1). $[Pt(en)_2Cl_2]$

1

Co-ordination number → 6

Oxidation state → +2 [Pt(II)]

2). FeO has a non-stoichiometric composition due to metal deficiency defect due to cationic vacancies.

1

In the crystal some Fe^{2+} ions are missing and the nearby Fe^{2+} atoms/ions are oxidised to Fe^{3+} to maintain electrical neutrality. So for every 3 Fe^{2+}, only 2 Fe^{3+} are present and one vacancy is created.

The composition thus becomes $Fe_{0.95}O$.

3).

chloro-benzene

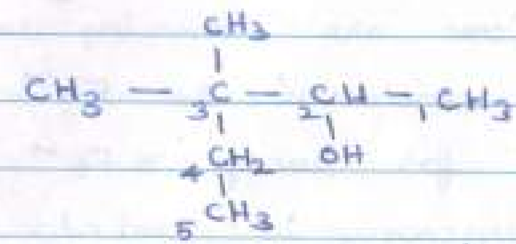
benzyl chloride

1

Benzyl chloride is hydrolysed easily because the benzyl carbocation formed is more stable.

On the other hand, C–Cl bond in chlorobenzene acquires partial double bond character due to resonance and the carbon is sp^2 hybridised. Also, phenyl carbocation formed is highly unstable. There is possible repulsion between approaching nucleophile and electron rich arene. This is more in case of chlorobenzene than benzyl chloride.

4)



3, 3 -dimethyl pentan-2-ol

5) These reaction shows the selectivity of the catalyst. It is the ability of the catalyst to direct the reaction to yield particular products.

Example:

$$CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$$

$$CO + 2H_2 \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH$$

$$CO + H_2 \xrightarrow{Cu} HCHO$$

6) NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3

(a) PH_3

(b) NH_3

(c) NH_3

(d) BiH_3

---

7) Mass of glucose , $W_2 = 60g$

Molar mass of glucose , $M_2 = 180\,g\,mol^{-1}$

Mass of water , $W_1 = 250g$

$K_f = 1.86\ K\,Kg\,mol^{-1}$

Molality of the solution , $m = \dfrac{W_2 \times 1000}{M_2 \times W_1}$

$$m = \frac{60g \times 1000}{180\,g\,mol^{-1} \times 250g}$$

$$m = 1.333\,mol\,Kg^{-1}$$

Depression in freezing point , $\Delta T_f = K_f \times m$

$$\Delta T_f = 1.86\ K\,Kg\,mol^{-1} \times 1.333\,mol\,Kg^{-1}$$

$$\Delta T_f = 2.474K$$

$$\Delta T_f = 2.48\,K$$

log(1.86) = 0.2695

log(1.33) = 0.1249

antilog(0.3944)

2.479

$\therefore \quad T_f^\circ - T_f = \cancel{2.474K}\ 2.48\,K$

$273.15K - T_f = \cancel{2.474K}\ 2.48\,K$

$T_f = 273.15\,K - \cancel{2.474K}\ 2.48\,K$

$T_f = \cancel{270.676K}\ 270.67\,K$

(or)

$T_f = \cancel{-2.474^\circ c}\ -2.48\,K$

$\begin{array}{r} 273.15 \\ 2.48 \\ \hline 270.67 \end{array}$

18 $\therefore$ The freezing point of the solution is 270.67 K or $-2.48\,^\circ c$

8). (a) 2

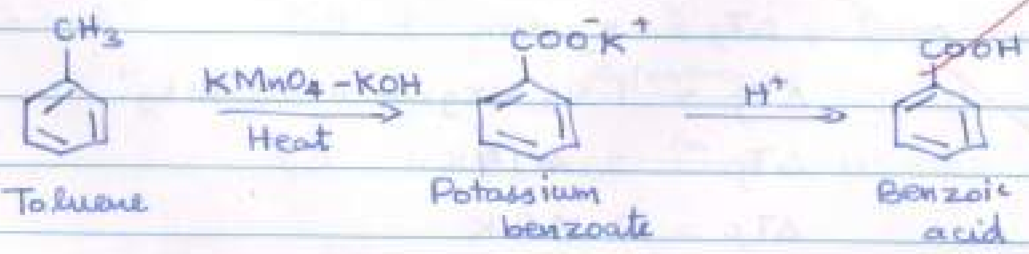
$$CH_3-\overset{H}{\overset{|}{C}}=O \xrightarrow{CH_3MgBr} \left[CH_3-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O^-\overset{+}{Mg}Br\right] \xrightarrow[-Mg(OH)Br]{H_2O / H^+} CH_3-\overset{OH}{\overset{|}{CH}}-CH_3$$

