radii of zirconium atomic No 40 is the same as Hafnium atomic No 72.
15. Define lanthanoid contraction.
16. Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
17. Enthalpy of atomization is lowest for Zn in 3d series.
18. Transition metals and their compounds act as catalyst.
19. The metallic radii of third (5d) series of transition metals are virtually the same as those of the corresponding group members of the second series (4d) series.
20. Name the element of 3d series which show maximum number of oxidation state stertes. Why does it show so.
21. Which transition metal of 3d has positive ($E°$ (M^{2+}/M) value and why?

22. Out of Cr^{3+} and Mn^{3+} which is a stronger oxidizing agent and why?

23. Name a member of lanthanoid series which known to exhibit +2 oxidation.

24. How will you prepare $K_2Cr_2O_7$ from its ore.

25. How will youpreparedKMnO$_4$ from MnO_2.

26. $K_2Cr_2O_7$ is orange but turn yellow in alkaline mediums.

27. Draw the structures of $Cr_2O_7^{2-}$ and CrO_4^{2-}.

28. Name the 3d series element which exhibit +1 oxidation state more frequently and why.

29. Which of the following cations are coloured in aqueous solution and why Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+}.

30. Complete the following ionic equations:

acidic medium

(i) $Cr_2O_7^{2-} + Fe^{2+} \longrightarrow$

(ii) $MnO_4^{-} + NO_2^{-} \longrightarrow$

(iii) $MnO_4^{-} + SO_3^{2-} \longrightarrow$

(iv) $MnO_4^{-} + C_2O_4^{2-} \longrightarrow$

(v) $Cr_2O_7^{2-} + S^{2-} \longrightarrow$

(vi) $Cr_2O_7^{2-} + I^{-} \longrightarrow$

(vii) $MnO_4^{-} + SO_2 + H_2O \longrightarrow$

Basic medium

(viii) $MnO_4^{-} + S_2O_3^{2-} \longrightarrow$

(ix) $MnO_4^{-} + I^{-} \longrightarrow$

(x) $MnO_4^{-} + Mn^{2+} \longrightarrow$

31. (a) How would you account for the following:

(i) Actinoid contraction is greater than lanthanoid contraction.

(ii) Transition metals form coloured compounds.

(b) Complete the following equation:

$2MnO^{-}_4 + 6H^+ + 5NO_2^{-} \longrightarrow$ **2015**

32. What are the transition elements? Write two characteristics of the transition elements. **2015**

UNIT 9: Co-ordination Compounds

1. Write IUPAC name of the following complexes.

Ans. $[Cr(NH_3)_4Cl_2]^+$ what type of isomerism does it exhibit.

2. Which of the following is more stable complex and why?

   $[CO(NH_3)_6]^{3+}$ and $[CO(en)_3]^{3+}$

Ans. $[Co(en)_3]^{3+}$ethylenediamine is bidentate ligand.

3. Write IUPAC names of

   (i) $[Cr(NH_3)_3Cl_2]$ (ii) $K_3[Fe(CN)_6]$ (iii) $[CoBr_2(en)_2]^+$

4. Write IUPAC names of $Li[AlH_4]$.

5. Write the Isomer in the following compound

   (i) $[Co(NH_3)_5NO_3)Br$ (ii) $[Cu(NH_3)_4][PtCl_4]$

   (iii) $[Cr(H_2O)_6]Cl_3$ (iv) $[Co(NH_3)_5NO_2]^{2+}$

   (v) $[Co(en)_3]$ (vi) $[Pt(NH_3)_2Cl_2]$

6. Explain bonding in the following complexes according to valence bond theory.

   $[Fe(CN)_6]^{4-}$, $[Ni(CN)_4]^{2-}$ $[NiCl_4]^{2-}$ $[CoF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

7. Explain crystal field splitting of d orbital. What happens when (i) $\Delta o < P$ (ii) $\Delta o > P$

8. Write an example used as homogeneous catalyst for hydrogenation of alkenes.

9. Which complex is used for treatment of

   (i) Lead possaning (ii) Ramoval of excess of copper

   (iii) Removal of excess of iron from living beings.

10. Name one complex used as chemotherapentic agent for treatment of tumours.

11. Give formula of the following coordination entities.

    (i) Co^{3+} ion is bond to one Cl^-, one NH_3 molecule and two bidentate ethyleneiamine (en) molecules

    (ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

12. (i) Write down the IUPAC name of the following complex:

    $[Cr(NH_3)_2 Cl_2 (en)] Cl$ (en = ethylenediamine)

    (ii) Write the formula for the following complex:

    Pentaamminenitrito-o-Cobalt (III). **2015**

13. (i) Draw the geometrical isomers of complex $[Pt(NH_3)_2Cl_2]$.

    (ii) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_0 < P$.

    (iii) Write the hybridization and magnetic behavior of the complex $[Ni(CO)_4]$.

    (At. No. of Ni = 28) **2015**

NAME REACTIONS

SANDMEYER'S REACTION

Benzenediazonium chloride is treated withCu_2X_2/HX to form halo/cyanobenzene.

$$C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl$$

$$C_6H_5N_2Cl \xrightarrow{Cu_2Br_2/HCl} C_6H_5Br$$

$$C_6H_5N_2Cl \xrightarrow{Cu_2(CN)_2/HCl} C_6H_5CN$$

FINKELSTEIN REACTION

Iodoalkanes are prepared by treating chloroalkane and bromoalkanes with sodium iodide in acetone.

$$C_2H_5Cl + NaI \xrightarrow{acetone} CH_3CH_2I + NaCl$$

SWARTS REACTION

Flouro-alkanes are prepared by treating chlorolkane and bromoalkanes with AgF, SbF_5 etc.

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

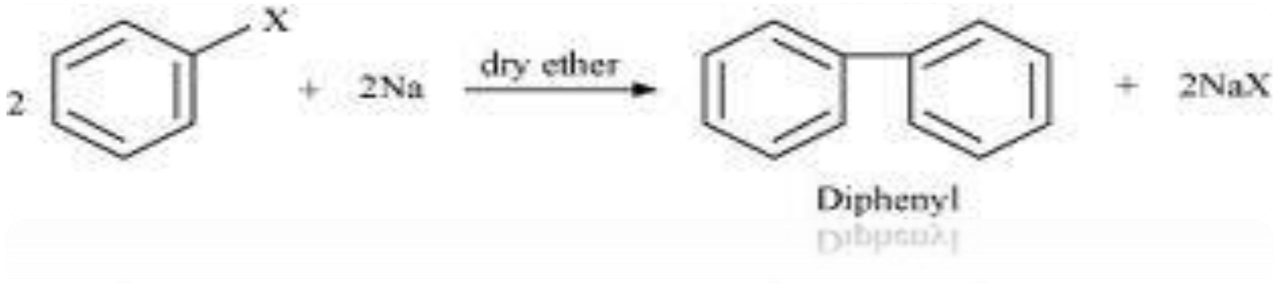
WURTZ REACTION

Haloalkanesare treated with sodium in dry ether to form alkane.

$2CH_3I + 2Na \xrightarrow{\text{dryether}} CH_3CH_3 + 2NaI$

FITTIG REACTION

Haloarenes are treated with sodium in dry ether to form diphenyl.



WURTZ-FITTIG REACTION

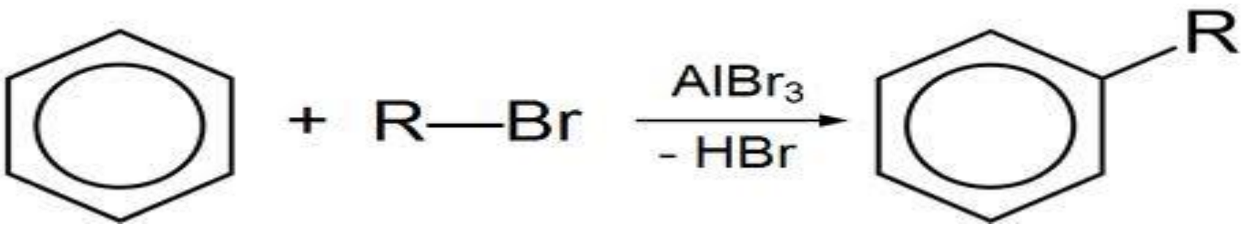
An equimolar mixture of haloalkane and haloarene are treated with sodium in dryether to form alkylated benzene.

$C_6H_5Cl + 2Na + Cl\ CH_3 \longrightarrow C_6H_5\text{- }CH_3 + 2NaCl$

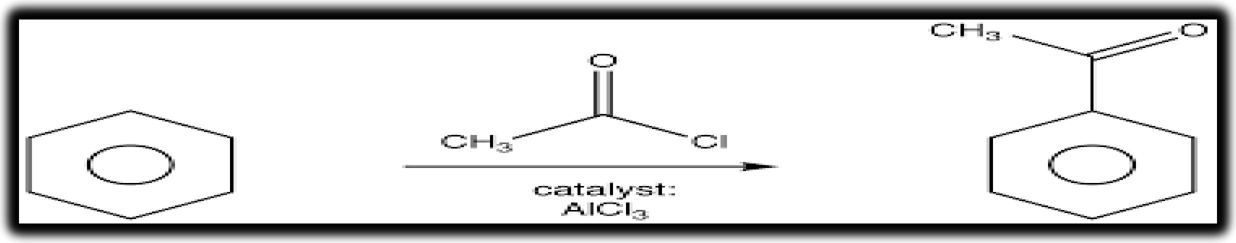
FRIEDEL CRAFT REACTION

Addition of alkyl, acetyl, acyl or benzoyl group to benzene in presence of anhydrous $AlCl_3$.

(i)**Alkylation**:-addition of alkyl group to benzene ring.



(ii)**Acetylation**: - addition of acetyl group to benzene ring.



(iii)**Acylation**: - addition of acyl group to benzene ring.

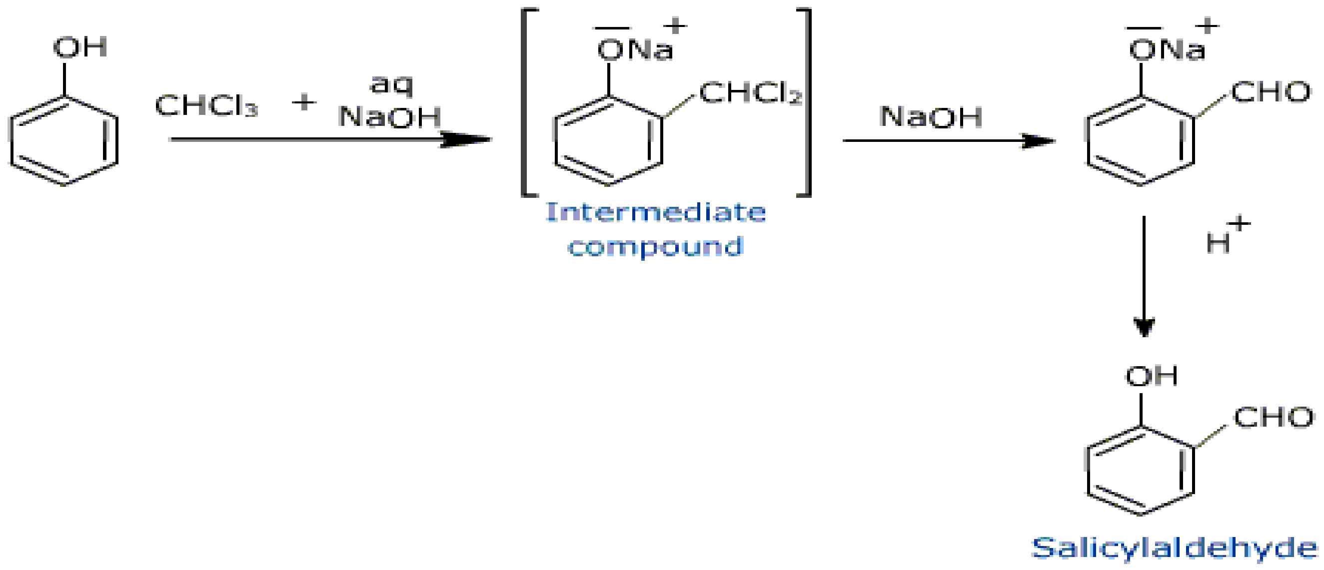
$$C_6H_6 + CH_3CH_2COCl \xrightarrow{\text{Anhyd AlCl}_3} C_6H_5\text{-}COCH_2\,CH_3 + HCl$$

(iv)**Benzoylation**: - addition of benzoyl group to benzene ring.

$$C_6H_6 + C_6H_5COCl \xrightarrow{\text{Anhyd AlCl}_3} C6H5\text{-}COC_6H_5 + HCl$$

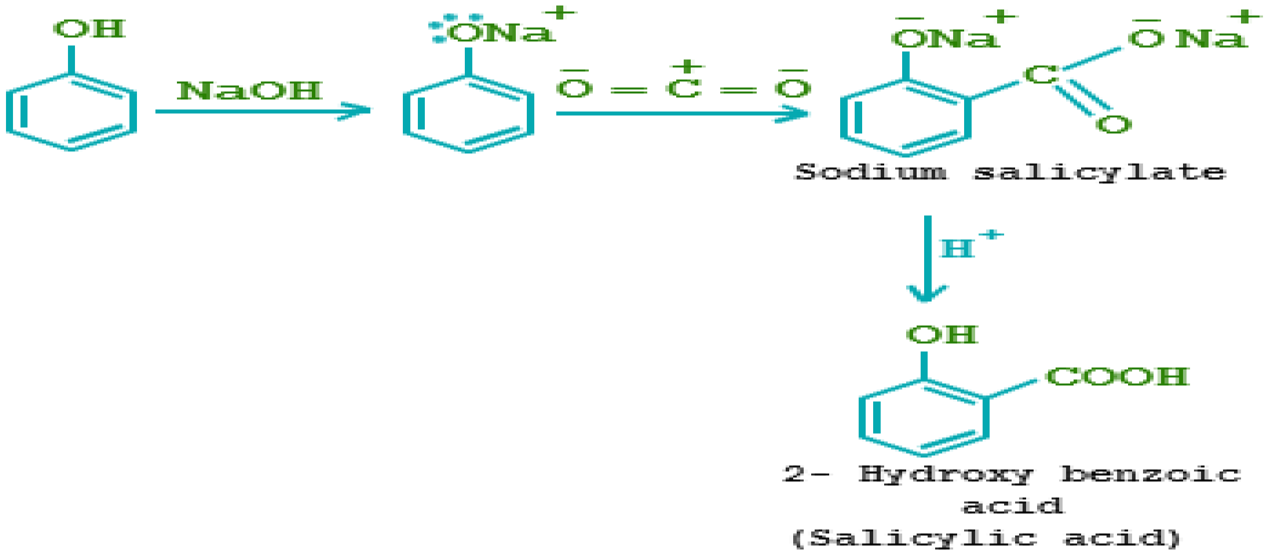
RIEMER TIEMAN REACTION

Phenol is treated with chloroform in alkaline medium to form ortho-salicyldehyde.



KOLBE’S REACTION

Phenol is treated with NaOH to from sodium phenoxide which is further treated with CO_2 followed by HCl to form ortho salicylic acid.



WILLIAMSON SYNTHESIS

Alkyl halides are treated with sodium alkoxide with to form symmetrical and unsymmetrical ethers.

