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MODULE : 3

3. GREEN CHEMISTRY AND CATALYSIS

(T+N + Reaction = 8-10 Marks)

Objective:- To promote safe environment free from pollutants.

To reduce the use of hazardous materials that deteriorate the condition of our ~~envio~~ surroundings

Major pollution in the atmosphere is because of manufacturing units and combustion of fuel (petrol, diesel, etc).

General Reaction of manufacturing of any chemical:-

$$\underbrace{A + B + C}_{\text{Reactants}} \xrightarrow{X \rightarrow \text{Catalyst}} \underbrace{P}_{\text{Product}} + \underbrace{D}_{\text{By product}}$$

During manufacturing of any compound, one should follow 12 principles of Green Chemistry:-

1. Prevention of waste :- (Try to have 100% reaction By product should not be formed) — P
2. (Numerical) Maximize % Atom Economy — M
3. Non Hazardous chemical or Raw material — N
4. Safer Chemicals: — S
5. Auxiliary Substance: — (Inorganic Solvent) — A
6. Energy Efficiency — E
7. Renewable Feedstock — R
8. Avoid d
   Eg:-
9. Use
10. Deg
11) New
12) Acc
(wa
App
Cer
* Num
%

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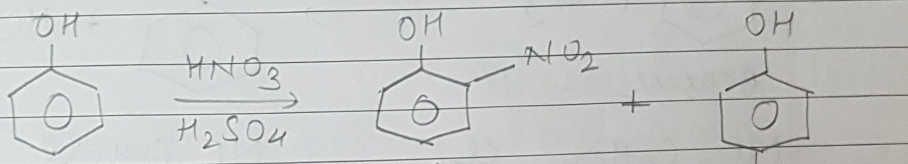
8. Avoid derivatisation

Eg:-



(0%) ✗ (100%) ✓

This should be formed in minimum amount

9. Use of Catalyst in stoichiometric amount

10. Degradable product

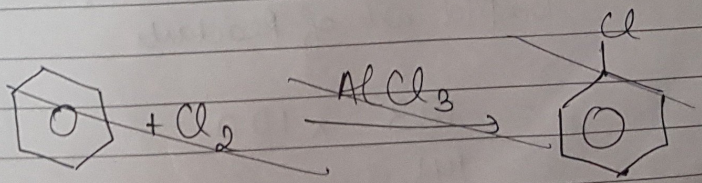
11) New Analytical Method

12) Accidental prevention

(Way to remember: Prime Minister Need Some Applied Engineering Research Development Center to Develop National Asset)

* Numerical based on % atom economy.

% Atom Economy = $\frac{\text{Molecular weight of product}}{\text{Total M.W of Reactants}} \times 100$



MF :- Molecular Formula

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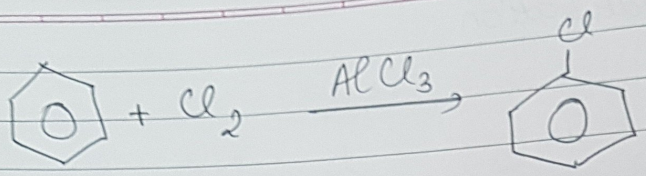


Benzene

MF = C_6H_6 Cl_2 MF = C_6H_5Cl

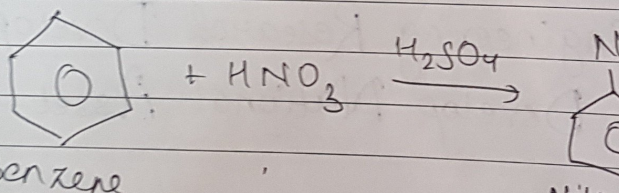
MW = 78 71 MW = 112.5

$$\% AE = \frac{\text{Mol wt of Products}}{\text{Total mol wt of Reactants}} \times 100$$

$$= \frac{112.5}{(78+71)} \times 100$$

$$= \frac{112.5}{149} \times 100$$

$\therefore \%.A.E = 75.5\%.$



Benzene

MF = C_6H_6 MF = HNO_3 MF = $C_6H_5NO_2$

MW = 78 MW = 63 MW = 123

Nitrobenzene

$$\therefore \%.A.E = \frac{\text{Mol wt of Products}}{\text{Total Mol wt of Reactants}} \times 100$$

$$= \frac{123}{141} \times 100$$

$\%.A.E = 87.23\%.$

227

93 + 134 = 135

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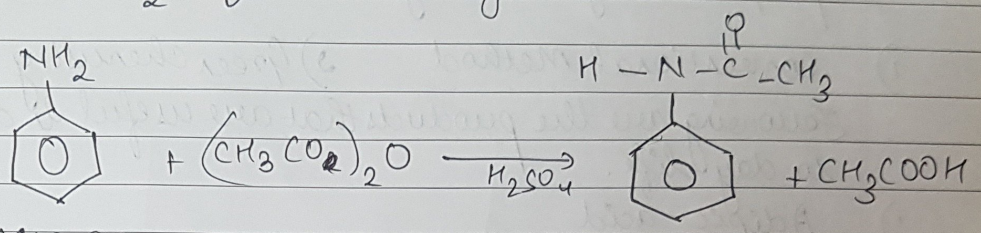
Q Aniline on acetilation using acetic anhydride $(CH_3CO)_2O$ gives N-acetyl aniline