Ethanal — adduct — propan-2-ol

$$\downarrow CrO_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Propanone

(b) 

9). (a) $Fe^{2+} + MnO_4^- + H^+ \longrightarrow$

2

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^- \times 5$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(b) $MnO_4^- + H_2O + I^- \longrightarrow$

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^- \times 2$$

$$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$$

$$2MnO_4^- + I^- + H_2O \longrightarrow 2MnO_2 + IO_3^- + 2OH^-$$

10) $\frac{d[NO_2]}{dt} = 2.8 \times 10^{-3}\,Ms^{-1}$

2

$$Rate = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\therefore -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

$$\frac{d[N_2O_5]}{dt} = -\frac{\cancel{2}^{1}}{\cancel{4}_{2}} \times \cancel{2.8}^{1.4} \times 10^{-3}\,Ms^{-1}$$

$$\frac{d[N_2O_5]}{dt} = -1.4 \times 10^{-3}\ Ms^{-1}$$

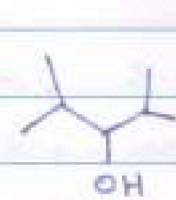
∴ The rate of disappearance of N_2O_5 is $1.4 \times 10^{-3}\ Ms^{-1}$

3

11) (a)

(i)

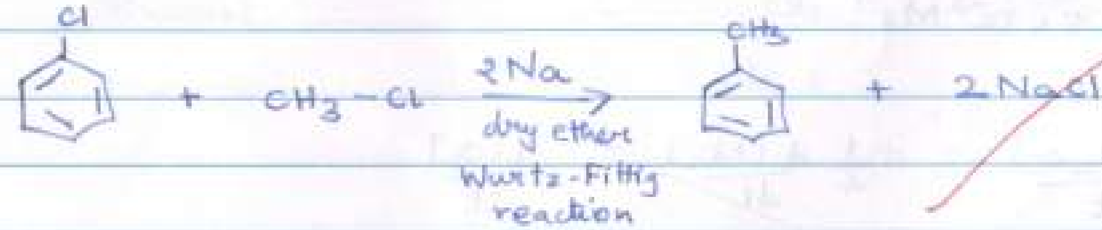
and



(ii)

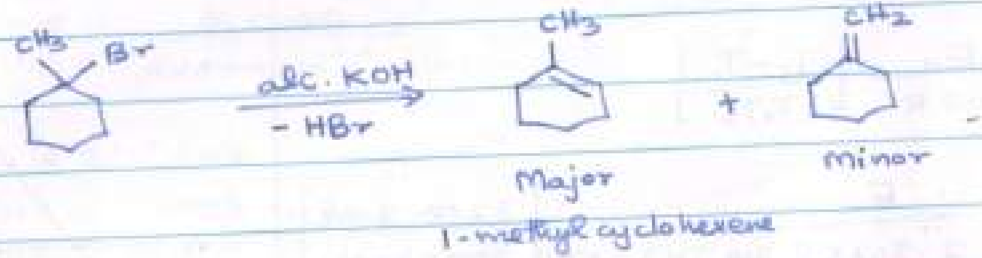
∴ (i) is chiral due to presence of one asymmetric carbon.