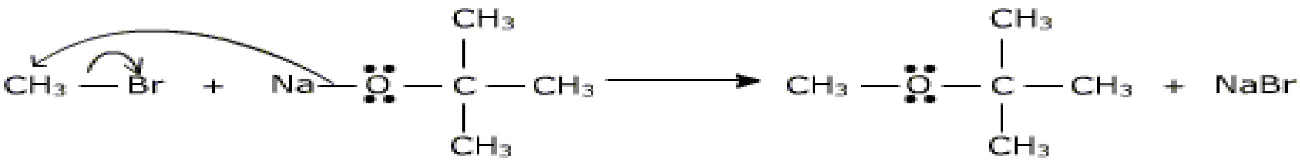
$$\boxed{R \quad X + Na} \, OR' \longrightarrow R{-}O{-}R' + NaX$$

Sodium alkoxide Ether

$$CH_3CH_2Br + Na^+OCH_3{-} \longrightarrow CH_3CH_2OCH_3 + NaBr$$

Sodium methoxide Methoxy ethane
(Methyl ethyl ether)

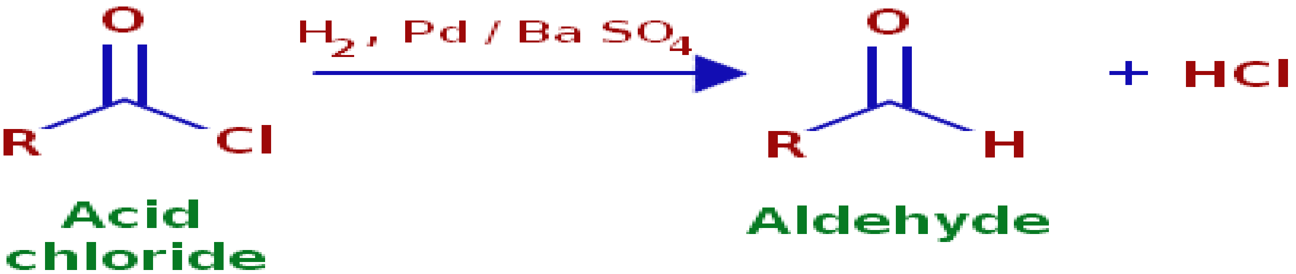
In secondary and tertiary ethers larger R is taken as alkoxide and primary halide.



Limitation:-If tertiary halides are treated with primary alkoxide, the product is alkene.

ROSENMUND REACTION

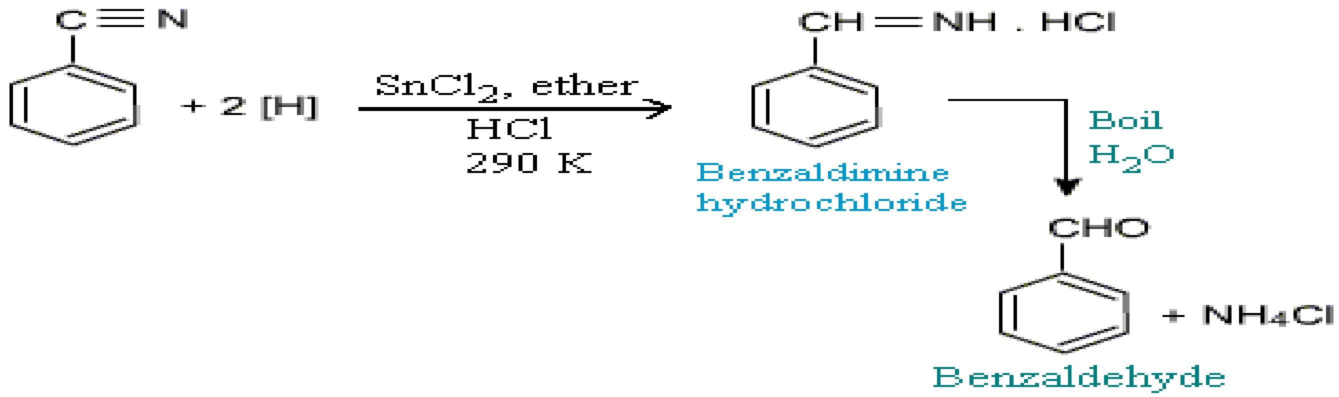
Acid chlorides are hydrogenated over catalyst palladium suspended over $BaSO_4$ inquinoline or xylene to form aldehyde.



$BaSO_4$ + S act as poison to catalyst Pd, deactivate it and prevent further reduction of aldehyde to alcohol.

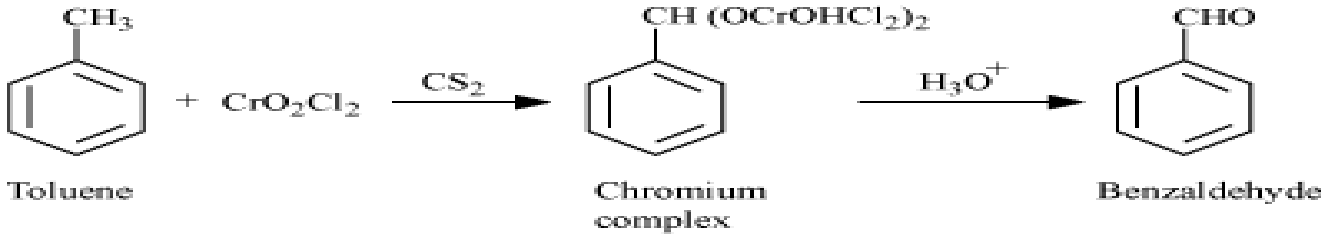
STEPHEN REACTION

Nitriles are reduced to corresponding imine with stannous chloride in presence of hydrochloric acid which on hydrolysis gives an aldehyde.



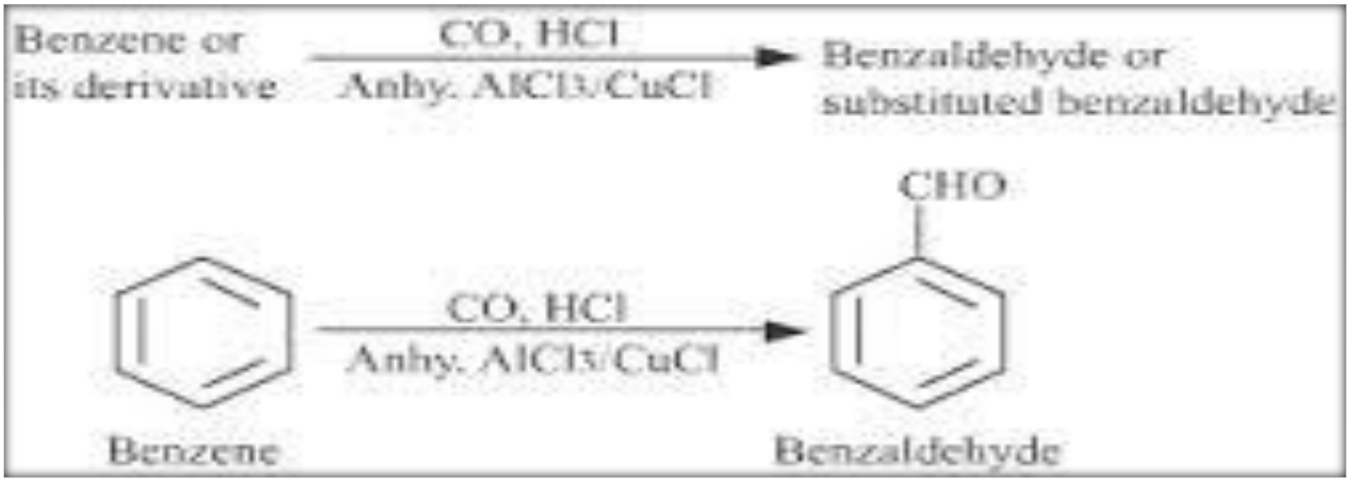
ETARD REACTION

Toluene is oxidized with chromyl chloride to form a complex which on hydrolysis formbenzaldehyde.



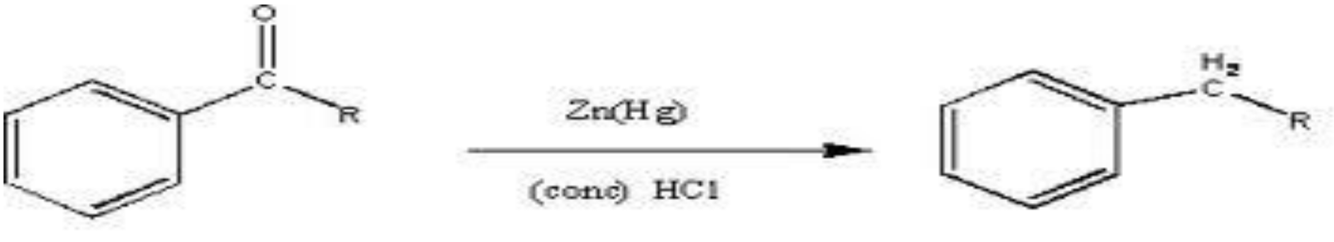
GATTERMAN - KOCH REACTION

Benzene is treated with carbon monoxide and hydrogenchloride in presence of anhydrous aluminium chloride or cuprous chloride to give benzaldehyde.



CLEMMENSEN REDUCTION

Carbonyl group of aldehyde and ketones is reduced to $-CH_2$ on treatment with zinc- amalgam and concentrated hydrochloric acid.

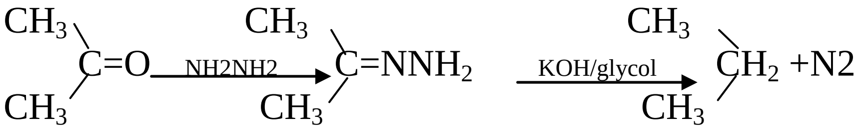


The Clemmensen reduction uses zinc amalgam and concentrated hydrochloric acid

WOLFF-KISHNER REDUCTION

Carbonyl group is treated with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol to form alkane.

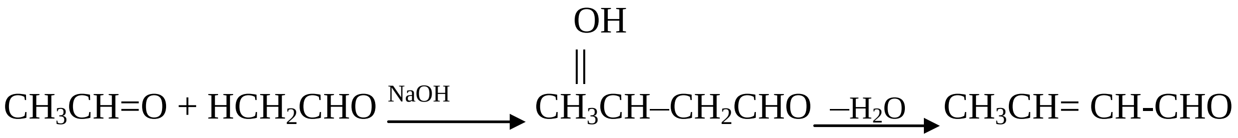
$CH_3CH=O \xrightarrow{NH2NH2} CH_3CH=NNH_2 \xrightarrow{KOH/glycol} CH_3CH_3 + N_2$



$$\underset{CH_3}{\overset{CH_3}{C}}=O \xrightarrow{NH2NH2} \underset{CH_3}{\overset{CH_3}{C}}=NNH_2 \xrightarrow{KOH/glycol} \underset{CH_3}{\overset{CH_3}{C}}H_2 + N2$$

ALDOL CONDENSATION

Aldehydes which consist of α-H-atom when condensed with dil. NaOH, form aldol (β-hydroxyaldehyde)

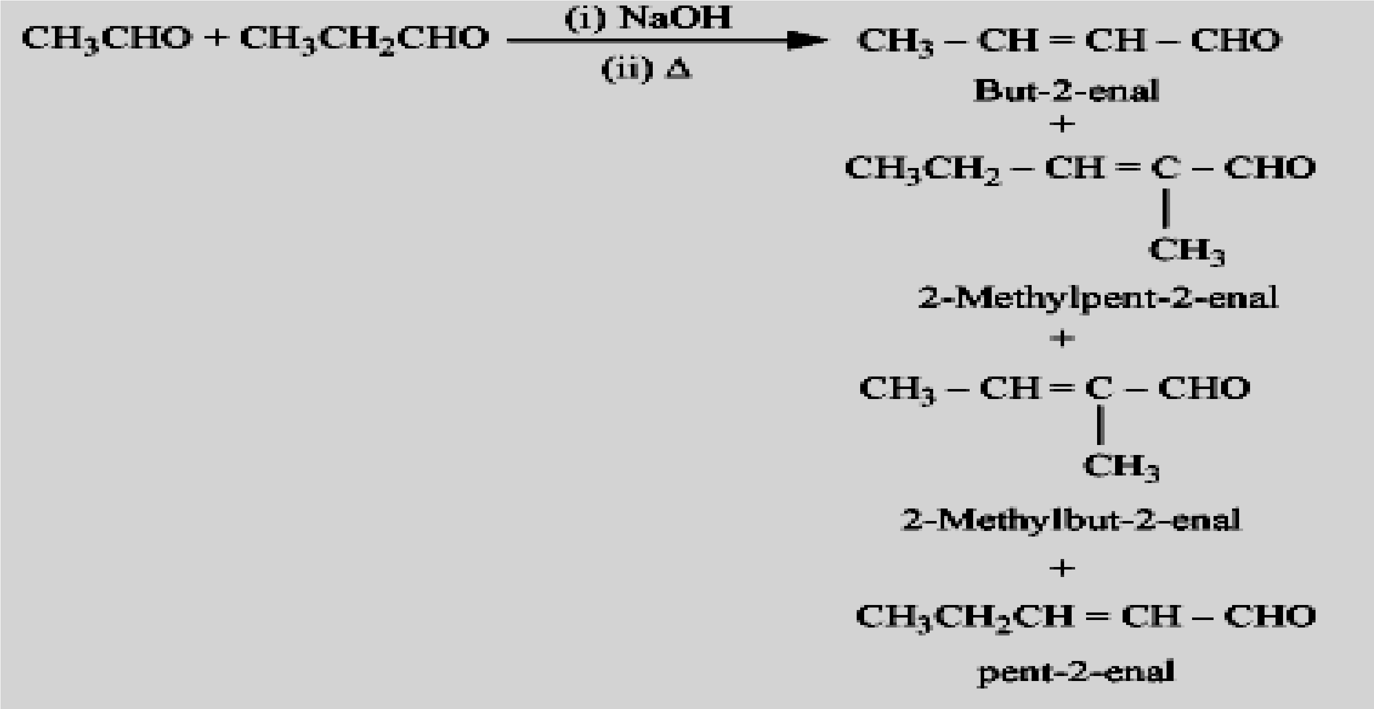


$$CH_3CH=O + HCH_2CHO \xrightarrow{NaOH} CH_3\overset{\overset{OH}{||}}{CH}–CH_2CHO \xrightarrow{–H_2O} CH_3CH= CH\text{-}CHO$$

β –hydroxy aldehyde looses H_2O molecules to form unsaturated aldehyde. Whatever is the size of aldehyde, attack comes from α and product is β

CROSS ALDOL CONDENSATION

When two different aldehydes having α-H atom , when condensed with dil.NaOH, mixed products are obtained.



$$CH_3CHO + CH_3CH_2CHO \xrightarrow[(ii)\ \Delta]{(i)\ NaOH} CH_3-CH=CH-CHO$$

But-2-enal

+

$$CH_3CH_2-CH=\underset{\displaystyle |\atop CH_3}{C}-CHO$$

2-Methylpent-2-enal

+

$$CH_3-CH=\underset{\displaystyle |\atop CH_3}{C}-CHO$$

2-Methylbut-2-enal

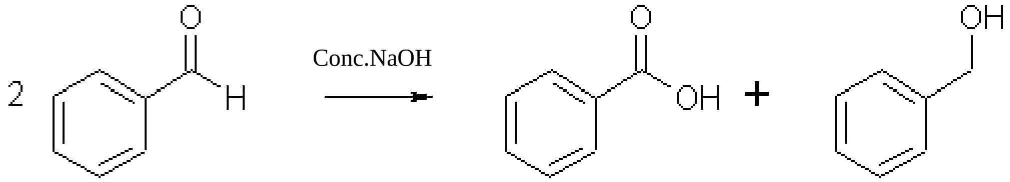
+

$$CH_3CH_2CH=CH-CHO$$

pent-2-enal

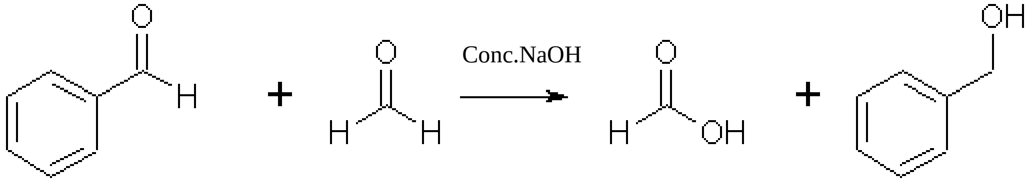
Cannnizaro reaction

Aldehydes which do not have α-H atom when condensed with conc.alkali,undergo disproportionation to form one molecule each of alcohol and sodium salt of an acid.



