Q. No. 2 Part (i) # THERMAL DECOMPOSITION OF NITRATES

a) $LiNO_3$

$LiNO_3$ decomposes to lithium oxide, nitrogen dioxide and oxygen.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

Lithium nitrate — Lithium oxide — nitrogen dioxide — oxygen

b) $NaNO_3$

$NaNO_3$ decomposes on heating to corresponding nitrite.

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$

Sodium nitrate — Sodium nitrite — oxygen

c) $Mg(NO_3)_2$

It decomposes on heating to MgO, NO_2 and oxygen.

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

Q. No. 2 Part (ii) **ELECTRONIC CONFIGURATION**

Chromium (24) :-

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$

$[Ar]\ 4s^1, 3d^5$

[Ar] | 1 | 1 | 1 | 1 | 1 | 1 |

Copper (29) :-

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

$[Ar]\ 4s^1, 3d^{10}$

[Ar] | 1 | 1↓ | 1↓ | 1↓ | 1↓ | 1↓ |

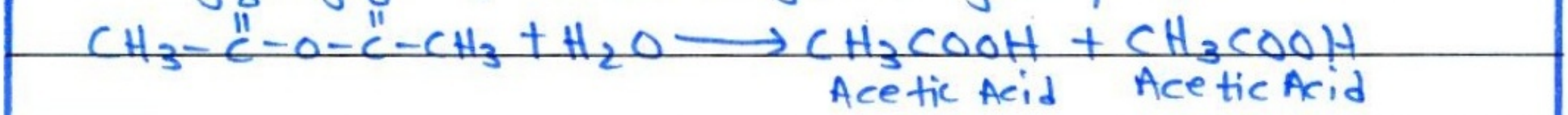
Reason :-

These electronic configuration violate Aufbau's principle because extra stability is possessed/attained by half filled or completely filled d orbital ($3d^5$/$3d^{10}$)

Q. No. 2 Part (iii) **REACTION OF ACETIC ANHYDRIDE**

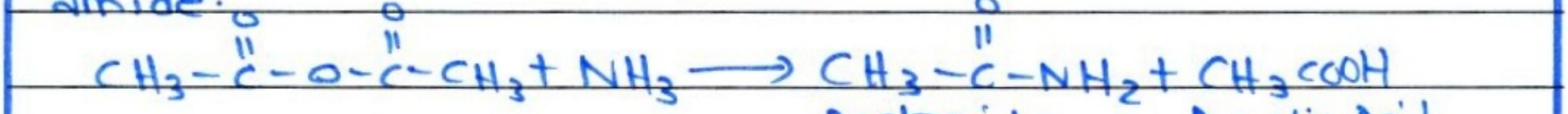
a) H_2O

Hydrolysis of acetic anhydride give parent acids.



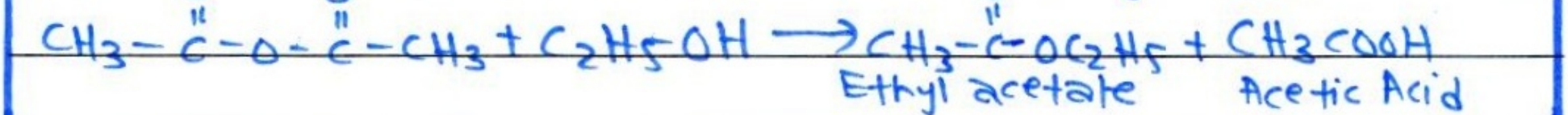
b) NH_3

Acetic anhydride reacts with NH_3 to give acid and amide.



c) C_2H_5OH

Acetic anhydride react with ethanol to give ester.



Q. No. 2 Part (iv) Aldehyde and ketone can by distinguished by i) Fehling solution Test ii) Tollen's test.

Fehling solution Test :- Fehling solution is a mild oxidizing agent made of Cu^{2+} ions, basic solution, sodium/potassium Tartarate. Ketone don't give this test. Aldehyde on reaction with it form brick red ppt of Cu_2O. CH_3CHO is oxidized to CH_3COO^-, Cu^{2+} is reduced to Cu^+.

$$CH_3CHO + Cu^{2+} + 2OH^- + \underset{\text{Tartarate}}{\text{sodium}} \longrightarrow CH_3COO^- + \underset{\text{(red ppt)}}{Cu_2O} + H_2O$$

Tollen's Test :- Tollen test consist of solution of silver nitrate (basic solution), ammonia which on reaction with aldehyde form silver mirror (Ag). It is also called silver mirror test.