(b)

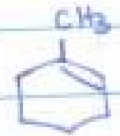


→ Methyl benzene or Toluene

(c)



The major product is



1-methyl cyclohex-1-ene

12) At 300K,

Half life of the reaction, $T_{1/2}(300K) = 40$ mins

Rate constant, $K_1 = \frac{0.693}{T_{1/2}} = \frac{0.693}{40 \text{ mins}}$ 0.17325

$$K_1 = 0.017325 \text{ mins}^{-1}$$

3

At 320 K,

Half life of the reaction, $T_{1/2}(320) = 20$ mins

Rate constant $k_2 = \frac{0.693}{20 \text{ mins}^{-1}}$ 0.2465 $= 0.02465 \text{ mins}^{-1}$

We have:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log \frac{0.02465}{0.01\cancel{7}325} = \frac{E_a}{2.303 \times 8.314\,JK^{-1}mol^{-1}}\left[\frac{320K-300K}{300K \times 320K}\right]$$

$$E_a = \frac{(\log 4 - \log 2) \times 2.303 \times 8.314\,JK^{-1}mol^{-1} \times 300 \times \overset{16}{\cancel{320}}}{\cancel{20}}$$

$$E_a = 0.3011 \times 2.303 \times 8.314 \times 300 \times 16 \ J/mol$$

$$E_a = 2.767 \times 10^4 \ J/mol$$

$$\boxed{E_a = 27.67 \ kJ/mol}$$

$\therefore$ The activation energy of the reaction is 27.67 kJ/mol.

0.6021
0.3010
0.3011

log 0.3011 = $\bar{1}$.4787
log 2.303 = 0.3623
log 8.314 = 0.9198
log 300 = 2.4771
log 16 = 1.2041
4.4420

2767 x10^4

---

13). Edge length, $a = 400\,pm = 400 \times 10^{-10}\,cm$

Atomic Mass, $M = 40\,g\,mol^{-1}$

For f.c.c structure, number of atoms per unit cell, $Z = 4$

Density, $d = \frac{ZM}{a^3 N_A}$

$$d = \frac{4 \times 40\,g\,mol^{-1}}{(4 \times 10^{-8})^3\,cm^3 \times 6.022 \times 10^{23}\,mol^{-1}}$$

3

$$d = \frac{4 \times 40}{4 \times 4 \times 4 \times 10^{-24} \times 6.022 \times 10^{23}} \ g\,cm^{-3}$$

$$d = \frac{100}{4 \times 6.022} \ g\,cm^{-3}$$

$$\boxed{d = 4.152 \ g\,cm^{-3}}$$

$\log 25 = 1.3979$
$\log 6.022 = 0.7797$
0.6182
4.152

$\log 4 = \bar{1}.6021$ (0.6021)
$\log 4.152 = 0.6182$
$\bar{1}.9839$
0.9636

$\log 0.9636 = \bar{1}.9839$
$\log 64 = (-23)\ 1.8062$
$\bar{2}.1777$
1.505×10^{-2}

Volume of one unit cell $= a^3$

$$= (4 \times 10^{-8})^3 \ cm^3$$

$$= 64 \times 10^{-24} \ cm^3$$

Volume of 4g of X $= \frac{\text{Mass}}{\text{Density}}$

$$= \frac{4g}{4.152\,g\,cm^{-3}}$$

$$= 0.9636 \ cm^3$$

Number of unit cells $= \frac{\text{Volume of 4g}}{\text{Volume of unit cell}}$

$$= \frac{0.9636 \ cm^3}{64 \times 10^{-24} \ cm^3}$$

$$\boxed{= 1.505 \times 10^{22} \text{ unit cells}}$$

∴ The density of X is $4.152\ g\,cm^{-3}$ and the number of unit cells in 4g of X is 1.505×10^{22} unit cells.

14). (a) The measurement of osmotic pressure is ~~prefferred~~ preferred for the determination of molar masses of macromolecules such as proteins and polymers because

3

(i) Molarity is used instead of molality.

(ii) Observation is made around room temperature. Since, biomolecules are unstable at high temperature, this is best method.

(iii) Its value is large even for very dilute solution. So, polymers having poor solubility can use this method to find their molar mass.

(b) Solute + Solvent $\rightleftharpoons$ Solution + Heat

Dissolution is an exothermic process and it is in equilibrium. So, according to Le Chatelier's principle, the solubility increases with decrease

in temperature. So, more oxygen dissolves in water at low temperature.
So aquatic animals are more comfortable is cold water than in warm water.