CrossCannnizaro reaction

When two different aldehydes which do not have α-hydrogenatom when condensed withconc.NaOH, aldehyde is reduced to alcohol and smaller is oxidized.



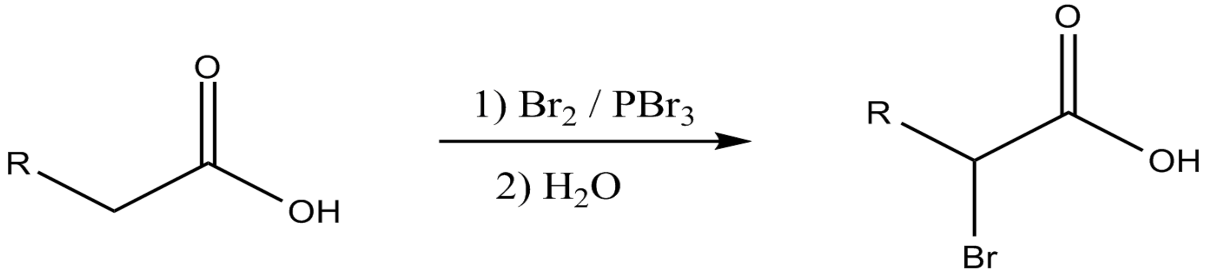
Claisen condensation

Benzaldehyde is condensed with acetaldehyde to form cinnamaldehyde.

$$C_6H_5CH=O + H_2CHCHO \xrightarrow{NaOH} C_6H_5CH=CHCHO + H_2O$$

HELL- VOLHARD ZELINSKY REACTION

Carboxylic acids having a α-hydrogenatom are halogenated at the α-position on treatment with chlorine or bromin e in presence of red phosphorous to give α-halo carboxylic acids.



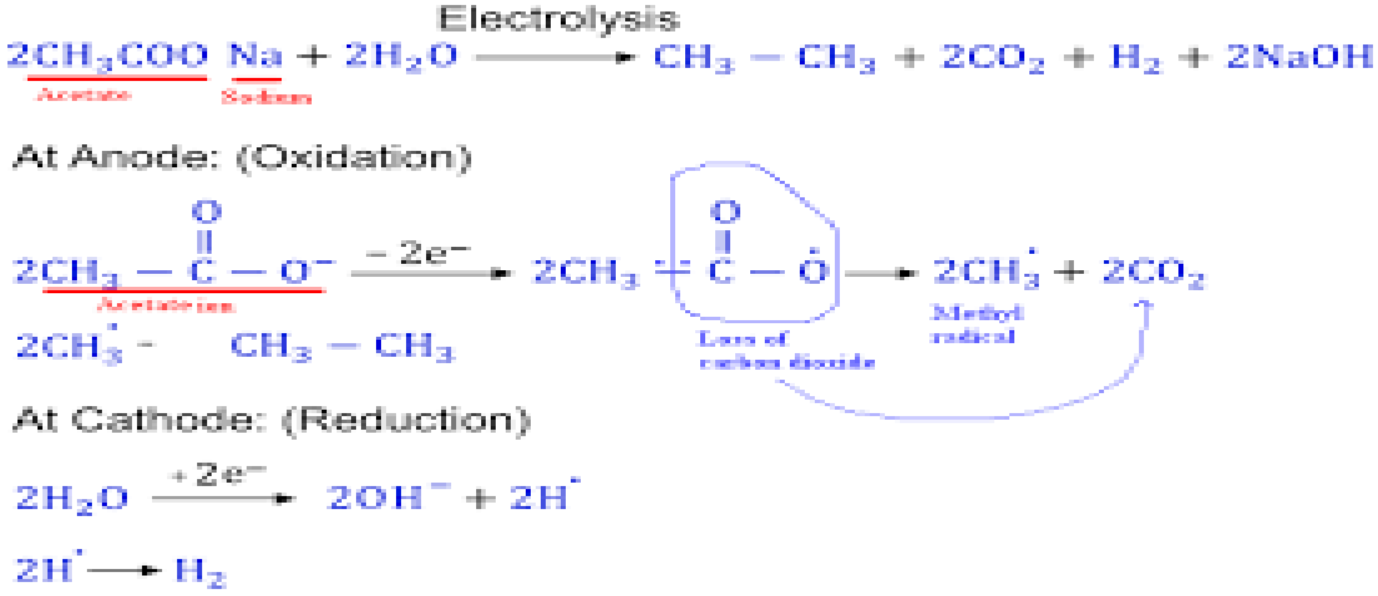
DECARBOXYLATION

Sodium salt of an acid is treated with sodalime to form hydrocarbon having one C-atom less than carboxylic acid.

$CH_3COONa \xrightarrow{NaOH/CaO/Heat} CH_4+Na_2CO_3$

KOLBE'S ELECTROLYSIS

Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aq solution and form hydrocarbon having twice the number of C- atoms present in the alkyl group of acid.



$\underbrace{2CH_3COO}_{Acetate}\ \underbrace{Na}_{Sodium} + 2H_2O \xrightarrow{Electrolysis} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$

At Anode: (Oxidation)

$\underbrace{2CH_3-\overset{O}{\overset{\|}{C}}-O^-}_{Acetate\ ion} \xrightarrow{-2e^-} 2CH_3 + \boxed{\overset{O}{\overset{\|}{C}}-\dot{O}} \longrightarrow \underset{Methyl\ radical}{2\dot{C}H_3} + 2CO_2$

Loss of carbon dioxide

$2\dot{C}H_3 - \quad CH_3-CH_3$

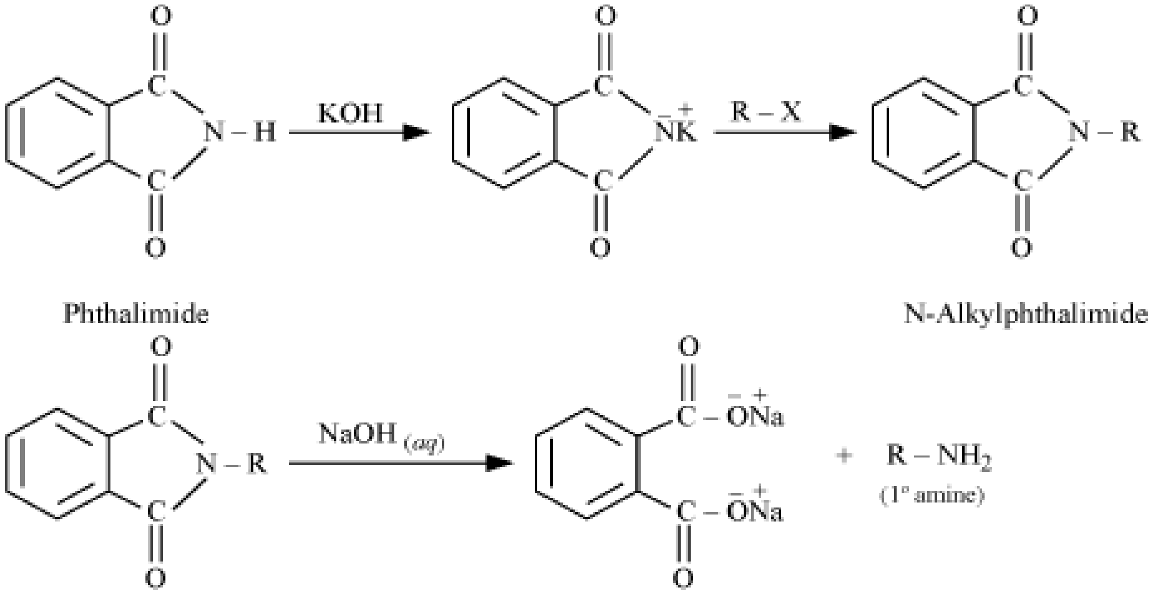
At Cathode: (Reduction)

$2H_2O \xrightarrow{+2e^-} 2OH^- + 2H^\cdot$

$2H^\cdot \longrightarrow H_2$

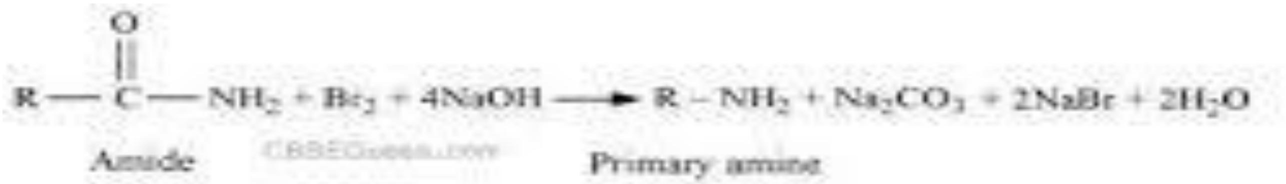
GABRIEL PTHALIMIDE SYNTHESIS

Pthalimideis treated with eyhanolic potassium hydroxide forms potassium Salt of pthalimide which on heating with alkyl halide followed by alkaline hydrolysis produce pure primary amine.



HOFFMANN BROMAMIDE REACTION

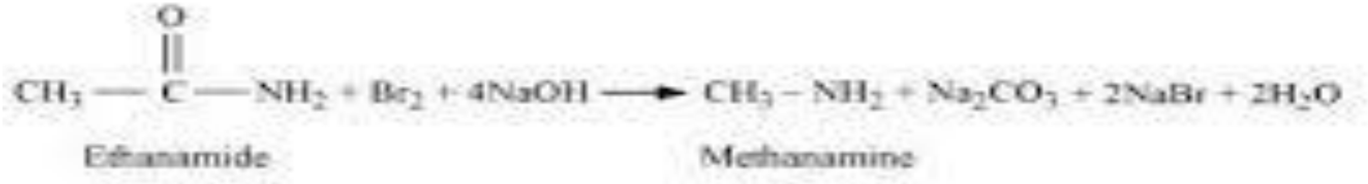
Amides are treated with bromine in an aqueous or ethanolic solution of sodium hydroxide to form a primary amine containing one C- atom less than amide.



$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Amide Primary amine

For example,



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow CH_3-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Ethanamide Methanamine

$$C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Benzamide Aniline

CaRBYL AMINE REACTION

Aliphatic and aromatic primary amine on heating with chloroform and ethanolic potassium hydroxide form isocyanide or carbylamines which are foulsmelling substance.

$CH_3NH_2 + CHCl_3 + 3\ KOH \xrightarrow{heat} CH_3NC + 3KCl + 3H_2O$

GATTERMANN REACTION

Chlorine and bromine can be introduced in the benzene ring by treating the diazonium salt solution in presence of copper powder.

$$C_6H_5N_2Cl \xrightarrow{Cu/HCl} C_6H_5Cl + N_2$$

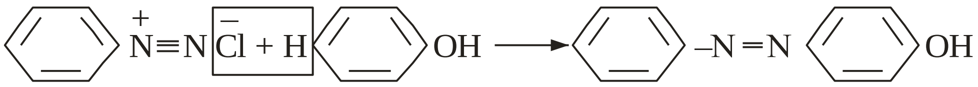
$$C_6H_5N_2Cl \xrightarrow{Cu/HBr} C_6H_5Br + N_2$$

COUPLING REACTION

Benzene diazonium chloride reacts with phenol to form p-hydroxyazobenzene

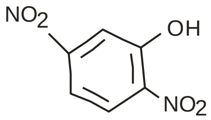
(Orange dye) and aniline to form p-aminoazobenzene (yellow dye).

The aromatic ring joined through –N=N- bond.

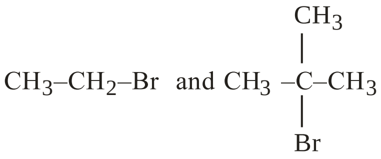


2015

1. Write the IUPAC name of the given compound:

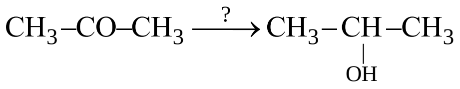


2. Which would undergo S_N2 reaction faster in the following pair and why?



$$CH_3–CH_2–Br \text{ and } CH_3–\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_3$$

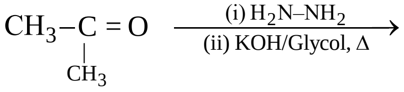
3. Name the reagents used in the following reactions:

(i) 

$$CH_3–CO–CH_3 \xrightarrow{?} CH_3–\underset{\underset{OH}{|}}{CH}–CH_3$$

(ii) $C_6H_5–CH_2–CH_3 \xrightarrow{?} C_6H_5–COO^{-}K^{+}$

4. Predict the products of the following reactions:

(i) 

$$CH_3–\underset{\underset{CH_3}{|}}{C}=O \xrightarrow[\text{(ii) KOH/Glycol, }\Delta]{\text{(i) }H_2N–NH_2}$$

(ii) $C_6H_5{-}CO{-}CH_3 \xrightarrow{NaOH/I_2} + ? + ?$

(iii) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$

5. How do you convert the following.

(i) Phenol to anisole

(ii) Propan-2-ol to 2-methylpropan-2-ol

(iii) Aniline to phenol

6. (a) Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2{-}O{-}CH_2CH_3$$

(c) Write the equation involved in the acetylation of salicylic acid.

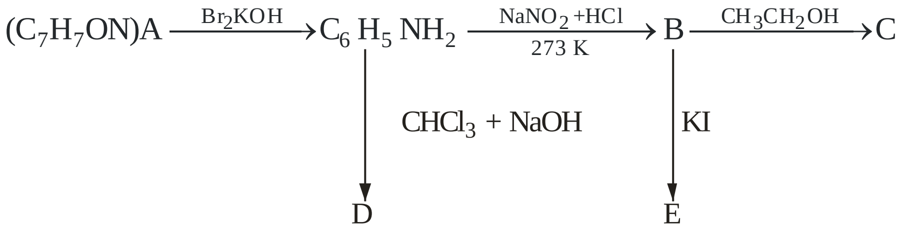
7. Give reasons.

(a) n-Bytyl bromide has higher boiling po8nt than t-butyl bromide.

(b) Racemic mixture is optically inactive.

(c) The presence of nitro group ($-NO_2$) at o/p positions increases the reactivity of haloarenes towards uncleophilic substitution reactions.

8. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions.



$$\begin{tikzcd}
(C_7H_7ON)A \arrow[r, "Br_2KOH"] & C_6H_5NH_2 \arrow[r, "NaNO_2+HCl", "273\ K"'] \arrow[d, "CHCl_3 + NaOH"] & B \arrow[r, "CH_3CH_2OH"] \arrow[d, "KI"] & C \\
 & D & E &
\end{tikzcd}$$

OR

(a) Write the structures of main products when aniline reacts with the following reagents:

(i) Br_2 water
(ii) HCl
(iii) $(CH_3CO)_2O$/Pyridine

(b) Arrange the following in the increasing order of their boiling point.

$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

(c) Give a simple chemical test to distinguish between the following pair of compounds:

$(CH_3)_2$ NH and $(CH_3)_3$ N

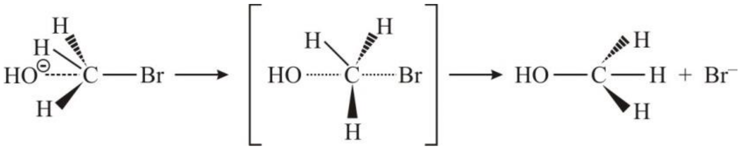
Reaction Mechanisms

1.Substitution Nucleophilic Bimolecular (SN^2)

Proposed be Edward Davis Hunghes and Sir Christopher Ingold (1937).