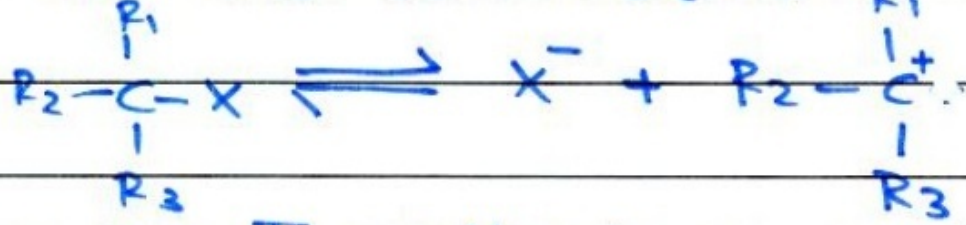
$$CH_3CHO + 2[Ag(NH_3)_2]^+ + OH^- + H_2O \longrightarrow \underset{\text{mirror}\downarrow}{2Ag(s)} + 2NH_3 + 2NH_4^+ + CH_3COO^-$$

Ketones don't give this test.

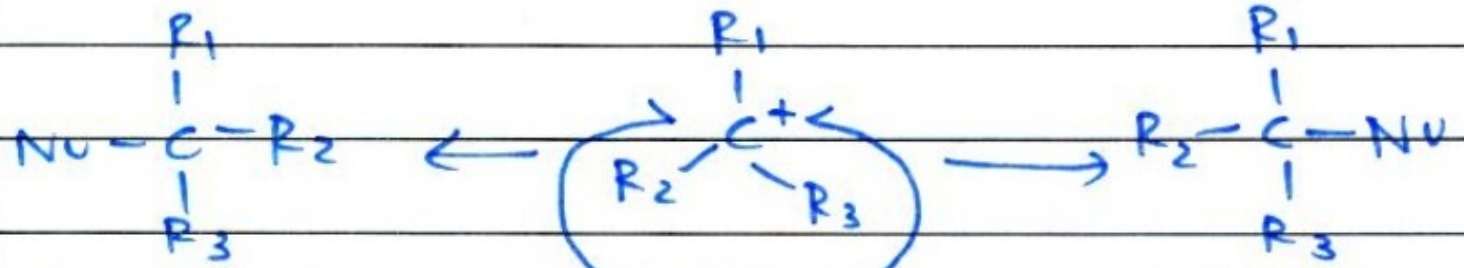
Q. No. 2 Part (v) **MECHANISM OF SN_1 reaction :-**

This reaction takes place in two steps. 1st is slow and rate determining step and 2nd is the fast step.

Step 1 :- Alkyl halide ionizes reversibly into halide ion and carbocation.



Step 2 :- The attack on nucleophile from either side to form the product.



Inversion of configuration

retention of configuration

Order of reaction = 1 ; Rate = $k[R-X]$

Q. No. 2 Part (vi) **CHROMATE-DICHROMATE CHEMISTRY**

Chromates (CrO_4^{2-}) are highly soluble in water resulting in a brilliant yellow solution. If a small amount of acid is added in solution, dichromate ions ($Cr_2O_7^{2-}$) are formed having orange colour, an equilibrium is attained.

$$\underset{\text{(yellow)}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{(orange)}}{Cr_2O_7^{2-}} + H_2O$$

If a small amount of base is added in solution, the concentration of H^+ ions decreases which shifts the reaction towards backward direction. Hence chromate (CrO_4^{2-}) are formed again.

$$\underset{\text{(orange)}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{(yellow)}}{2CrO_4^{2-}} + H_2O$$