(c) Elevation in boiling point is a colligative property and depends only on number of solute particles and not on their nature.
KCl is a strong electrolyte and dissociates completely into K^+ and Cl^-. Thus 1 M KCl produces two ions which can be considered as double the particles (nearly).
But ~~gluco~~ sugar does not undergo dissociation.
Thus number of particles in 1M KCl is nearly double that of 1 M sugar solution.
Since, Elevation in boiling point $\propto$ Number of solute particles
The Elevation in boiling point is also nearly double for 1MKCl solution than 1M sugar solution.

15). (a) When freshly prepared precipitate of $Fe(OH)_3$ is shaken with a small amount of $FeCl_3$ solution, peptization takes place and a reddish brown coloured colloid is formed. It adsorbs Fe^{3+} ions and becomes positively charged.

3

(b) When persistent dialysis is carried out, traces of electrolyte is also removed, the colloidal particles lose ~~loose~~ their charge and coagulation or precipitation takes place.

(c) When an emulsion is centrifuged, demulsification takes place and the two liquids separate out.

16). EXTRACTION OF GOLD:

3

The ore containing the gold is leached in aqueous NaCN in free access of air to form a complex.

$$4Au + 8CN^- + 2H_2O + O_2 \longrightarrow 4[Au(CN)_2]^- + 4OH^-$$

Then Zn is used to reduce this complex to give pure gold.

$$2[Au(CN)_2]^- + Zn \longrightarrow \underset{\text{Pure gold}}{2Au} + [Zn(CN)_4]^{2-}$$

Dilute NaCN is used as a complexing and oxidising agent which oxidises Au to Au^+.
Zn is used as a reducing agent to reduce Au^+ to pure gold.

17) The possible isomers of a carbonyl compound with molecular formula C_4H_8O are

I: $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

II: $CH_3-CH_2-CH_2-CHO$

III: $CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-CHO$

Since isomer (B) does not give Tollen's test. It must be a Ketone and it gives iodoform test, so it is a methyl Ketone. ∴ Structure of B is I.

3

(A) and (C) give positive Tollen's test, so both are aldehyde.
Since (A) and (B) give same product on reduction with $Zn(Hg)/conc.\ HCl$

$$\underset{(B)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3} \xrightarrow[HCl]{Zn(Hg)} \underset{(D)}{\cancel{CH_3}CH_2CH_2CH_3}$$

$$\underset{(A)}{CH_3-CH_2-CH_2-CHO} \xrightarrow[HCl]{Zn(Hg)} \underset{(D)}{CH_3CH_2CH_2CH_3}$$

∴ Structure of (A) is II

∴ Structure of (C) is III

(a) (A) → $CH_3-CH_2-CH_2-CHO$
Butanal

(B) → $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$
Butan-2-one

(C) → ${}_3CH_3-{}_2\underset{\underset{CH_3}{|}}{CH}-{}_1CHO$

2-methyl propanal

(a) $\rightarrow$ $CH_3-CH_2-CH_2-CH_3$
Butane

(b) (B) $\rightarrow$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ is least reactive towards HCN addition.

18). (a) Bithional is added to soaps to ~~enhance its~~ impart antiseptic properties to soaps.

(b) 2-3 per cent of iodine in alcohol - water mixture is called tincture of iodine.
It is used as an antiseptic for wounds and cuts.

(c) Sodium benzoate acts as a food preservative.

19). (a) $Fe_4[Fe(CN)_6]_3$

(b) Ionisation isomerism is exhibited by the complex
$[Co(NH_3)_5Cl]SO_4$

(c) $[CoF_6]^{3-}$

Oxidation state of Co = +3

Electronic configuration:

Co – $3d^7 4s^2$

Co^{3+} – $3d^6$

F^- is a weak ligand, so it forms outer orbital high spin complex.