The reaction between a primary halide and a nuclophile follows second order Kinetics i.e., rate depends on the concentration of alkyl halide as well as nucleophile.

e.g., rate α [alkyl halide] [nucleophile]



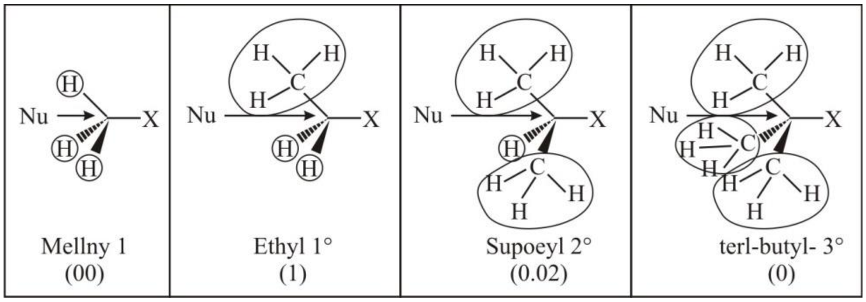
Solid wedge ▲ represents the bond coming out of the paper dashed ⋯ line represent bond going down the paper and a straight line represent bond in the plane of the paper.

The incoming nucleophile interact with the alkyl halide causing the C–X bond to break while forming a new C—OH bond. These two processes takes place in a single step simultaneously and no intermediate is formed. Inversion of configuration take place during the process. Carbon atom in the transition state is simultaneously bonded to five atom, therefore unstable and cannot be isolated.

Tertiary halides do not undergo SN^2 mechanism due to steric hinderance.

Since the nucleophile attacks from opposite side of halide atom, the three alkyl groups do not permit the nucleophile to attack on carbon a tom, the order of reactivity followed is

Primary halide > Secondary halide > Tertiary halide



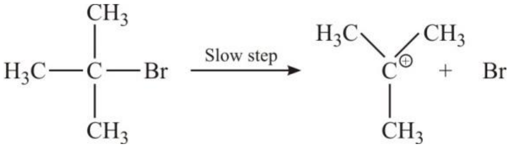
2. Substitution NucleophilicUnimolecular (SN^1)

Tertiary halide proceeds via SN^1 mechanism, Rate of reaction depends only on the concentration of alkyl halide

rate $\propto$ [alkyl halide]

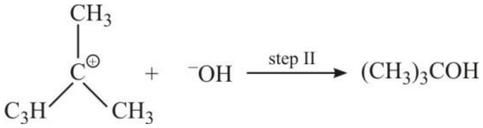
The reaction takes place in two steps.

Step I. The polarized C—X bond undergo slow cleavage to produce a carbocation and a halide ion.



Step I is slow and reversible.

Step II. The carbocation thus formed is attacked by nucleophile to complete the substitution reaction.



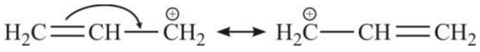
Effect of Solvent:SN^1 reaction are favoured in protic solvent (a) as step I involves the C—Br breaking for which the energy is obtained through salvation of halide ion with proton of protic solvent.

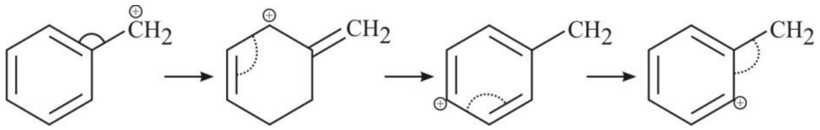
(b) Polar solvent promote ionization of halide ion.

Since the reaction proceeds through formation of carbocation, so greater the stability of carbocation, faster will be the rate of reaction therefore

$$Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H > Ph\overset{+}{C}H_2 > \text{allyl} > (CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

For this reason allylic and benzylic halides show high reactivity toward SN^1 mechanism. The carbocation thus formed get stabilised through resonance.





For alkyl group, the reactivity of halides R — X follow the same order in both mechanisms.

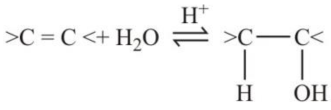
R — I > R — Br > R — Cl> R — F

Vinyl halides neither undergo SN^1 nor SN^2 mechanism SN^2 mechanism is hindered by the fact that carbon atom attains a negative charge and SN^1 mechanism is hindered by resonance and no ionization possible.

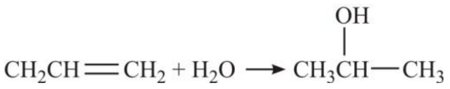
SN^2	**SN^1**
1. SN^2 reaction follow 2nd order kinetics.	SN^1 reaction follow first order kinetics.
2. Inversion of configuration takes place.	Retention of configuration and also racemisation takes place.
3. No effect of solvent.	More polar solvent more is the rate or reaction.

3. AcidCatalysed Hydration Alkene

Alkene reacts with H_2O in presence of mineral acid as catalyst to form alkenes. In unsymmetrical alkene the reaction proceed according to Markovnikov rule.

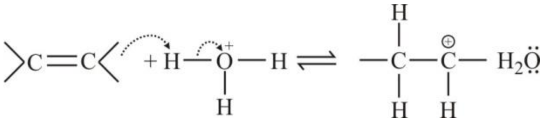


$$>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >\underset{H}{C}-\underset{OH}{C}<$$

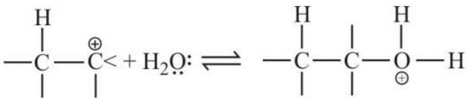


$$CH_2CH{=}CH_2 + H_2O \longrightarrow CH_3\overset{OH}{C}H-CH_3$$

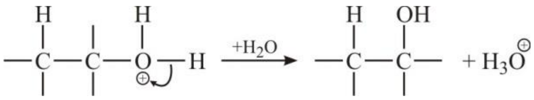
Step 1. Protonation of alkene to form carbocation by electrophilic attack of hydronium ion (H_3O^+).



Step 2. Nucleophilic attack of water on carbocation.

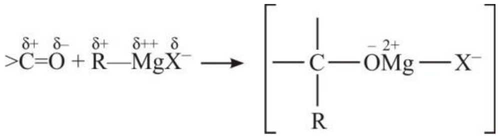


Step 3. Deprotonation to form alcohol.



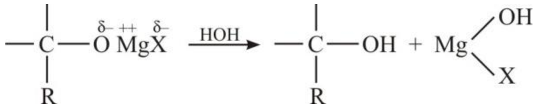
4. Addition of Grignard Reagent on Carbonyl Compounds

Step I. Nucleophilic addition of Grignard reagent to carbonyl group to form an adduct.



Bond in Grignard Reagent is highly polar carbon being non-metal and magnesium metal, So Mg reactes to oxygen to form adduct.

Step II. Hydrolysis of adduct yield alcohol.

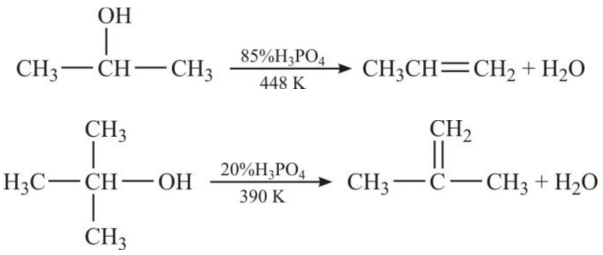


5. Acid Catalysed Dehydration of Alcohol

Alcohols undergo dehydration by heating with concentrated H_2SO_4.

$$CH_3CH_2OH \xrightarrow[445\,K]{H_2SO_4} H_2C = CH_2 + H_2O$$

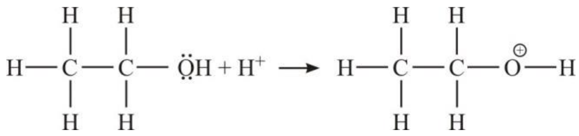
Secondary and tertiary alcohols are dehydrated under milder conditions.



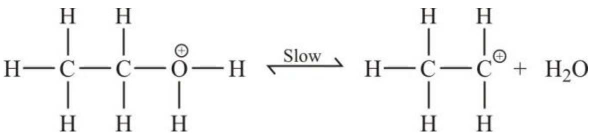
The reaction proceed in three steps.

Setp 1. Formation of protonated alcohol.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$



Step 2. Formation of carbocation: It is slowest step and rate determining step.



Step 3. Elimination of Proton.

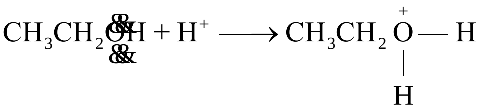
6. Acid catalysed dehydration of alcohol to form ether.

$$CH_3CH_2OH \xrightarrow[413K]{H_2SO_4} C_2H_5OC_2H_5$$

Formation of ether is a nucleophilic bimolecular reaction SN^2 involving attack of alcohol molecule on a protonated alcohol.

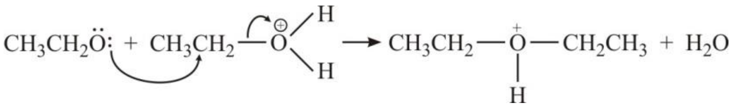
$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

(i) Protonation of alcohol

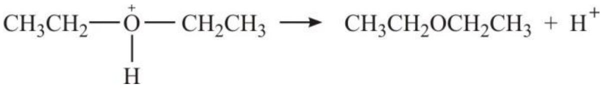


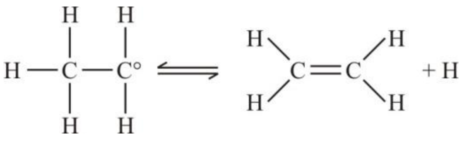
$$CH_3CH_2\ddot{O}H + H^+ \longrightarrow CH_3CH_2\underset{\underset{H}{|}}{\overset{+}{O}}-H$$

(ii) Attack of alcohol molecule.



(iii) Deprotonation

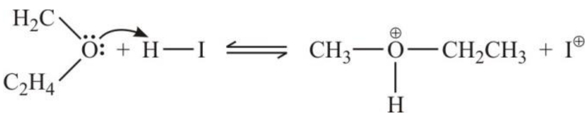




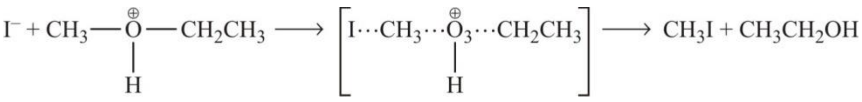
The acid used in step 1 is released in step 3. To drive the equilibrium to the right ethene is removed fast.

7. Reaction of Ether with HI

Step 1. The reaction start with protonation of ether.

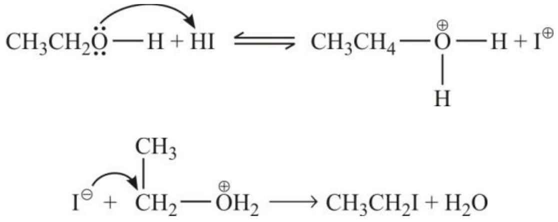


Step 2. Iodide is a good nucleophile. It attack the least substituted carbon atom of the oxonium ion formed is step 1 and displaces an alcohol molecule by SN^2 mechanism. Thus in the cleavage of mixed ethers with two different alkyl group, the lower group, the lower alkyl group forms alkyl iodide and larger forms alcohol.



When HI is in excess and reaction is carried at high temperature alcohol reacts with another molecule of HI to form another alkyl iodide.

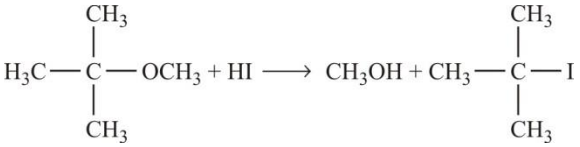
Step 3.



$$CH_3CH_2\ddot{O}-H + HI \rightleftharpoons CH_3CH_4-\overset{\oplus}{O}(H)-H + I^{\oplus}$$

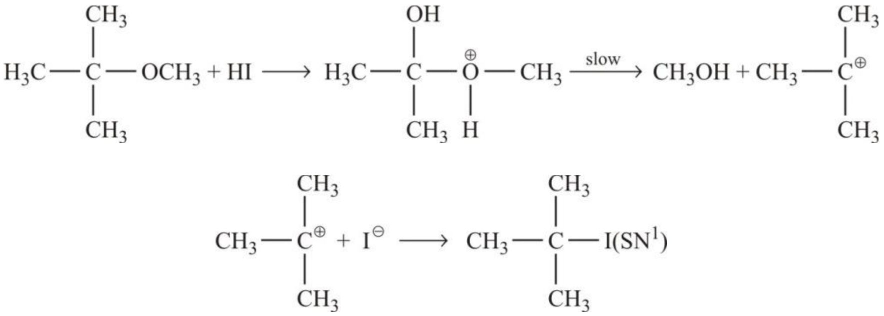
$$I^{\ominus} + \overset{CH_3}{CH_2}-\overset{\oplus}{O}H_2 \longrightarrow CH_3CH_2I + H_2O$$

When one of the alkyl group is tertiary, the halide formed is a tertiary halide.



$$H_3C-C(CH_3)_2-OCH_3 + HI \longrightarrow CH_3OH + CH_3-C(CH_3)_2-I$$

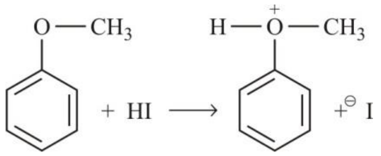
Due to formation of tertiary carbocation (stable).



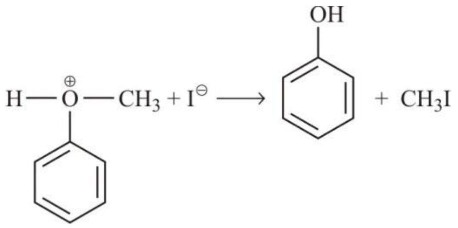
$$H_3C-C(CH_3)_2-OCH_3 + HI \longrightarrow H_3C-C(OH)(CH_3)-\overset{\oplus}{O}(H)-CH_3 \xrightarrow{slow} CH_3OH + CH_3-\overset{\oplus}{C}(CH_3)_2$$

$$CH_3-\overset{\oplus}{C}(CH_3)_2 + I^{\ominus} \longrightarrow CH_3-C(CH_3)_2-I(SN^1)$$

In anisole:

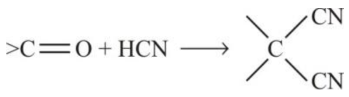


The CH_3—O bond is weaker then C_6H_5—O bond because the carbon atom of benzene ring is sp^2hybridised and there is a partial double bond character. There attack of I^O break the CH_3—O bond from CH_3I.



8. Addition of HCN to >C = O

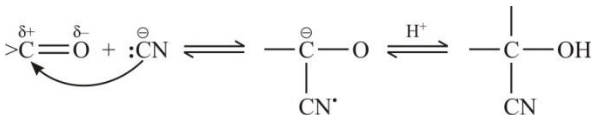
The reaction proceeds by attack of nucleophile.



Step 1. Generation of nucleophile.

$$HCN + \overset{\ominus}{O}H \rightleftharpoons :\overset{\ominus}{C}N + H_2O$$

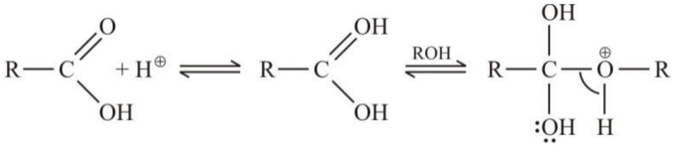
Step 2. Nucleophilic attack of CN^- on carbonyl group.



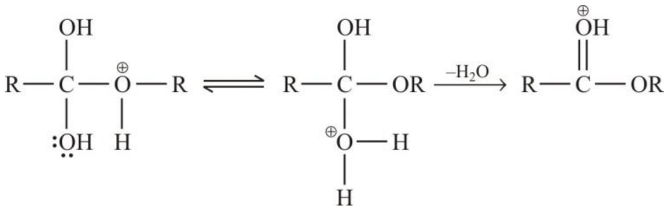
9. Esterification

$$CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

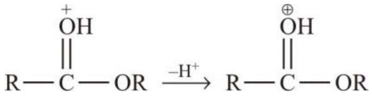
Step 1. Protonation of carbonyl oxygen activate the carbonyl group towards nucleophilic addition of alcohol. Proton transfer in the tetrahedral intermediate convert the OH– group into $(\overset{+}{O}H_2)$.