Q. No. 2 Part (vii) **GREEN HOUSE EFFECT**

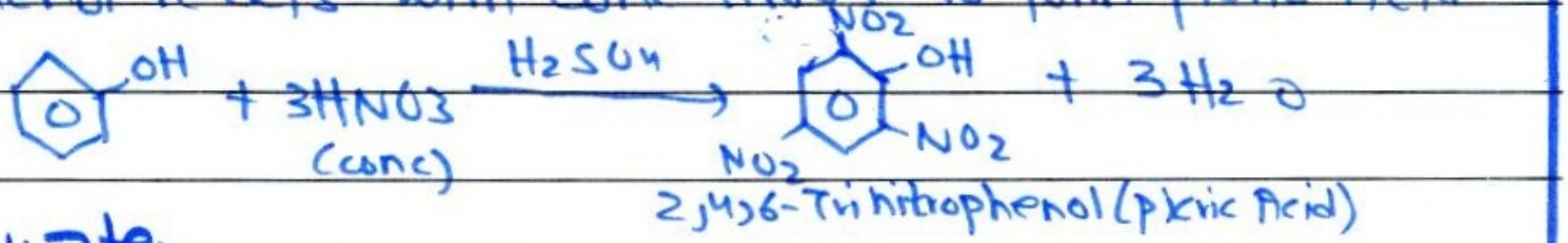
Heat radiations coming from sun are of shorter wavelength, cause atoms, molecules on earth surface to vibrate and radiate heat and IR radiations of longer wavelength. Some substances in atmosphere, CO_2, H_2O absorb these IR radiations of longer wavelength and result in the rise of temperature. Some energy must be emitted by the earth but CO_2, H_2O act as a thick blanket and prevent escaping of these radiations producing a warming effect.

Definition :- "The absorbtion of Radiations (heat and IR of longer wavelength) on earth by CO_2 and H_2O present in the atmosphere is known as greenhouse effect." It produce warming effect.

Q. No. 2 Part (viii) **REACTION OF PHENOL**

i) Conc. HNO_3

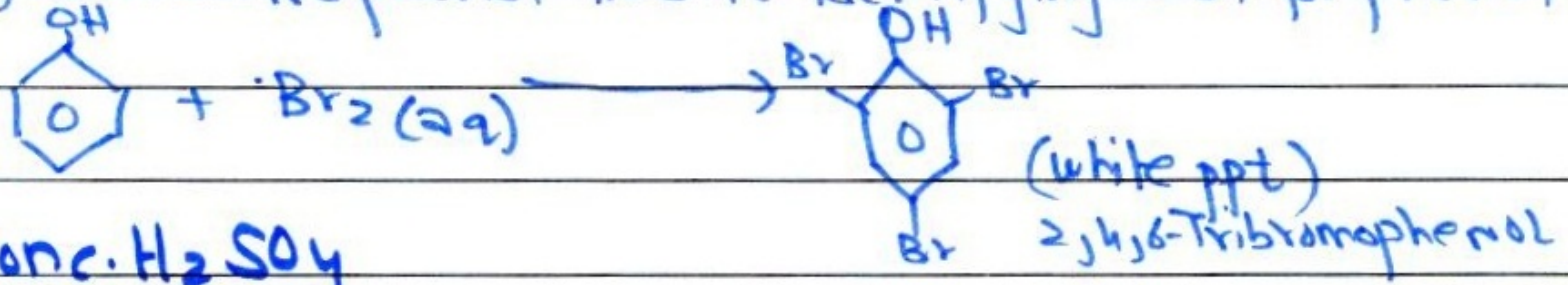
phenol reacts with conc. HNO_3 to form picric Acid.



2,4,6-Trinitrophenol (picric Acid)

iii) Br_2 water

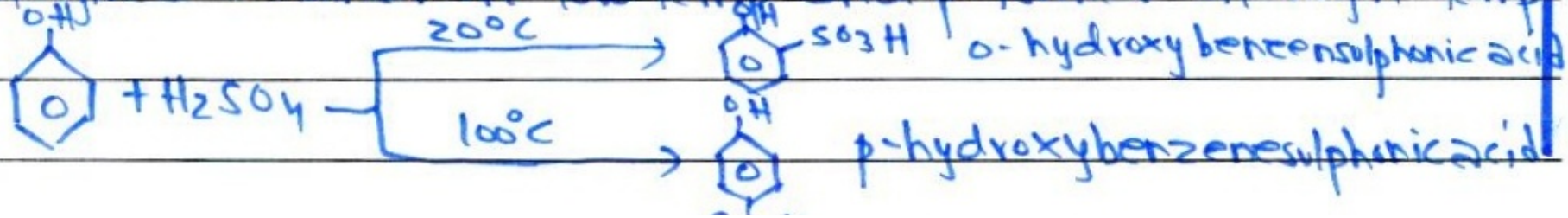
phenol reacts with bromine water to give white ppt of 2,4,6-Tribromophenol. This is identifying test for phenol.