	$3d$	$4s$	$4p$	$4d$
	$3d^7$	$4s^2$	$4p^0$	$4d^0$
Co →	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{}\boxed{}\boxed{}$	$\boxed{}\boxed{}\boxed{}\boxed{}\boxed{}$
	$3d^6$	$4s^0$	$4p^0$	$4d^0$
Co^{3+} →	$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$	$\boxed{}$	$\boxed{}\boxed{}\boxed{}$	$\boxed{}\boxed{}\boxed{}\boxed{}\boxed{}$

$\underbrace{4s\ 4p\ 4d}_{sp^3d^2 \text{ hybridisation}}$

$3d^6$

$[CoF_6]^{3-}$ → $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\boxed{xx}\boxed{xx}\boxed{xx}\boxed{xx}\boxed{xx}\boxed{xx}$

$\uparrow F^-$ $\uparrow F^-$ $\uparrow F^-$ $\uparrow F^-$ $\uparrow F^-$ $\uparrow F^-$

3

Hybridisation – sp^3d^2

Number of unpaired electrons – 4

20) (a) POLYSACCHARIDES:

Carbohydrates that yield more than ten (or a large number) of monosaccharide units on hydrolysis are called as polysaccharide.

Example: Starch, Cellulose, Glycogen.

These are also called non-sugars.

(b) DENATURED PROTEIN:

Proteins in biological system with unique three dimensional structure and biological activity is called native protein.

When a protein in its native form is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds get disturbed.

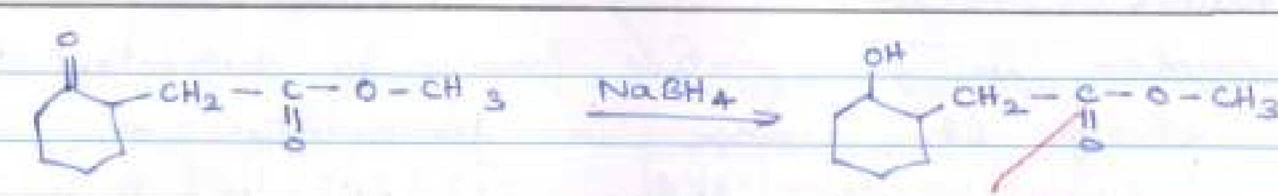
Due to this, globules unbind and helix get uncoiled and protein loses its biological activity.

This protein is called denatured protein and the phenomenon is called denaturation of proteins.

During denaturation, secondary and tertiary structure are destroyed but primary structure remain intact.
Example: Curdling of milk due to lactic acid, coagulation of egg while heating it.

(c) ESSENTIAL AMINO ACIDS:
The amino acids which can not be produced in human body and must be taken through diet are called as essential amino acids.
Example: Valine, Leucine.

21) (i)



(ii)

(iii) 

Phenol Iodoethane

3

22) (a) $Mn^{3+} \rightarrow 3d^4$ $Fe^{3+} \rightarrow 3d^5$

$Mn^{2+} \rightarrow 3d^5$ $Fe^{2+} \rightarrow 3d^6$

Mn has very high third ionisation enthalpy due to stable d^5 (half-filled) configuration of Mn^{2+}. So oxidation to Mn^{3+} is difficult.

On the other hand Fe^{2+} readily loses one electron to form Fe^{3+} due to stable half-filled d^5 electronic configuration.

Thus E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(b) Iron (Fe) $\rightarrow 3d^6 4s^2$ $\rightarrow$ 4 unpaired electrons

Copper (Cu) $\rightarrow 3d^{10} 4s^1$ $\rightarrow$ 1 unpaired electron

In iron, there is contribution of 4 unpaired electron from 3d orbital for bonding while in copper

there is only one unpaired electron in 4s orbital.
Greater the number of unpaired electrons, greater will be the interatomic interaction, stronger will be the metallic bonding and higher the enthalpy of atomisation.
Thus, Iron has higher enthalpy of atomisation than that of copper.

(c) $Sc^{3+} \rightarrow 3d^0$
$Ti^{3+} \rightarrow 3d^1$
Sc^{3+} does not have any unpaired electron in its d-orbital and thus no d-d transition takes place and hence it is colourless.
While Ti^{3+} has one unpaired electron which can undergo d-d transition and absorb light in visible region and thus become coloured.
Thus Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured.

3

23) (a) Social responsibility and environmental concern.