Step 2. Transfer of Proton.



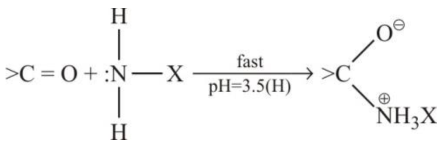
Step 3. $\overset{+}{O}H_2$ is a better leaving group and eliminated as H_2O. Protonated ester so formed finally loses a H^+ (Proton) to give ester.



10. Mechanism

Addition of NH_3, NH_2 OH, NH_2NH_2, $C_6H_5NHNH_2$ or $NH_2CONHNH_2$ to >C = O.

Step-1. Addition of ammonia derivative to >C = O



Step-2. Elimination of H_2O to form product.

Where X = –H, –R, –OH, $–CONHNH_2$ or $–NHC_6H_5$

The pH of the reaction is controlled at 3.5, in strongly acidic medium proton is captured by amino group to form salt

$$R\ddot{N}H_2 + H^+ \longrightarrow R\overset{+}{N}H_3$$

In basic medium, OH^- cannot attack to electro-negative oxygen atom.

$$>\overset{\delta+}{C}=\overset{\delta-}{O}+\overset{-}{O}H \longrightarrow \text{No reacation}$$

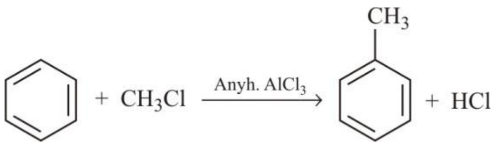
Hence no product is formed in strongly acidic or basic medium.

11. Some Important Reactions

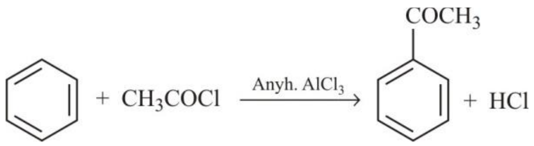
(a) Friedel Craft Reaction

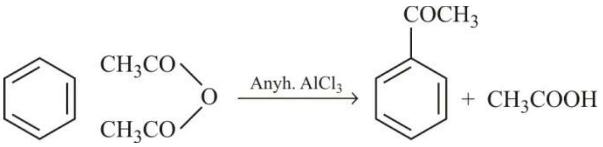
Addition of alkyl (R) or aryl group (COR) to benzene nucleus in presence of Anhydrous $AlCl_3$ (Lewis acid).

(a) Alkylation

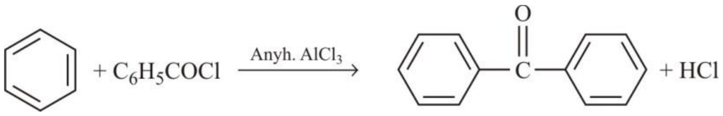


(b) Acetylation or Acylation





(c) Benzoylation

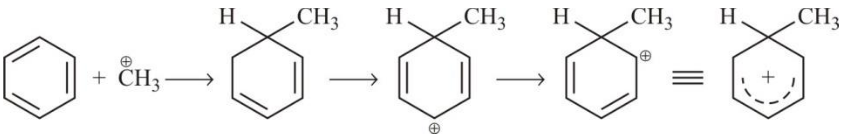


Mechanism

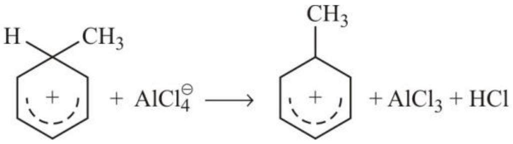
Step I. Generation of elecrophile, $AlCl_3$ is Lewis acid and generate electrophile.

$$CH_3Cl + AlCl_3 \longrightarrow AlCl_4^- + \overset{+}{C}H_3$$

Step II: Formation of intermediate.

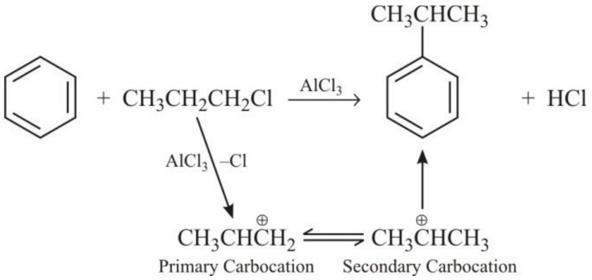


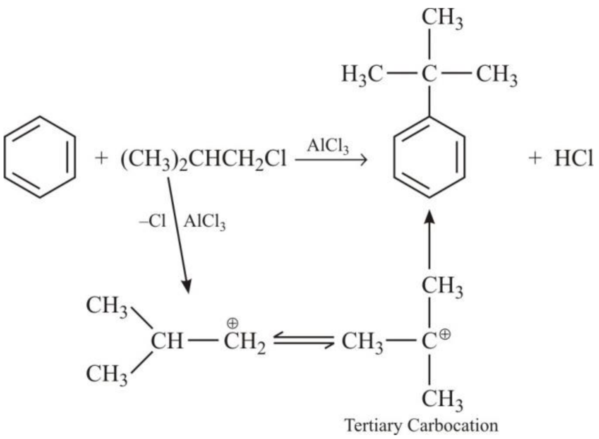
Step III.



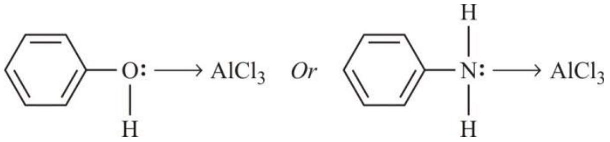
Characteristics:

1. More stable carbocation will form the product, e.g.,



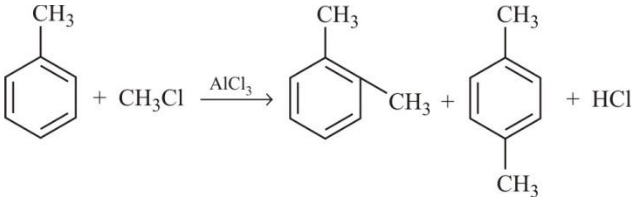


2. Phenol and aniline form addition product with AlCl$_3$donot form carbocation.



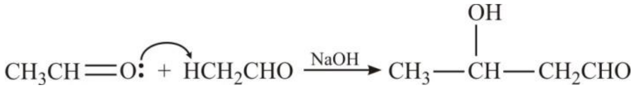
3. Chlorobenzene and vinyl chloride do not form carbocation.

4. Addition product will be determined by ortho, meta and para directing group e.g.,



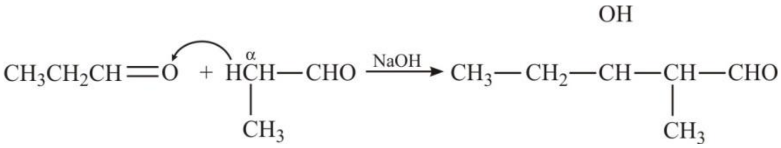
(B) Aldol Condensation

Aldehyde and ketones having one or more α-H-atom when warmed withdilute base undergo self addition reaction known as aldol condensation.



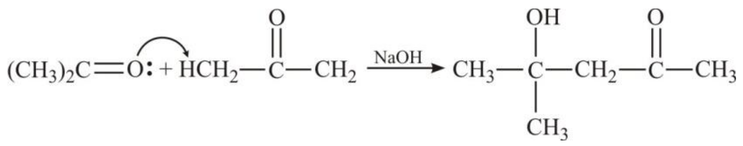
$$CH_3CH{=}\ddot{O} + HCH_2CHO \xrightarrow{NaOH} CH_3-\overset{\displaystyle OH}{CH}-CH_2CHO$$

Whatever be the size of aldehyde, attack comes from α-H-atom and product is β.



$$CH_3CH_2CH{=}O + \underset{\displaystyle CH_3}{H\overset{\alpha}{C}H}-CHO \xrightarrow{NaOH} CH_3-CH_2-\overset{\displaystyle OH}{CH}-\underset{\displaystyle CH_3}{CH}-CHO$$

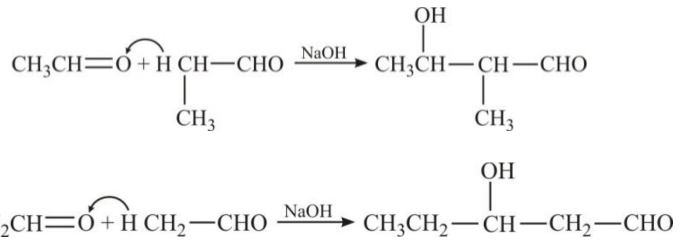
Ketones also undergo self addition to form ketol.



$$\mathrm{(CH_3)_2C{=}\ddot{O}{:} + HCH_2-\overset{O}{\overset{\|}{C}}-CH_2 \xrightarrow{NaOH} CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}$$

(C) Cross Aldol Condensation Reaction

When two different aldehydes are condensed together 4 products are formed.



$$\mathrm{CH_3CH{=}O + H\,\underset{CH_3}{CH}-CHO \xrightarrow{NaOH} CH_3\overset{OH}{CH}-\underset{CH_3}{CH}-CHO}$$

$$\mathrm{CH_3CH_2CH{=}O + H\,CH_2-CHO \xrightarrow{NaOH} CH_3CH_2-\overset{OH}{CH}-CH_2-CHO}$$

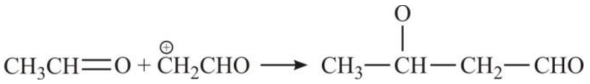
Mechanism:

Step I. Formation of carbonation.

$$\mathrm{CH_3CH{=}O + \bar{O}H \rightleftharpoons CH_2-CH{=}O \longleftrightarrow \overset{+}{C}H_2{=}CH-\bar{O} + H_2O}$$

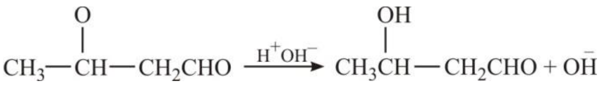
α-H-atom is removed by base as H_2O.

Step II.



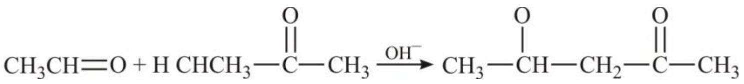
$$\mathrm{CH_3CH{=}O + \overset{\oplus}{C}H_2CHO \longrightarrow CH_3-\overset{O}{CH}-CH_2-CHO}$$

Step III.



$$\mathrm{CH_3-\overset{O}{CH}-CH_2CHO \xrightarrow{H^+OH^-} CH_3\overset{OH}{CH}-CH_2CHO + \bar{O}H}$$

Cross Aldol Involving Aldehyde and Ketone

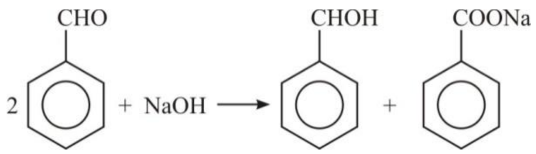


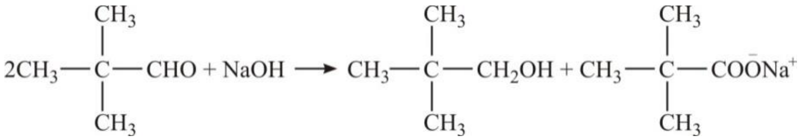
$$\mathrm{CH_3CH{=}O + H\,CHCH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{OH^-} CH_3-\overset{O}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}$$

(D) Cannizzaro Reaction

Disproportionation of an aldehyde lacking α-H-atom like HCHO CHCHO RC–CHO to salt of an acid and a primary alcohol is known as Cannizzaro Reaction.

$$\mathrm{2HCHO + NaOH \longrightarrow CH_3OH + HCOONa}$$

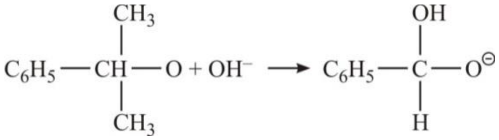




$$2CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CHO + NaOH \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2OH + CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CO\bar{O}Na^+$$

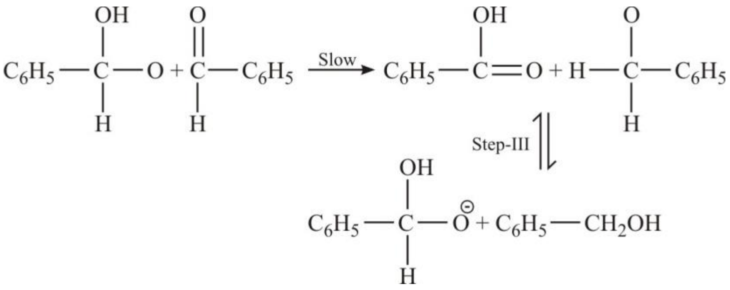
Mechanism:

Step I. Reversible addition of OH to >C=O.



$$C_6H_5-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{CH}}}}-O + OH^- \longrightarrow C_6H_5-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-O^{\ominus}$$

Step II. Transfer of hydride ion (H) to another aldehyde.



$$C_6H_5-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-O + \underset{H}{\overset{O}{\underset{|}{\overset{\|}{C}}}}-C_6H_5 \xrightarrow{\text{Slow}} C_6H_5-\overset{OH}{\overset{|}{C}}=O + H-\underset{H}{\overset{O}{\underset{|}{\overset{|}{C}}}}-C_6H_5$$

$$\xrightleftharpoons{\text{Step-III}} C_6H_5-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-\overset{\ominus}{O} + C_6H_5-CH_2OH$$

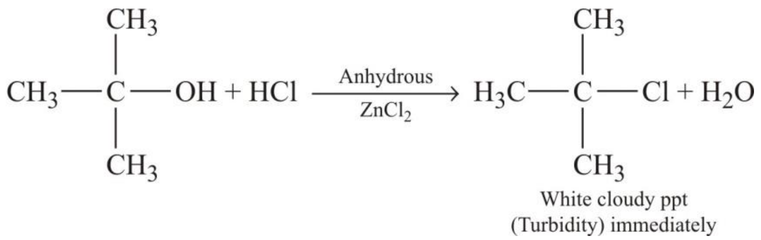
Distinguish Between

Primary Secondary and Tertiary alcohol

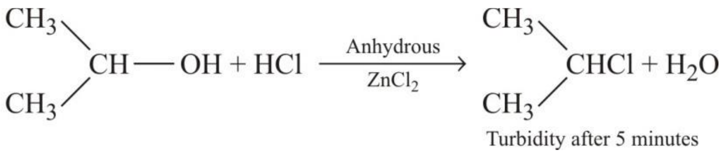
Test	**Primary**	**Secondary Alcohol**	**Tertiary alcohol**
1. Add Lucas reagent Anhydrous $ZnCl_2$ + Conc. HCl.	No Change	Turbidity after 5 minutes	Turbidity immediately
2. Add Victor Meyer reagent	Red	Blue	No change

Lucas Test

3°


White cloudy ppt
(Turbidity) immediately

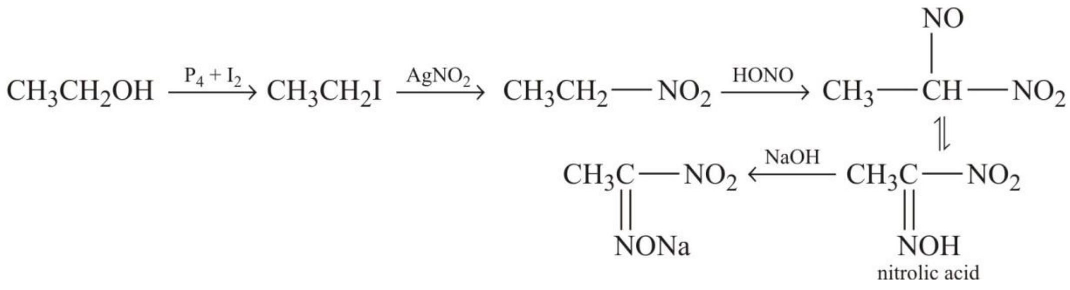
2°

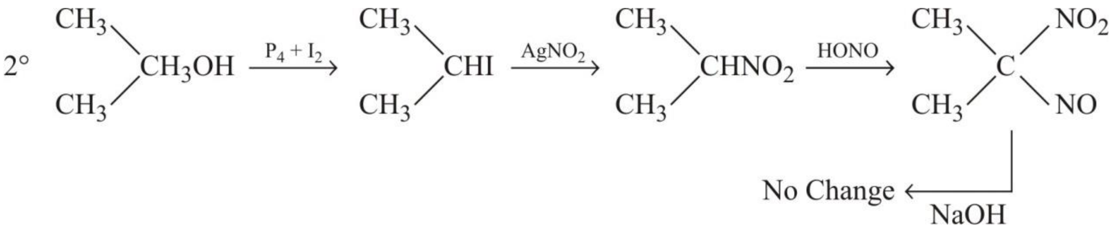

Turbidity after 5 minutes

1° $CH_3CH_2OH + HCl \xrightarrow[ZnCl_2]{Anhydrous}$ no reaction at ordinary temp