(white ppt)
2,4,6-Tribromophenol

iii) Conc. H_2SO_4

It gives o-isomer at low temp and p-isomer at high temp



o-hydroxybenzenesulphonic acid

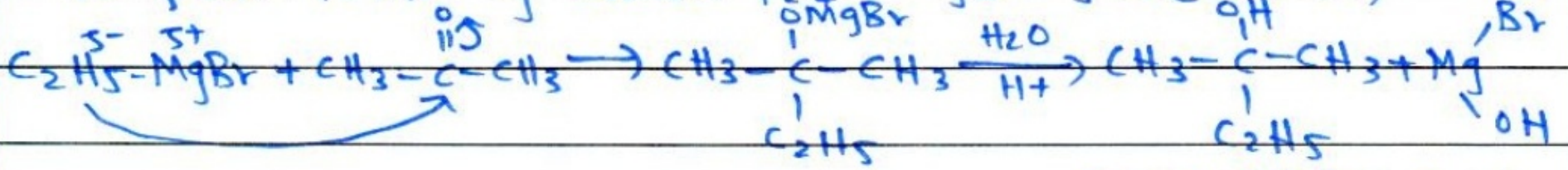
p-hydroxybenzenesulphonic acid

Q. No. 2 Part (ix)

E_1	E_2
1) It is two step mechanism	1) It involves single step
2) First step is slow and 2nd one is fast	2) It has one step only, that is slow.
3) Rate = $k[R-X]$ depend on conc. of R-X only and nothing else	3) Rate = $k[R-X][B]$ depend on conc. of R-X and base.
4) order = 1st order because only molecule involved in RDS	4) order = 2nd order because two molecule react in RDS
5) unimolecular reaction	5) Bimolecular reaction
6) favored in polar solvent.	6) favored in nonpolar solvent

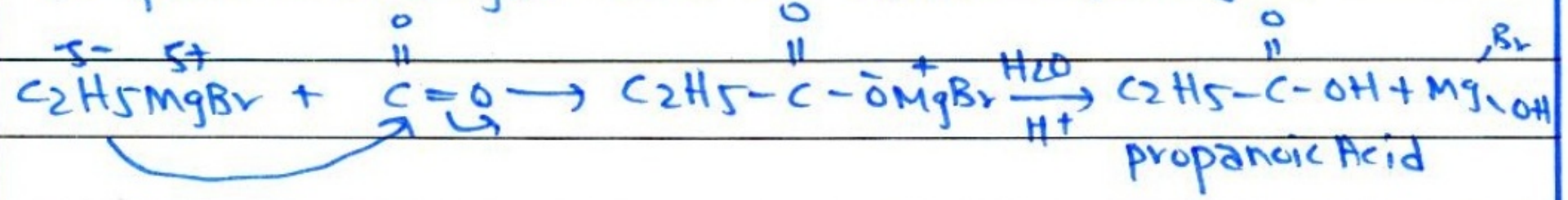
Q. No. 2 Part (x) **REACTION OF C_2H_5-MgBr**

a) Acetone: It reacts with acetone in dry ether to form tertiary alcohol on hydrolysis (acidic).



2-methyl-butan-2-ol
(Tertiary alcohol)

b) Carbondioxide: It reacts with CO_2 in dry ether to form carboxylic acid on acidic hydrolysis.



propanoic Acid

Q. No. 2 Part (xi) **REACTIVITY OF ALDEHYDE / KETONE**

Reactivity of aldehyde/ketone depends upon the substituent group:-

i) Size of substituent → large sized groups tend to sterically hinder the approach of nucleophile.

ii) electronic effect of substituent → Alkyl groups are weak electron donating groups that make carbon of $-\overset{O}{\overset{\|}{C}}-$ less electrophillic and less reactive toward nucleophile.

Acetaldehyde more reactive than acetone

$CH_3-\overset{O}{\overset{\|}{C}}-H$ → Acetaldehyde $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (Acetone)

since acetaldehyde has 1H and 1 alkyl group as compared to two alkyl groups in acetone, thus carbonyl carbon is more electrophillic in case of acetaldehyde and hence more reactive than acetone.

Q. No. 2 Part (xii) **ROLE OF CFC'S**

CFCs stand for Chloro-flouro-carbon or chloro flouro methanes e.g: Freon 1 ($CF(l_3)$ Freon 2($CF_2(l_2)$ CFCs are used as refrigerants, fire fighting reagent and solvent for clearing electrical components. Their CFCs are inert when in atmosphere. When they go to stratosphere, The CFCs absorb ultraviolet radiations of sun and decompose into free atomic radicals. The Chlorine free radical attacks ozone and breaks it into O_2.

$$CF_2Cl_2 \xrightarrow{h\nu} \dot{C}F_2Cl + \dot{C}l$$

$$Cl^{\bullet} + O_3 \longrightarrow \dot{C}lO + O_2$$

$$Cl^{\bullet}O + O_3 \longrightarrow Cl^{\bullet} + 2\,O_2$$

Thus CFCs play role in ozone depletion. HFCs should be used.