(b)

LOW DENSITY POLYTHENE	HIGH DENSITY POLYTHENE
* Low density polythene is slightly or heavily branched.	* High density polythene is linear in its structure.
* It is flexible	* It is hard
* It is used in making squeeze Bottles, flexible pipes.	* It is used in making dustbins

(c) Because polythene bags are made up of non biodegradable polymer and they cause environmental pollution. They spoil soil fertility, dangerous to aquatic lives, harmful if consumed by animals, etc.
So, government have banned polythene bags in many areas, so Shyam who is a good citizen refused to

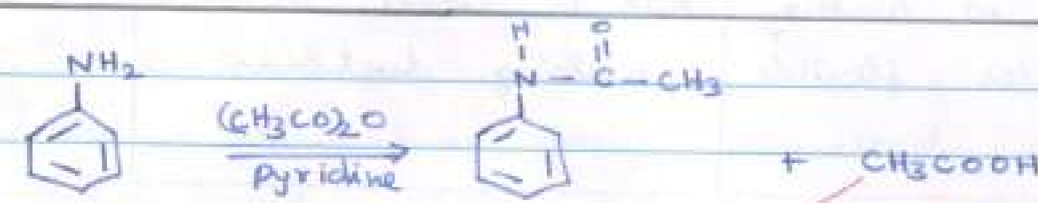
accept it.

(d) Biodegradable polymer is a polymer which can be degraded by the micro-organisms within a certain time, so they don't cause any damage to the environment.

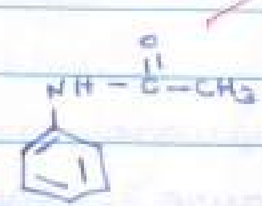
Example: PHBV – poly β-hydroxy butyrate –co-β-hydroxy valerate and nylon-2-nylon-6.

4

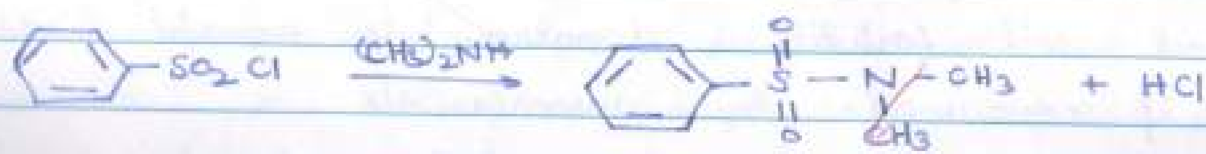
24) (a) (i)



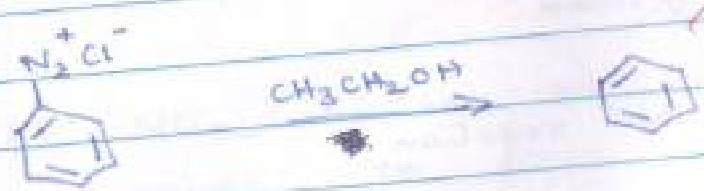
(ii) The main product is



(ii)



∴ The main product is 

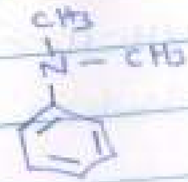
(iii) 

+ CH_3CHO + N_2 + HCl

∴ The main product is  (benzene).

(b) 