Victor Meyer Test

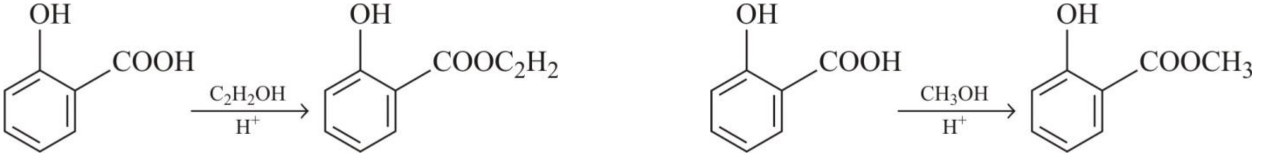
1°





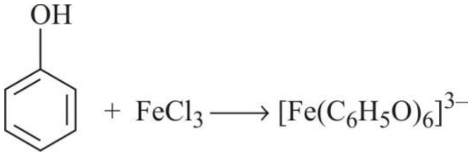
Test	Propan-1-ol $CH_3CH_2CH_2OH$	**Propan-2-ol** $CH_3\underset{OH}{\underset{\vert}{CH}}CH_3$
1. Add Lucas reagent Anhydrous $ZnCl_2$ + HCl.	No Change	Turbidity after 5 min.
2. Add Victor Meyer reagent	Red	Blue
3. Add I_2/NaOH	No change	Yellow ppt.
$6NaOH + 4I_2 + CH_3\underset{OH}{\underset{\vert}{CH}}-CH_3 \longrightarrow CHI_3 + CH_3COONa + 5NaI + 3H_2O$		

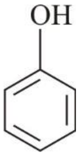
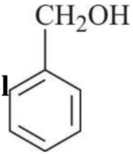
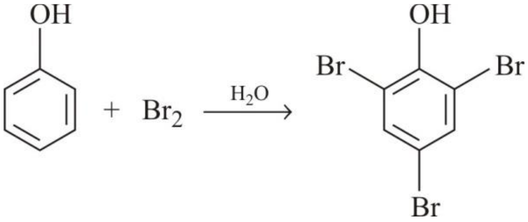
Test	Ethanol	Propan-1-ol
1. Add I_2/NaOH	Yellow iodoform	No change
$6NaOH + 4I_2 + C_2H_5OH \longrightarrow CHI_3 + HCOONa + 5NaI + 3H_2O$		

Test	Ethanol	Methanol
1. Add I_2/NaOH	yellow ppt.	No change
2. Add salicyclic acid	Pleasant odour	Odour of oil of winter green grass
		

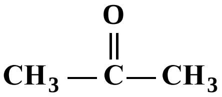
Test	**Ethanol CH_3CH_2OH**	**Propan-2-ol** $CH_3\overset{OH}{\overset{\vert}{CH}}CH_3$
1. Add Lucas reagent Anhydrous $ZnCl_2$ + HCl.	No Change	Turbidity after 5 min.

Test	**Ethanol**	**Phenol**

1. Add I_2/NaOH	Yellow iodoform	No change
2. Add neutral $FeCl_3$	No Change	Violet colour
		

Test	**Phenol** 	**Benzyl alcohol** 
1. Add neutral $FeCl_3$	Violet colour	No change
2. Add Br_2/H_2O	Red colour of Br_2decolourised	No change
		

Test	**Phenol**	**Benzoic acid**
1. Add neutral $FeCl_3$	Violet colour	No change
2. Add $NaHCO_3$	No Change	Effervescence of CO_2
$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2$		

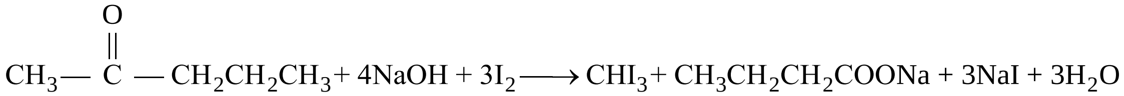
Test	**Acetaldehyde CH_3CHO**	**Acetone**  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$
1. Add fehling solution	Red ppt	No change
2. AddTollens reagent	Silver mirror	No change
A+ B $CH_3CHO + 2Cu^{2+} + 5OH \longrightarrow CH_3COO^{-} + CH_2O + 3H_2O$ $2[Ag(NH_3)_2]^{+} + CH_3CHO + 3OH + CH_3COO^{-} + 2Ag + 4NH_3 + 2H_2O$		

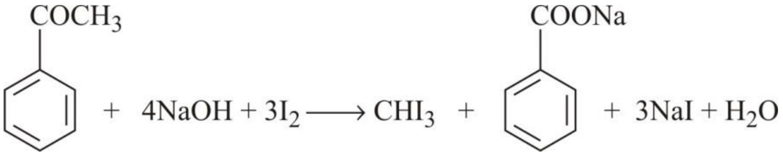
Test	**CH_3CHO Acetaldehyde**	**HCHO Formaldehyde**
1. Add I_2/NaOH	Yellow ppt	No change
$4NaOH + 3I_2 + CH_3CHO \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$		

2. Add $KMnO_4 + H^+$ $CH_3CHO \xrightarrow{O} CH_3COOH$	Vinegar odour	Formica Odour and effervescence of CO_2. $HCHO \xrightarrow{O} HCOOH \xrightarrow{O} CO_2 + H_2O$

Test	**Acetaldehyde**	**Benzaldehyde**
1. Add I_2/NaOH	Yellow ppt	No change
2. Add fehling solution A + B	Red ppt	No change

Test	**Formaldehyde**	**Benzaldehyde**
1. Add Fehling solution A + B	Red ppt	No change
2. Add $KMnO_4/H_2SO_4$	Effervescence of CO_2.	White ppt C_6H_5OOH

Test	**Pentan-2-one**	**Pentan-3-one**
1. Add I_2/NaOH	Yellow ppt	No change
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3 + 4NaOH + 3I_2 \longrightarrow CHI_3 + CH_3CH_2CH_2COONa + 3NaI + 3H_2O$		

Test	**Acetophenone**	**Benzophenone**
1. Add I_2/NaOH	Yellow ppt	No change
		

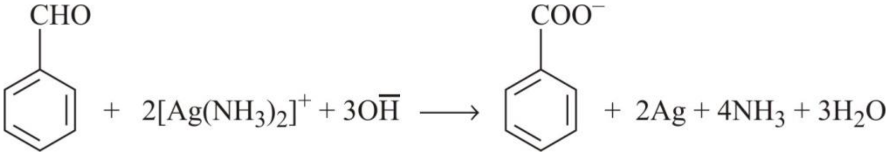
Test	**HCOOH Formicacid**	**CH_3COOH acetic acid**
1. Add Tollen's reagent	Silver mirror	No change
$HCOOH + [Ag(NH_3)_2]^+ \longrightarrow Ag + 2N\overset{+}{H}_4 + CO_2$		

Test	**CH_3COOH acetic acid**	**Benzoic acid C_6H_5OOH**
1. Odour	Characteristic vinegar	Odour less.
2. Add $P_4 + Br_2$	Red colour of Br_2decolourises	No change

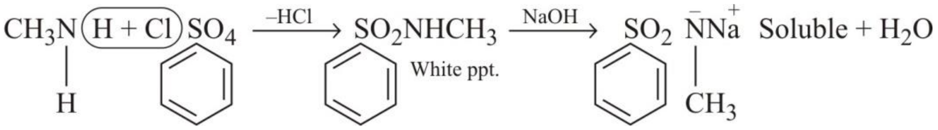
	$CH_3COOH \xrightarrow{P_4 + Br_2} Br\ CH_2COOH$	

Test	**Ethanol**	**Propanal**
1. Add I_2/NaOH	Yellow ppt	No change

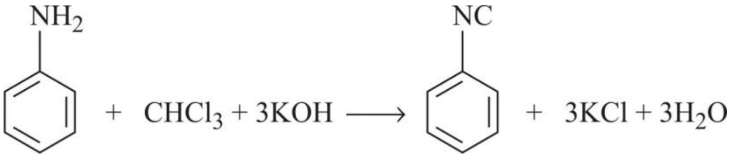
Test	**Benzoic acid**	**Ethyl Benzoate**
1. Add $NaHCO_3$	Effervescence of CO_2	No change

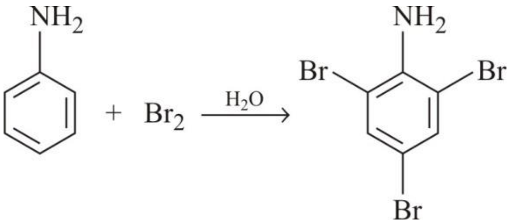
Test	**Benzaldehyde**	**Acetophenone**
1. Add I_2/NaOH	No change	Yellow ppt
2. Add Tollen’s reagent	Silver mirror	No change
		

Test	**Acetone**	**Acetic acid**
1. Add Feh soln. A + B	Red ppt.	No change
2. Add $NaHCO_3$	No change	Effervescence of CO_2.
$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$		

Test	**Primary Amine**	**Secondary Amine**	**Tertiary Amine**
1. Add Hinsburg agent $C_6H_5SO_2Cl$	White ppt Soluble in NaOH	White ppt Insoluble in NaOH	No change
			

Test	**Methanamine CH_3NH_2**	**N-Methyl methanamine CH_3NHCH_3**
1. Add H.B reagent $C_6H_5SO_2Cl$	White ppt soluble in NaOH	White ppt insoluble in NaOH
2. Add $CHCl_3$ + KOH	Foul odour	No change
$CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3N \equiv C + 3KCl + 3H_2O$		

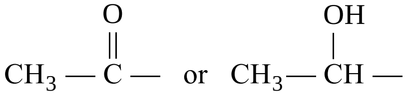
Test	**Aniline NH_2**	**N-methyl aniline $NHCH_3$**
1. Add Hinsbergreagent	White ppt solution in NaOH	White insoluble in NaOH
2. Add $CHCl_3$ + KOH	Foul odour	No change
		

Test	**CH_3NH_2Methanamine**	**Aniline NH_2**
1. Add Br_2/H_2O	No change	Red colour of Br_2 of decolourised
		

Tests

1. Lucas test: 1° 2° 3° alcohol: Isocyanide Test + Primary Amine.

2. Neutral $FeCl_3$ Test: Phenol form violet colour.

3. Iodoform Test: 

$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} -$ or $CH_3 - \overset{\overset{\displaystyle OH}{|}}{CH} -$

4. Hinsberg Test: 1 ° 2° 3° amine.

5. $NaHCO_3$ Test: acid releases CO_2 from carbonates.

6. Fehling solution: All aldehyde form red ppt except Benzaldehydes.

7. Tollen's Test: All aldehyde +HCOOH: Silver mirror

8- Br_2/H_2O: Phenol & aniline decolourises red colour of Br_2.

Give Reason

1. Alkyl holide react with KCN to form nitrile but product is isonitrile with AgCN.

Ans. $CH_3Cl + KCN \longrightarrow CH_3CN + KCl$

$CH3Cl + AgCN \longrightarrow CH_3N \overset{|}{=} C + AgCl$

$\overset{+}{K}\overset{-}{C}N$ is an ionic compound and provide $:\overset{-}{C}N$ is solution, which attach through C-atom which consists of pair of electron not through N-atom since C—C bond is stronger than C—N bond $Ag: C \equiv N$ is a covalent compound and nitrogen $.C \equiv N:$ attack through line pair of e^- to form isocyanide as main product.

2. Grignord reagent is prepared under anhydrous conditions.

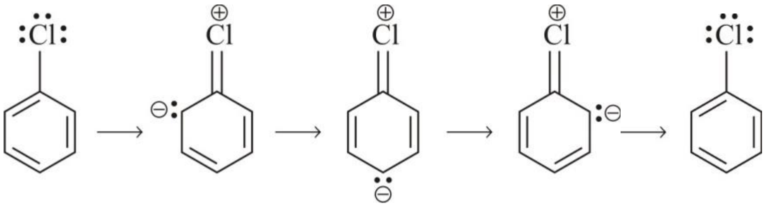
Ans. In Grignord reagent C—M bond is highly polar, with carbon pulling electrons from electropositive magnesium and Mg—X bond is ionic $\overset{\delta-}{R}-\overset{\delta+}{Mg}\ \overset{\delta-}{X}$

So Grignard reagent is highly reactive and react with any source of proton donor like H_2O, alcohol, amine to form hydrocarbon. $R-Mg-X+HOH \longrightarrow RH+Mg\begin{smallmatrix}/OH\\ \backslash X\end{smallmatrix}$

So Grignard reagent is prepared under anhydrous conditions.

3. Chlorobenzene is less reactive than chloroethane.

Ans. Eachcatom of benzene ring is sp^2hybridised and and is electron withdrawing. The electron pairs an halogen atom is conjugation with π electrons of the ring and remain delocalized over the ring.



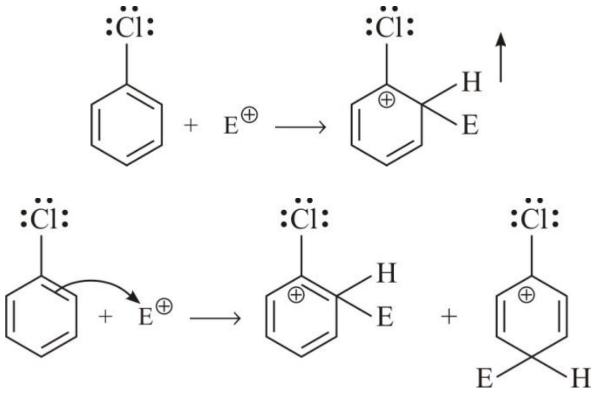
C-Cl bond aquire a partial double bond character due to resonance.

In halo alkanes, carbon atom attached to halogen is sp^3hybridised less s-character.

C—Cl bond length in halo arene is 169 pm as compared to 177 pm in haloalkane so larger amount of energy is required to break the bond.

4. Although chlorine is an electron withdrawing group yet it is ortho and para directing in electrophilic aromatic substitution reactions.

Ans. Chlorine withdraws electron though-I effect and release electrons through resonance. Though reasonance. Though inductive effect chlorine destabilizes the intermediate carbocation formed during electrophilic substitution.



Through reasonance halogen tends to stabilize the carbocation and effect is more pronounced at ortho and para position. The inductive effect is stronger than resonance and causes net electron withdrawl and cause de-activation.