Q. No. 2 Part (xiii) **RELATIVE ATOMIC MASS**

GIVEN

Mg^{24} (78.7%) , Mg^{25} (10.13%) , Mg^{26} (11.17%)

REQUIRED

relative atomic mass = ?

FORMULA

$$\text{relative atomic mass} = \frac{M_1P_1 + M_2P_2 + M_3P_3}{100}$$

∴ M = mass
P = percentage

SOLUTION

$$\text{relative atomic mass} = \frac{M_1P_1 + M_2P_2 + M_3P_3}{100}$$

$$= \frac{24 \times 78.7 + 10.13 \times 25 + 11.17 \times 26}{100}$$

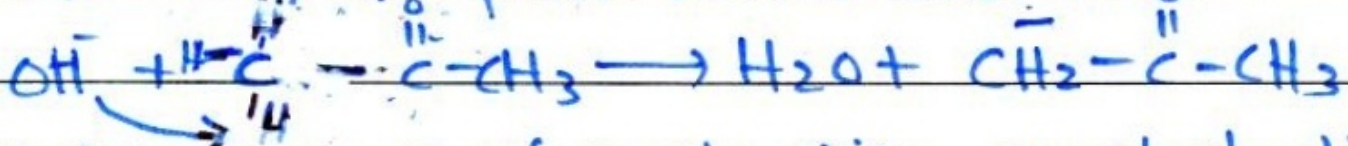
$$= 24.3247 \text{ amu}$$

RESULT

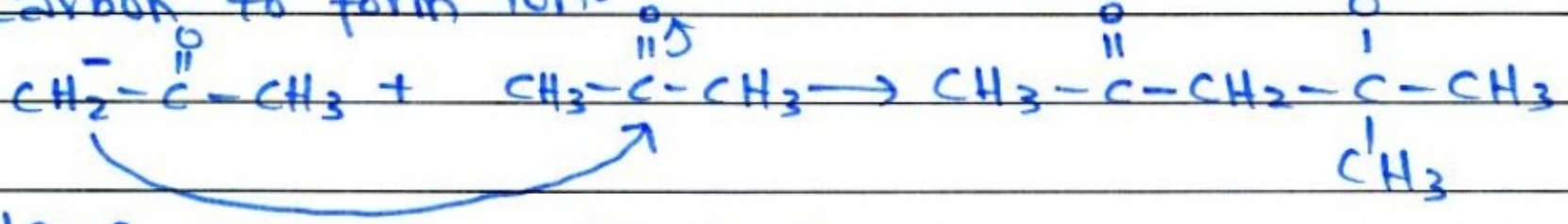
relative atomic mass of Mg is 24.3247 amu.

Q. No. 2 Part (xiv) # MECHANISM OF ALDOL

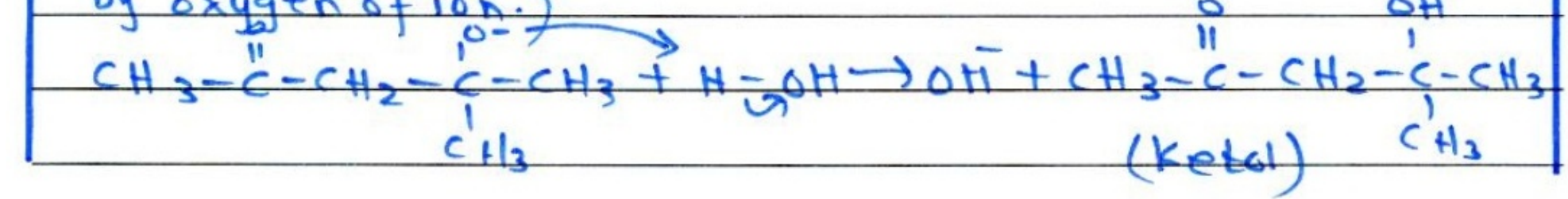
① **step 1**:- Formation of nucleophile :- The hydroxide/base attacks on the α-hydrogen (hydrogen on carbon next to C=O) to form water and ion.



② **step 2**:- Attack of nucleophile on electrophillic carbon to form ion.



③ **step 3** :- Formation of ketol (by deprotonation of water by oxygen of ion.)