Aniline



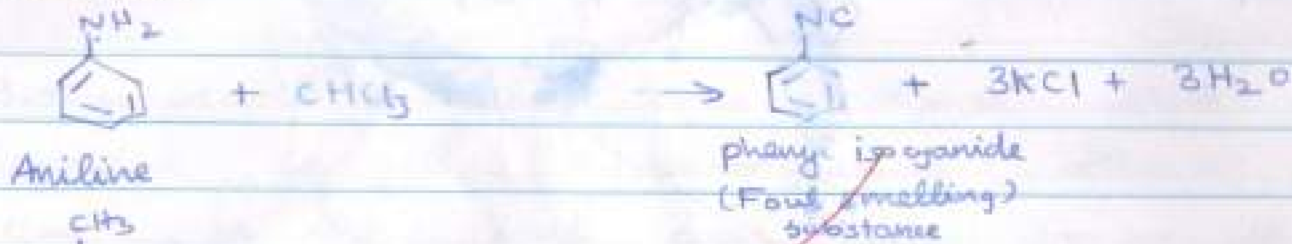
N,N-dimethyl aniline

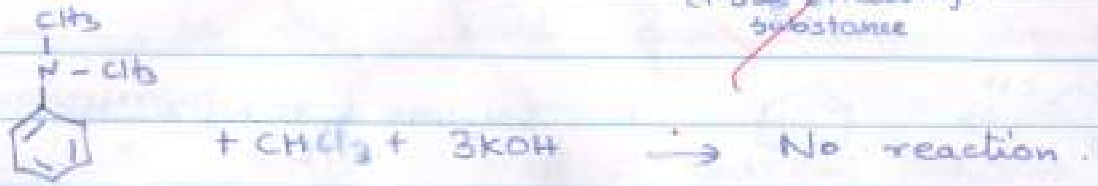
Distinguishing Test: Isocyanide Test / Carbylamine Reaction

Test: Treat the compound with chloroform in the presence of KOH.

Aniline forms a foul smelling substance while N,N-dimethyl aniline does not.

Reaction:





(c) Increasing order of pK_b:

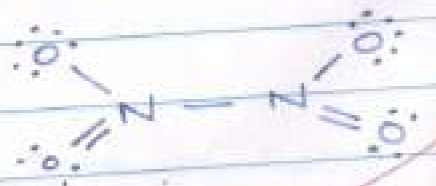
$C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$

25) (a) (i) (A) – NO_2

(B) – N_2O_4

(ii) Structure of A (NO_2):

Structure of (B) – N_2O_4:



(iii) (A) – NO_2 is an odd electron species, so on cooling it dimerises to form (B) – N_2O_4 which is a solid.

$$2\dot{N}O_2 \underset{hot}{\overset{cool}{\rightleftharpoons}} \underset{\text{(solid)}}{N_2O_4}$$

(b) Decreasing order of their reducing character:

$$HI > HBr > HCl > HF$$

(c) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$

5

26). (a) $Sn_{(s)} / Sn^{2+} (0.004 M) // H^+ (0.020 M) / H_{2(g)} (1 bar) / Pt_{(s)}$

· $E^\circ_{Sn^{2+}/Sn} = -0.14V$

Cell reaction:

Anode: $Sn_{(s)} \longrightarrow Sn^{2+}_{(aq)} + 2e^-$ $E^\circ_{Sn^{2+}/Sn} = -0.14V$

Cathode: $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ $E^\circ_{H^+/H_2} = 0.00V$

Overall reaction: $Sn_{(s)} + 2H^+_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + H_{2(g)}$

Number of electrons, $n = 2$.

$E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{Anode}$

$E^\circ_{cell} = 0.00V - (-0.14V)$

$E^\circ_{cell} = 0.14V$

From Nernst Equation,

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[Sn^{2+}]}{[H^+]^2}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[H^+]^2}$$

$$\begin{array}{r} 0.14\cancel{00} \\ 0.0295 \\ \hline 0.1105 \end{array}$$

$[Sn^{2+}] = 0.004\,M$

$[H^+] = 0.02\,M$

$E_{cell} = 0.14 - \frac{0.059}{2} \log \frac{0.004}{(0.02)^2}$

$E_{cell} = 0.14 - \frac{0.059}{2} \log \frac{0.004}{0.0004}^{10}$

$E_{cell} = 0.14 - \frac{\overset{0.0295}{0.059}}{\cancel{2}} \times 1$

$E_{cell} = 0.14 - 0.0295$

$E_{cell} = 0.1105\,V$

(or) $E_{cell} = 0.11\,V$ (approx.)

Thus the emf of the cell is 0.11V.

(b) (i) Cl_2 gas is liberated instead of O_2 due to overpotential. Some electrochemical process although feasible, they are kinetically very slow, that they don't seem to take place. So, extra potential called overpotential is applied which make such process more difficult to occur.

At anode: $Cl^-_{(aq)} \longrightarrow \frac{1}{2} Cl_{2(g)} + 1e^-$

$OH^-_{(aq)} \longrightarrow OH^{\cdot} + 1e^-$

$4OH^{\cdot} \longrightarrow O_{2(g)} + 2H_2O_{(l)}$

Actually lower E° value is preferred. So O_2 should be evolved but due to over potential, Cl^- is oxidised to Cl_2.

(ii) On dilution, the number of ions that carry the current per unit volume decreases, so conductivity of CH_3COOH decreases.