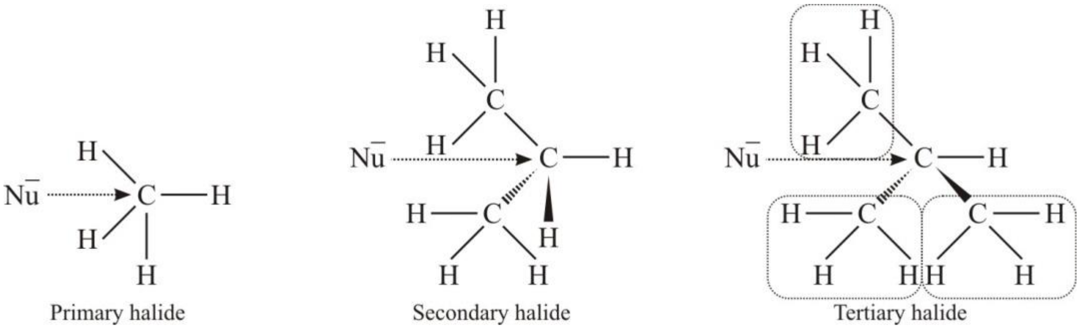
Resonance effect tends to oppose I effect and attack at ortho and para position. The reactivity is controlled by resonance effect and orientation is controlled by resonance effect.

5. $S_N{}^1$ reactions are favoured in protic solvent.

Ans. It involves the C—X bond breaking for which the energy is obtained through the salvation of halide ion with proton of protic solvent like H_2O.

6. Tertiary halides donot undergo SN^2 mechanism.

Ans. Three alkyl groups hinder the approach of nucleo-phile, in rear side attack.

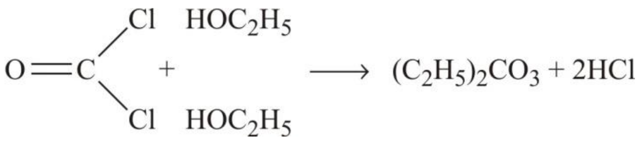


7. Why chloroform is stored in coloured bottles.

Ans. Chloroform is slowly oxidized by air in presence of sunlight to carbonyl chloride (Phosgene).

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl.$$

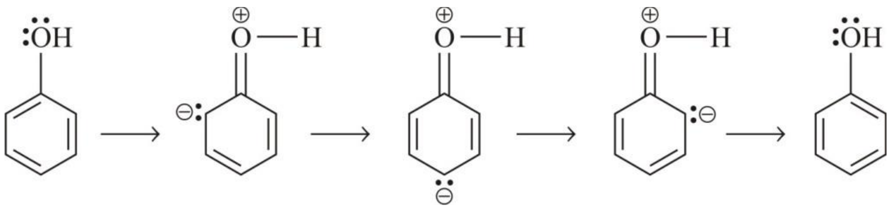
So chloroform is stored in coloured bottles to cut sunlight filled upto brim with a few drops of ethanol on top.



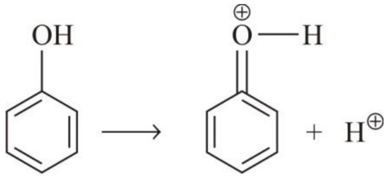
Ethanol form diethyl carbonate which form a layer on top and prevent further oxidation.

8. Phenol is acidic in nature.

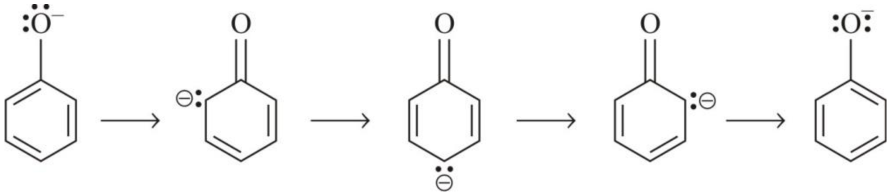
Ans. In phenols each caton of benzene ring is sp^{2}hybridised and is electron with drawing. Oxygen atom donate a long pair of electron and aquire (+) charge. The (–) change is stabilized on orthopara position by resonance.



This increases the polarity of O—H bond and results in an ionization of phenol.

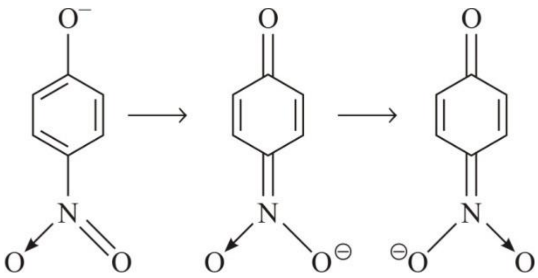


In phenoxide ion, the charge is delocalized makes phenoxide ion more stable (conjugate base) and favours ionization of phenol.



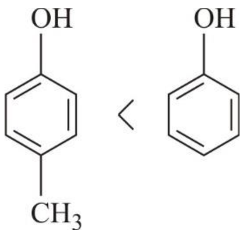
9. Whether paranitrophenol is more or less acidic than phenol and why?

Ans. Any electron withdrawing group eg No$_2$ pull the electron density away from benzene ring. Stabilises the phenoxide ion due to effective resonance.



10. Whether cresol is more or less acidic than phenol.

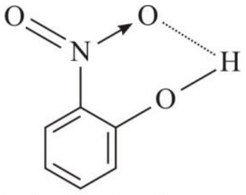
Ans. Any electron releasing group eg., CH_3, OCH_3 push the electron density over oxygen atom, destabilizes the phenoxide ion and H^+ cannot be donated effectively, Thus decreases the acidic strength of phenol. So cresol is less acidic than phenol.



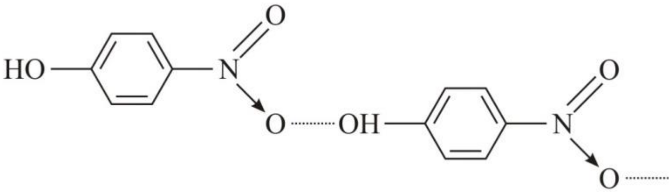
11. Orthonitrophenol is steam volatile where p-nitrophenol is not or

How will you separate a mixture of ortho and para nitro phenol.

Ans. Ortho nitro phenol is steam volatile due to intro molecular Hydrogen bonding while paranitrophenol is less volatile due to inter molecular H-bonding which causes association of molecules.



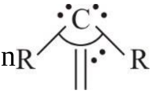
Orthonitrophenol



12. Ethers and insoluble in water.

Ans. Ethers can not form Hydrogen bond with water and ethers are less polar then water.

13. Ethers have two alkyl group but polar in nature.

Ans. There are two lone pairs of electron  on O-atom in ether which repel the bond pair to create net dipole. Dipole moment is the vector sum of all dipoles.

14. Boiling point of ethers and lower than isomeric alcohols.

Ans. Ethers cannot form inter molecular Hydrogen bond so their B.P. are lower than isomeric alcohol.

$$CH_3CH_2OH \longleftarrow C_2H_6O \longrightarrow CH_3OCH_3$$

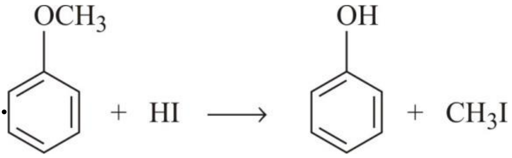
BP(k) 35175 249

$$CH_3CH_2CH_2CH_2OH \longleftarrow C_4H_{10}O \longrightarrow C_2H_5O_2H_5$$

BP(K) 391 309 K

15. Phenyl methyl ether react with HI to form phenol and methyl iodide not iodo benzene and methanol.

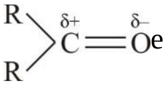
Ans.



(a) Each c atom of benzene ring is sp^2hybridised and is electron with drawing so C_6H_5O bond is stronger than CH_3–O bond where c atom of alkyl group is sp^3hybridised. So larger amount of energy is required to break the bond.

(b) Benzene ring after a steric hindirance to I^- nucleophile to attack C_6H_5O bond.

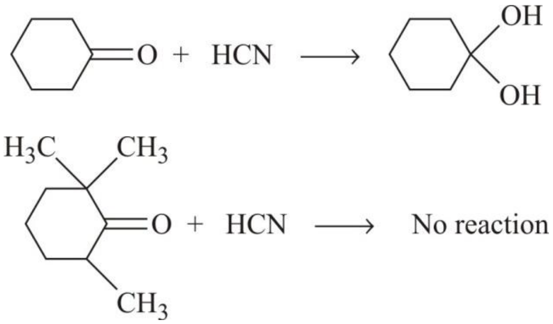
16. Aldehydes are more reactive towards nucleophite than ketones.

Ans.(a) Two alkyl group in ketones are  electron releasing push the electron density over carbonyl c-atom. Thus decreases its electrophilicity (net positive charge), so less pull force for nucleophile.

(b) Two alkyl group offer a steric hindrance to nucleophiles so perpendicular attack possible.

17. Cyclohexanone form cyanohydrins in good yield but 2, 2, 6 trimethylcyclohexanone does not

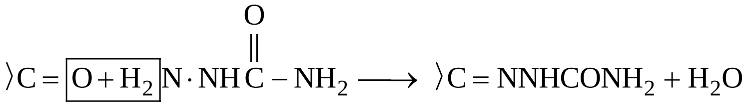
Ans.

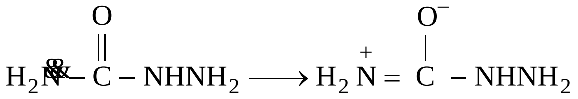


(a) Three methyl group push the electron density over carbonyl c-atom. This decreases its electrophiliaty.

(b) Three methyl group offer a steric hinderance to nucleophiles.

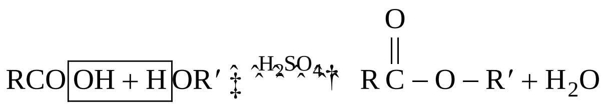
18. There are two —NH_2 groups in semi carbazide. However only one is involved in the formation of semicorbazones.

Ans. 
$$\rangle C=\boxed{O+H_2}N\cdot NH\overset{\overset{O}{\|}}{C}-NH_2 \longrightarrow \rangle C=NNHCONH_2+H_2O$$


$$H_2\overset{\&\&}{N}-\overset{\overset{O}{\|}}{C}-NHNH_2 \longrightarrow H_2\overset{+}{N}=\overset{\overset{O^-}{|}}{C}-NHNH_2$$

The lonepair of electron on N-atom nearer to $-\overset{\overset{O}{\|}}{C}-$ remain delocalized over O-atom and not available for reaction. Far —NH_2 cannot donate its lone pair of electron to $-\overset{\overset{O}{\|}}{C}-$ and involved is the reaction.

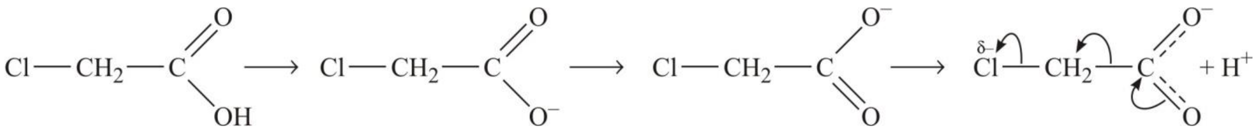
19. During the preparation of esters from carboxylic acid and an alcohol in foresence of an acid catalyst the esters are removed as fast as it is formed.

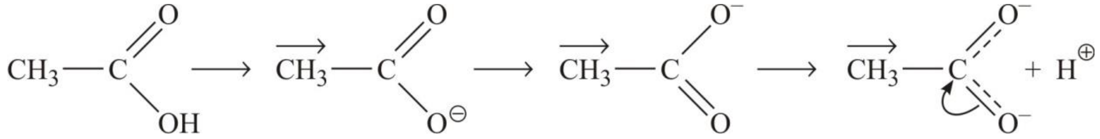
Ans. 
$$RCO\boxed{OH+H}OR' \xrightleftharpoons{H_2SO_4} R\overset{\overset{O}{\|}}{C}-O-R'+H_2O$$

Both esterification and hydrohysis of either are catalysed by acid. The reaction is reversible and an equilibrium is established, so esters are removed fast to avoid equilibrium and to favour the forward reaction.

20. Chloro acetic acid is stronger than acetic acid.

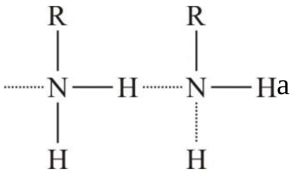
Ans. Any electron withdrawing like Cl, F, group pull the electron density away from COO^- (–I effect) stabilies the conujugate base by delocalization of charge over C—C—Chain and proton H^+ can be denoted easily. Thus increases the acidic strength of carboxylic acid.





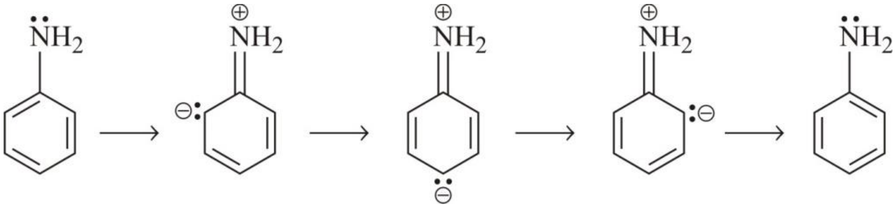
Ary e^- releasing group eg CH_3 push the electron density over COO^- (+I effect) denstabilise. The conjugate base and H^+ cannot be denoted easily. Thus decreases the acidic strength of Carboxylic acid.

21. Amines are higher boiling compound than hydrocarbon but lower than alcohols of comparable molecular masses.

Ans. Amines can form intermolecular  are higher than hydrocarbon. Hydrogen bond in amines between Nitrogen and Hydrogen are weaker than present in alcohols between O and H. Oxygen being more electronegative than Nitrogen. So their BP are lower than alcohols.

22. Pkb value of amiline is more than methanamine or Aniline is weaker base than methanamine.

Ans. In aniline, each c-atom of benzene ring is sp^2hybridised and is electron with drawing in aniling NH_2 group is directly attached to benzene ring. It results unshared electron pair on Nitrogen atom to be in conjugation with benzene ring and remain delocalized over the ring so less available for protonation.



23. Observed kb order is

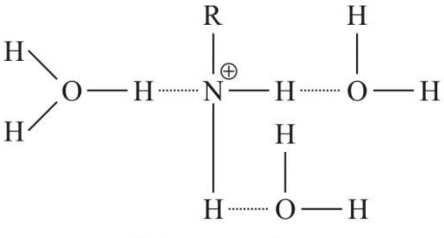
$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

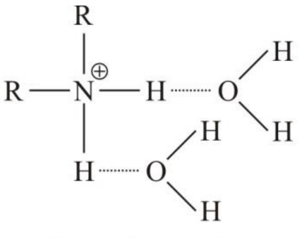
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

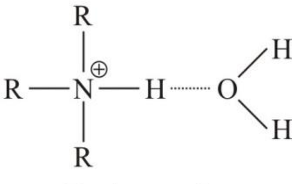
(a) In gasous phase, where solvent factor is missing larger the number of electron releasing group, more is basic strength. kb order should bes (+Inductive effect).

Tertiary Amine > Secondary Amine > Primary Amine > NH_3

(b) In aqueous solution amines form Hydrogen bond with H_2O protonated primary amine can form three Hydrogen bond. Secondary amine form two Hydrogen and tertiary amine form one Hydrogen bond.


Primary amine


Secondary amine


Tertiary amine

kb order should be

Primary Amine > Secondary Amine > Tertiary Amine

(c) There is steric hinderance in tertiary amine deponding on nature of alkyl group.

Combinine three factor (i) +I effect (ii) Solvation effect and (iii) Steric effect kb order is

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

24. Aromatic primary Amine cannot be prepared by Gabriel's phthalomide synthesis.

Ans. Anyl halides donot undergo nucleophilic substitution with the anion formed by phthalamide.