OXIDES OF GROUP IV

1) CO_2

CO_2 is an acidic oxide, it reacts with water to form acid and reacts with bases due to its acidic nature

Reaction with water :-

$$CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$$

Ions are formed, since H^+ is released, hence solution is acidic.

Reaction with base :-

CO_2 reacts with bases to form carbonates and bicarbonates.

$$CO_2 + NaOH \longrightarrow NaHCO_3$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

2) GeO_2

GeO_2 is amphoteric in nature, it reacts with both, acids and bases.

Reaction with acid :-

$GeCl_4$ is formed on reaction with acid.

$GeO_2 + 4HCl \longrightarrow GeCl_4 + 2H_2O$

$GeCl_4$ can react with halide ions to form hexa halo complex.

$GeCl_4 + 2Cl^- \longrightarrow [GeCl_6]^{2-}$

Reaction with base :-

GeO_2 reacts with base to form complex.

$GeO_2 + 2NaOH + 2H_2O \longrightarrow Na_2[Ge(OH)_6]$

3) SnO_2

SnO_2 is amphoteric in nature, it reacts with both acid and base.

Reaction with acid :-

$SnCl_4$ is formed on reaction with HCl.

$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$

$SnCl_4$ can form hexahalo complex with halide ions.

$SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{2-}$

Reaction with base :-

SnO_2 react with base to form complex

$SnO_2 + 2NaOH + 2H_2O \longrightarrow Na_2[Sn(OH)_6]$

4) PbO_2

PbO_2 is also amphoteric in nature. it reacts with acid and base.

Reaction with acid :-

$$PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$$

$PbCl_4$ react with Cl^- to give complex.

$$PbCl_4 + 2Cl^- \rightarrow [PbCl_6]^{2-}$$

Since +2 oxidation state is more stable than +4 in Pb, it forms $PbCl_2$.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2.$$

reaction with base :-

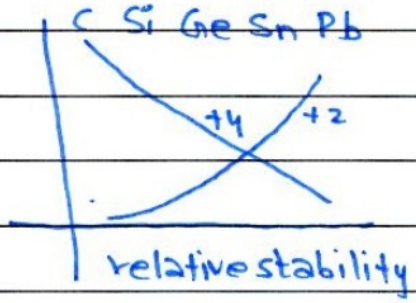
PbO_2 react with base to give a complex.

$$PbO_2 + 2NaOH + 2H_2O \rightarrow Na_2[Pb(OH)_6].$$

GROUP IV ELEMENTS

OXIDATION STATES

Carbon and Silicon show an oxidation state of +4 and other members of group show +2 oxidation number in addition to +4.



INERT PAIR EFFECT

The reason that Sn, Pb and Ge show +2 as well as +4 oxidation state is inert pair effect. The ns^2 electron pair becomes inert and doesnot take part in bond formation. This ns^2 electron pair is called inert pair and this effect as inert pair effect. Due to this effect, stability of +2 increases as we go down the group, and that of +4 decreases.

① $Ge^{+4} > Sn^{+4} > Pb^{+4}$ relative stability
② $Ge^{+2} < Sn^{+2} < Pb^{+2}$ relative stability

RELATIVE STABILITY OF +2, +4 O.N

$Ge^{+4} > Sn^{+4} > Pb^{+4}$; $Ge^{+2} < Sn^{+2} < Pb^{+2}$

Ge :-

In case of Ge, Ge^{+4} is more stable than Ge^{+2}, so Ge^{+2} is oxidized to Ge^{+4} and act as strong reducing agent, Ge^{+4} act as oxidizing agent.

$$Ge^{+2} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} Ge^{+4} \qquad (Ge^{+4} > Ge^{+2})$$

Sn :-

In case of Sn, Sn^{+4} is more stable than Sn^{+2}, so Sn^{+2} is oxidized to Sn^{+4} and act as strong reducing agent, Sn^{+4} act as oxidizing agent.

$$Sn^{+2} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} Sn^{+4} \qquad (Sn^{+4} > Sn^{+2})$$

Pb :-

In case of Pb, Pb^{+2} is more stable than Pb^{+4}. Hence Pb^{+4} is reduced to Pb^{+2} and act as strong oxidizing agent, Pb^{+2} act as reducing agent.

$$Pb^{+4} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} Pb^{+2} \qquad (Pb^{+2} > Pb^{+4}).$$

Order of stability

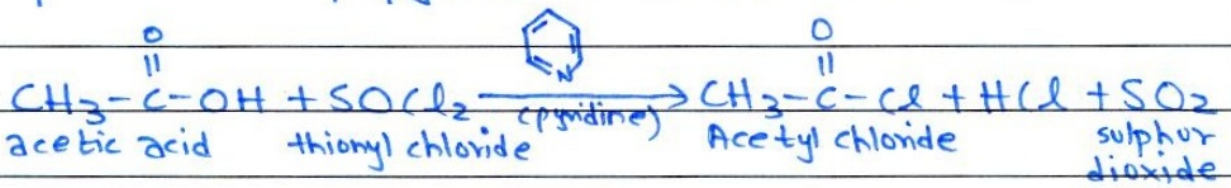
$Pb^{+2} > Pb^{+4}$; $Ge^{+2} < Ge^{+4}$; $Sn^{+2} < Sn^{+4}$

Q. No. 4 (Page 3)

ACETYL CHLORIDE

PREPARATION

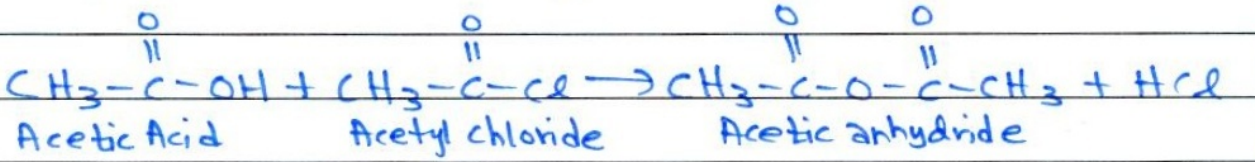
Acetyl chloride can be prepared by the reaction of acetic acid with thionyl chloride in presence of pyridine as solvent.



REACTIONS OF ACETYL CHLORIDE WITH

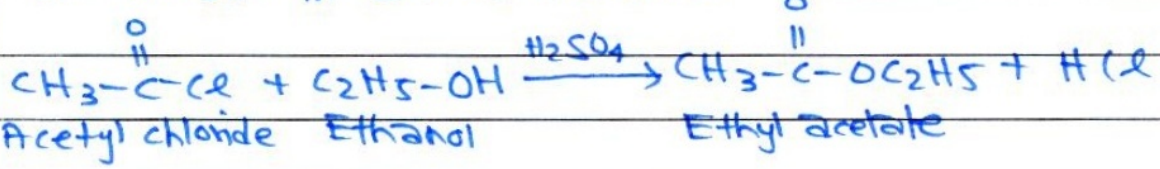
a) Acetic Acid

Acetyl chloride reacts with acetic acid to form acetic anhydride.



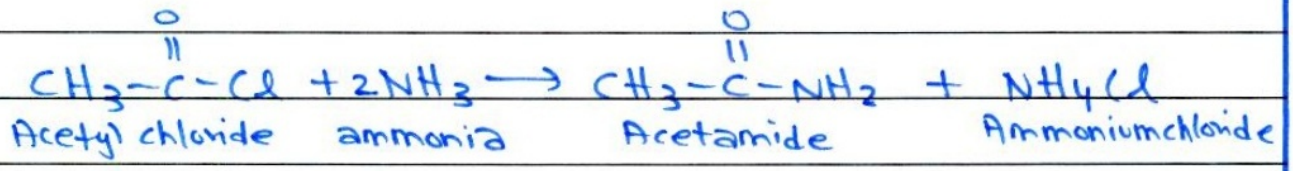
b) Ethanol

Acetyl chloride reacts with Ethanol to give an ester in acidic medium.



c) NH_3

Acetyl chloride will react with ammonia to give acetamide and ammonium chloride.



Q. No. 5 (Page 3)

MASS SPECTROMETRY

Definition

"Mass spectrometry is a technique used to detect and seperate gaseous ions according to their m/e ratio by varying the magnetic field and measurement of its intensity in form of a spectrum."

Principle

The device mass spectrometer detects the different isotopes of an element or organic molecule according to m/e ratio by variable magnetic field. It can tell about the no. of possible isotopes as well as their relative abundance. It can also be used the predict the molecular structure and weight.