25. Methyl amine in water react with ferricchloride to precipitate hydrated ferric axide.

Ans. Methyl amine in water behave as base react to form,

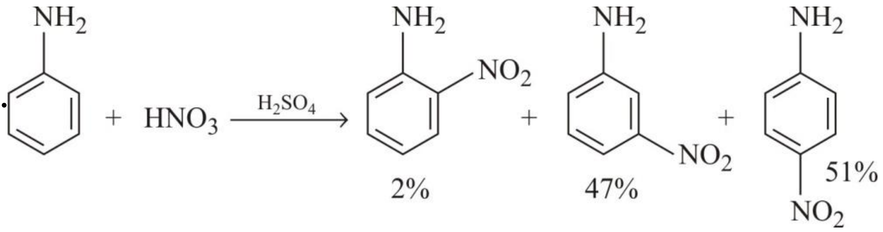
$$CH_3NH_2 + H_2O \longrightarrow [CH_3\overset{+}{N}H_3]\overset{-}{O}H$$

$$3[CH_3\overset{+}{N}H_3]\overset{-}{O}H + FeCl_3 \longrightarrow Fe(OH)_3 + 3[CH_3\overset{+}{N}H_3]Cl^-$$

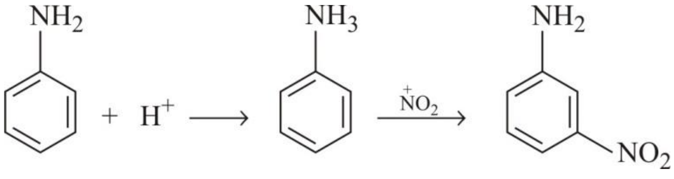
$$\downarrow Fe_2O_3 \cdot xH_2O \text{ red ppt.}$$

26. NH$_2$ group is ortho and para directing in aromatic electrophilic substitution reaction. Aniline on nitration gives a substiontial amount of meta-nitroaniline.

Ans.

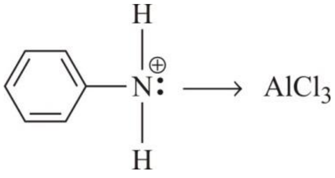


Aniline accept proton (H$^+$) from acids to form anilium.



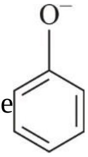
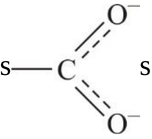
Which make the ring electron deficient and become meta-directing.

27. Aniline form salt with aluminium chloride Lewis acidwhich is used as a catalyst. Due to this Nitrogen



of amilineaquire positive charge and hence act as a strong deactivating group for further reaction.

28. Phenol is a weaker acid than carboxylic acid.

Ans. Phenoxide  has resonance only on one oxygen atom while carboxylate ion has resonance over 2-oxygen atoms  so more stable than phenoxide and can denote N^+ easily so has higher ionization than Phenol in aqueous solution.

29. $CH_3CHO$is more reactive than CH_3COCH_3toward reaction with HCN.

30. Carboxylic acid is stronger than acid than phenol.

UNIT 14: Biomolecules

1. Deficiency of which vitamin causes night blindness.
2. Name the Base that is found in nucleotide of RNA only.
3. Glucose on reaction with HI gives n-hexane, what does it suggest about the structure of glucose.
4. Deficiency of which vitamin causes scurvy.
5. What type of linkage is responsible for the formation of protein?
6. Write the product formed when glucose is treated with HI.
7. What is meant by (i) Peptide linkage (ii) Glycosidiclinkage?
8. Write any three reactions of glucose which cannot be explained by open chain structure of glucose.
9. What are common nitrogen bases in DNA and RNA.
10. Difference between

    (i) α-glucose and β-glucose

    (ii) amylose and cellulose

    (iii) Reducing sugar and non-reducing sugar

    (v) Fibrous protein and globular protein

    (v) DNA and RNA
11. What are carbohydrates? How many type of carbohydrates are? Give one example of each type.
12. Write briefly the primary, secondary structure of protein.
13. What are vitamins? How many types of vitamins are? Give example.
14. Write deficiency diseases of the following vitamins:

    Vitamin A, B_1, B_2, B_6, B_{12}, C, D, E, K
15. What are nucleoside and nucleotides?
16. Mention two chemical differences between DNA and RNA.
17. Name the product of hydrolysis of sucrose.

2013: After Watching a programme on TV about the advers effect of junk food and soft drinks on health of school children Sonali a student of class XII discuss the issue with the school principal. The

Principle immediately instructed the canteen contractor to replace the fast food with fibre and vitamins rich food like sprouts, salad, fruits etc. This decision was welcomed by parents and the students.

After reading the above passage, answer the following questions:

(a) What values are expressed by Sonali and the principal of the school?

(b) Give two examples of water soluble vitamins.

18. (i) Which one of the following is a disaccharide: Starch, Maltose, Fructose, Glucose?

(ii) What is the difference between fibrous protein and globular protein.

(iii) Write the name of vitamin whose deficiency causes bone deformities in children. **2015**

UNIT 15: Polymer

2014: After ban on plastic bags student of one school decided to make the people aware of the harmful effects of plastic bags on environment and Yamuna River. To make the awareness more impactful. They organised the rally by joining hands with other school and distributed paper bags to vegetable vendors, shopkeeper and departmental stores. All students pledged not to use polythene bags in future to save Yamuna River.

After reading the above passage, answer the following questions:

(i) What values are shown by students?

(ii) What are Biodegradable polymers? Give examples.

(iii) Is polythene a condensation or an addition polymer.

2013: (i) Write the names and structures of the monomers of the following polymers.

(i) Buna-S (ii) Neoprene (iii) Nylon-66

2012: Draw the structures of the monomers for each of the following polymers.

(i) Nylon-6 (ii) Polypropylene

1. What are elastomers and fibres? Give examples also.
2. Arrange the following polymers in the increasing order of strength. Natural Rubber, Nylon-66, PVC, Bakellite.
3. Write the mechanism of addition polymerisation.
4. Write the monomers of the following:

   Neoprene, Teflon, Terplene, PHBV.
5. How will you get the following polymers from their monomers:

   Buna-S, Buna-N, Bakelite, Alkyd resin, Urea formaldehyde resin, Melamine resin.
6. Define the term homopolymarisation and co-polymarisation. Give one example of each.
7. Write the name and structure of the monomers of the following polymers.

   (i) Polystyrene (ii) Dacron (iii) Teflon
8. Write the names and structures of the monomers of the following polymers:

   (i) Nylon-6, 6 (ii) PHBV (iii) Neoprene **2015**

UNIT 16: Chemistry in Everyday Life

1. What are the following substances? Give one example of each.

   (i) Tranquilizers (ii) Food Preservative (iii) Synthetic detergent

2. What are detergents? How many types of detergents are? Give example of each type.
3. Which one of the following is a food preservative?

   Equanil, Morphine, Sodium Benzoate.

4. Why is Bithionol is added to soap?
5. Which class of the drugs is used in sleeping pills?
6. Give two examples of macromolecules that are chosen as drug target.
7. What are antiseptics? Give one examples.
8. Why is use of aspartame limited to cold foods and soft drinks?
9. What are antiseptic and disinfectants. Give one example of each.
10. Give example of a substance used as antiseptic as well as disinfectant.
11. Which substance is added to shaving soaps to form lather well? (Rosin)
12. What are antacids? Give one example.
13. Where in India penicillin is manufactured?
14. What are Bacteriostatic and Bactericidalpenicillin.
15. Define spectrum of Penicillin. Give an example of Broad spectrum penicillin.
16. Eliminate the odd one - Equanil, seconal, veronal, bithional, Liaminal and why?
17. What are agonist and antagonist?
18. What are drug target? Give one example.
19. What are analgesics and antipyretics? Give one example of each.
20. Define antibiotics, who discovered penicillin.

Multi-Disciplinary Questions

UNIT: Electrochemistry

1. Fuel cells are voltaic cells, designed to convert the energy from the combustion of fuels such as H_2, CO, CH_4 etc. directly into electrical energy. The most common example is hydrogen-oxygen fuel cell. Many varities of fuel cells are possible and in some the electrolyte is a solid polymer membrane or ceramic. Recently a zinc air fuel cell (ZAFC) is developed in USA as a source of power in automobiles in which Zn metal is used in place of hydrogen gas. ZAFC have properties of both fuel cell as well as batteries. These have high energy density inexpensive to produce energy sizes ranges from button cells (mercury cell) to large batteries. H_2-O_2 fuel cell has been used for electric power in Apollo space programme.

   (i) Give two advantages of fuel cells.

   (ii) Which gas is oxidised at Anode in H_2-O_2 fuel cell?

   (iii) Give one disadvantage of ZAFC.

   (iv) What are ceramics?

   (v) What is the main compound used in solid polymer membrane?

Hints:

(i) High efficiency, pollution free

(ii) H_2

(iii) Non-Rechargeable

(iv) A ceramic is an inorganic, nonmetallic solid prepared by action of heat and subsequent cooling.

2. New research has established the “miracle material” called “graphene” as the world’s thinnest known coating for protecting metals against corrosion. Graphene coatings could be ideal corrosion-inhibiting coatings in applications where a thin coating is favourable, such as microelectronic components (e.g. aircraft components and implantable devices). Graphene, is a single layer of carbon atoms, many layers of which are in a lead pencils and charcoal and is the thinnest strongest known material. Copper coated by growing a single layer of graphene, corroded seven times slower than base copper and nickel coated by growing multiple layers of graphene corroded twenty times slower than base nickel.

   (i) Name the element present in Graphene.

   (ii) Give one important use of Graphene in mobile phones technology.

(iii) Is corrosion an electrochemical phenomenon?

(iv) Name the compound which is corroded form of copper.

(v) Will corrosion be slower or faster in presence of saline water?

Hints:

(i) Carbon

(ii) Specially-crafted graphene electrode can allow a lithium-ion battery (used in mobile phones) to store 10 times as much power and charge 10 times faster.

(iii) Yes

(iv) Copper sulphides (Cu_2S) (Green coating seen on copper wires)

(v) Faster

UNIT: General Principles and Processes of Isolation of Elements

1. One can do wonders if he or she has a scientific temperament and is attentive to observations. A washer woman while washing a miner's overalls, noticed that sand and similar dirt fell to the bottom of the wash tub, what was Peculiar, the copper bearing compounds that had come to the clothes from mines, were caught in the soapsuds and so they come to the top. One of their clients was a chemist, Mrs. Carrie Everson. The washer woman told her experience to Mrs. Everson. The latter thought that the idea could be used for separating copper compounds from rocky and earthy materials on large scale. This way an invention was born. At that time only those ores were used for extraction of copper which contain large amount of metal. Invention of the Froth Floatation method made copper mining profitable even from the low grade ores.

   (i) Which type of metal ores are mainly used in Froth Floatation Process.

   (ii) Name on more ore which can be concentrated by Froth Floatation Process in addition to copper sulphide ores.

   (iii) Name one important characteristic of washer woman.

   (iv) Name a Froth stabiliser used to stabilise the froth formed during floating process.

   (v) Is this method can be used to separate two sulphide ores?

Hints:

(i) Metal sulphides

(ii) Pbs

(iii) Attentive, innovative

(iv) Aniline

(v) Yes, (ZnS from PBS using NACN)

2. Nickel is an important element, the majority of nickel is used in corrosion-resistant alloys, such as stainless steel. Nickel steel is used for making cables automobiles and aeroplane parts, pendulum, chrome steel for cutting tools and crushing machines. Tubing made from a copper-nickel alloy is used in desalination plants. This alloy is naturally resistant to corrosion by sea water. Nickel is refined by heating impure nickel in a stream of carbon monoxide forming volatile complex, which on subsequent heating a higher temperature decomposes to give pure nickel , with cadmium nickel in used to form nickel-cadmium rechargeable battery.

   (i) Name the process used for refining nickel.

   (ii) Write the formula of volatile complex formed during refining of nickel.

   (iii) Is volatile complex formed toxic in nature?

(iv) Name the alloy in which copper, zinc and nickel are used.

(v) Is nickel-cadmium battery primary battery or a secondary battery?

Hints:

(i) Mond's Process

(ii) Ni(CO)4

(iii) yes

(iv) German silver

(v) Secondary battery

$$\begin{pmatrix} \text{Ni} - 40\text{-}50\% \\ \text{Cu} - 25\text{-}30\% \\ \text{Zn} - 25\text{-}30\% \end{pmatrix}$$

3. Cast iron, which is the most important form of iron is used for casting stoves, railway sleepers, gutter pipes toys etc. Cast iron is extremely hard and brittle and contains nearly 3% carbon. Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron. Wrought iron is used making anchors, wires, bolts, chains and agricultural implements.

   (i) how wrought iron is prepared from cast iron.

   (ii) Write the composition of cast iron.

4. Carbinol on treating with aq. NaOH and CO_2, followed by acidification forms an organic compound which is acidic in nature. The organic compound so formed on treatment with acetic anhydride, under acidic conditions produces "Aspirin", which is an antipyretic drug.

   (i) Draw structure of Aspirin.

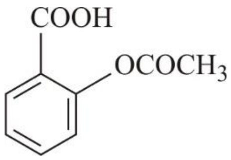
   (ii) Can Aspirin be used to reduce temperature of human body?

   (iii) Why Aspirin is used in prevention of heart attack?

   (iv) Give one test for identification of carbinol.

   (v) Name the intermediate compuond formed during preparation of 'Aspirin' from Carbinol.

Hints:

(i) 

(ii) Yes

(iii) Aspirin dilutes the blood

(iv) On treating with neutral $FeCl_3$carbinol gives violet colour

(v) Salicylic acid

UNIT: Alcohols, Phenols, Ethers

1. Biological oxidation of methanol and ethanol in the body produces the corresponding aldehyde followed by the acid. At times the alcoholics, by mistake, drink ethanol mixed with methanol also called denatured alcohol. In the body, methanol is oxidised first to methanol and them to methanoic acid, which may cause blindness and death. A methanol poisoned patient is treated by giving intravenous fusions of diluted ethanol. The enzyme responsible for oxidation of aldehyde (HCHO) to formic acid is swamped allowing time for kidneys to excrete methanol.

   (i) Name the compound used in denaturation of alcohol.

   (ii) Name the enzyme responsible for oxidation of aldehyde (HCHO) to methanoic acid.

   (iii) Name an oxidising agent to convert.

   (a) Methanol to formaldehyde

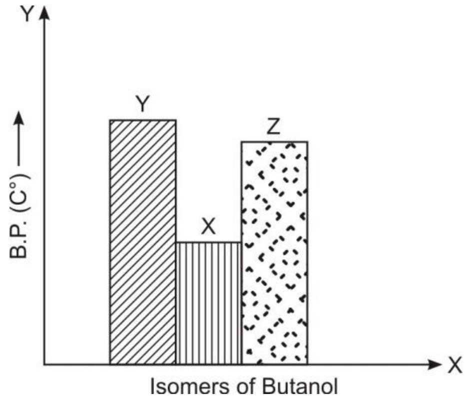
   (b) Methanol to formic acid.

Hints:

(i) CuSO4, Pyridine (ii) Quino protein Alcohol Dehydrogenase (QADH)

(iii) (a) PCC (b) $K_2Cr_2O_7.H^+$

2. The boiling points of three isomers of "Butanol" (n-Butylalcohol, sec-Butylalcohol, tert-Butyl alcohol) are represented by following bar diagram.



Answer the followings:

(i) Identify the three isomers in terms of X, Y, Z.

(ii) Give the structure of the product formed when 'X' is treated with Cu/573 K in vapour phase.

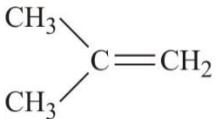
(iii) Convert Y into Z.

(i) Y – n-Butan-1-ol

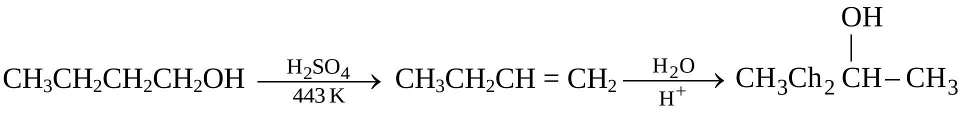
Z – Butan-2-ol

X – 2 methyl propan-2-ol

(ii)



(iii)



$$CH_3CH_2CH_2CH_2OH \xrightarrow[443\,K]{H_2SO_4} CH_3CH_2CH = CH_2 \xrightarrow[H^+]{H_2O} CH_3Ch_2\underset{}{\overset{\overset{\displaystyle OH}{|}}{CH}}-CH_3$$