Construction and Working

Mass spectrometer consist of following steps :-

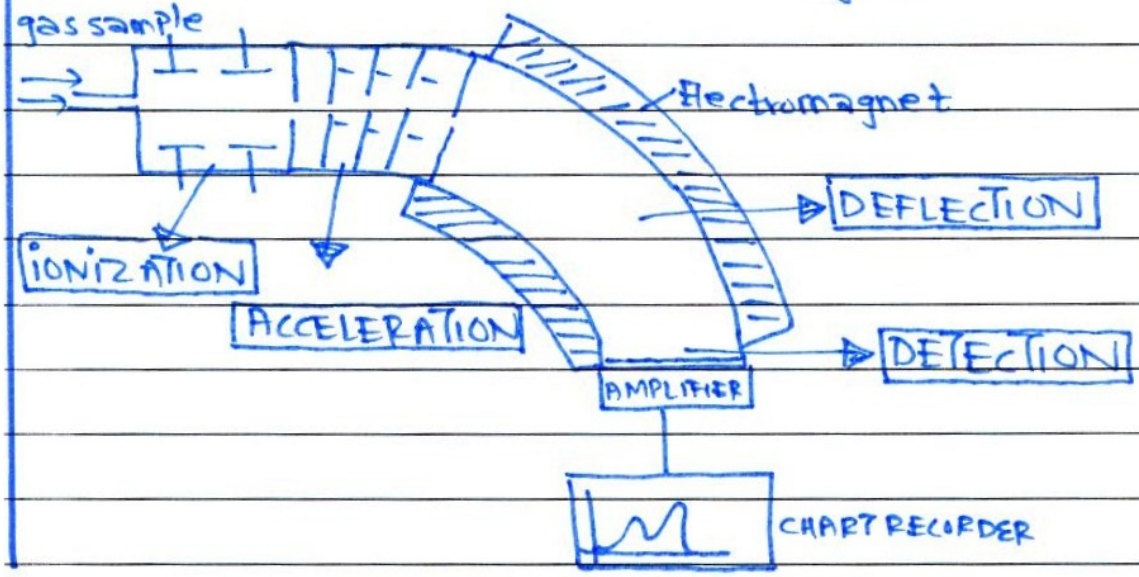
1) VAPORIZATION :- usually a gas is used as a sample but if a solid or liquid is injected it is evaporated in the evaporation chamber.

2) IONIZATION:- The conversion of gaseous atoms to gaseous ions by bombardment of high speed electrons (70 eV).

3) ACCELERATION:- The gaseous ions are accelerated by the application of suitable electric field of negative potential (500-2000V).

4) DEFLECTION:- Deflection of gaseous ions take place according to m/e ratio on application of variable magnetic field. The deflection angle (θ) is inversely proportional to the m/e ratio.

5) DETECTION:- These gaseous ions are detected when they strike the detector and are amplified. The detector can count the no. of ions striking it. Detector is in fixed position while the magnetic field is changed, so ions of particular m/e ratio can be focused into detector, that cause increase in current and signal on chart recorder.



MASS SPECTRUM

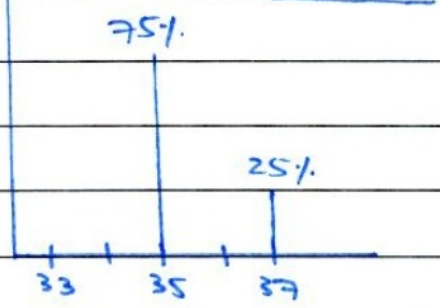
Mass spectrum tells about no. of possible isotopes (through lines) and relative abundance of isotope (through height). It can predict the relative atomic mass of element or compound.

Example

$$\text{relative atomic mass} = \frac{75 \times 35 + 25 \times 37}{100}$$

$$= 35.5 \text{ amu}$$

chlorine



+

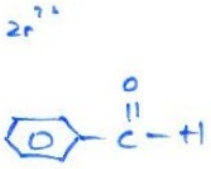
$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$

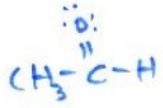
$CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$

$CO_2 + NaOH \rightarrow NaHCO_3$.

$XO_2 + 4HCl \longrightarrow XCl_4 + 2H_2O$

$XO_2 + 2NaOH + 2H_2O \longrightarrow Na_2[X(OH)_6]$

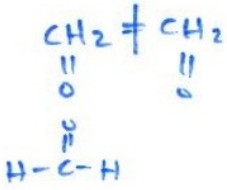




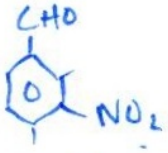
$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$

$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$



$CH_3CHO + OH^- + Cu^{2+} + \text{sodium tartarate} \longrightarrow Cu_2O +$



$H_2O + CH_3CHO + 2[Ag(NH_3)_2]^+ + OH^- \longrightarrow CH_3COO^- + Ag(s) +$