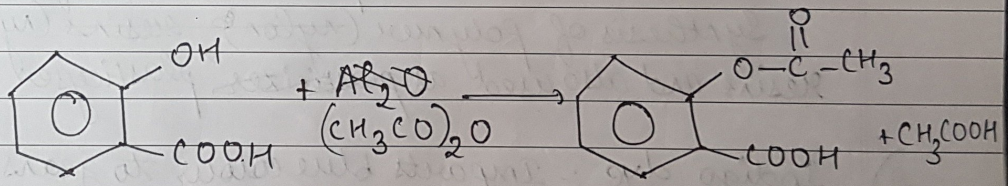
MW = 93 MW = 102 MW = 135

$$\% A.E = \frac{135}{93+102} \times 100$$

$$= 135/195 \times 100$$

$$= 69.23\%.$$

Q



S.A. Aspirin / Acetyl S.A

M.W = 138 MW = 102 M.W = 180

$$\% A.E = \frac{180}{138+102} \times 100$$

$$= \frac{180}{240} \times 100$$

$$= 75\%.$$

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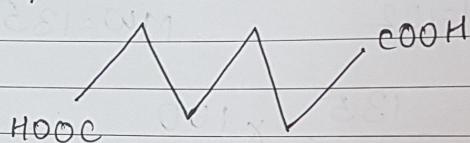
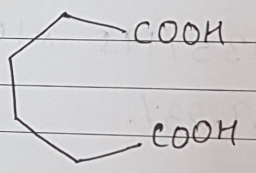
Commercial useful Chemical products can be prepared by 2 ways:-

1) Conventional Method 2) Green Chemistry Method

Following are the products that are useful in day to day life.

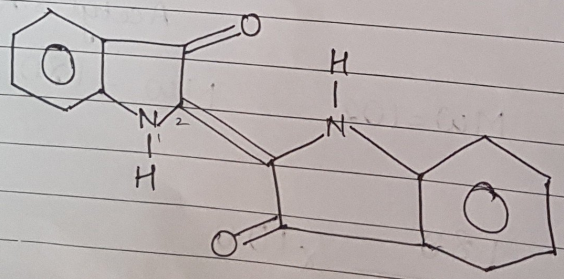
1) Adipic acid



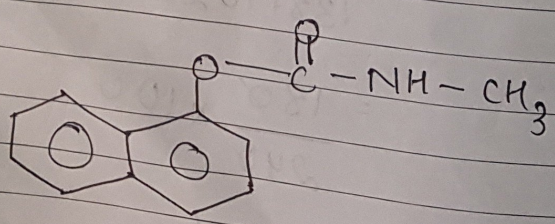


Uses:- Raw material (Adipic acid) used for Synthesis of polymer (~~nylon~~ ~~resins~~ (nylon 6,6), resins and also used as ~~plasticizer~~, plasticyser.

2) Indigo dye :- Imparts blue colour to jeans.

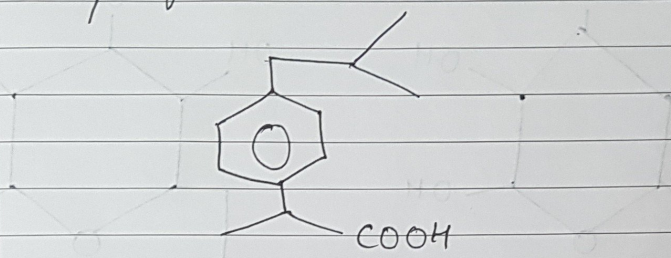


3) Carbaryl



used ~~as~~ to make pesticide.

4) Ibuprofen

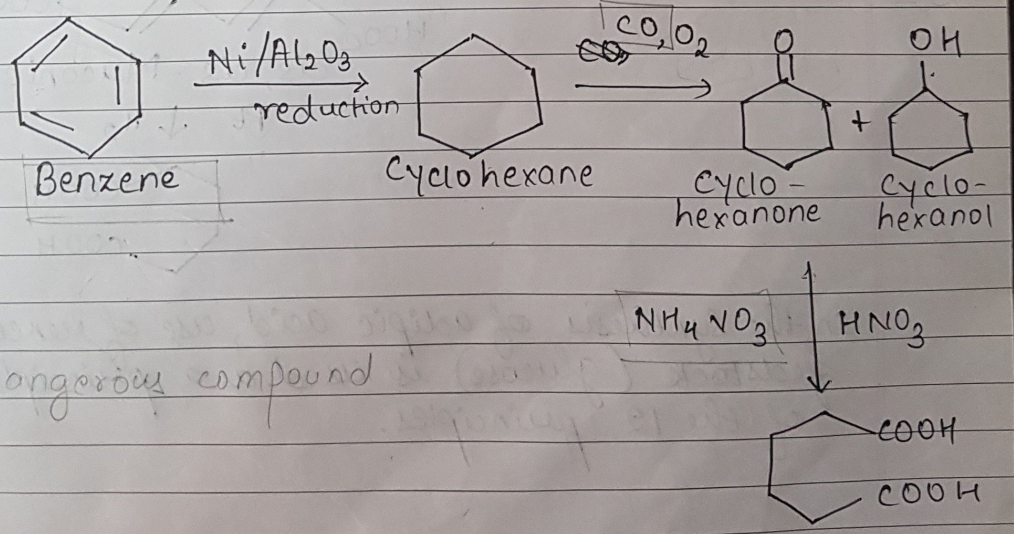


Used as analgesic (reduces fever and pain) pain ki~~ll~~ller

*** Give the synthesis of adipic acid by conventional method and green method. Which principle is involved for the synthesis of adipic acid?

⇒ A) Conventional Method:

Adipic acid in conventional method :- Benzene is used as the starting compound.

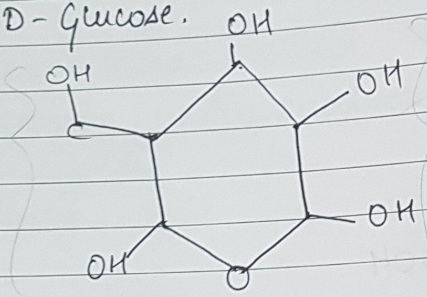


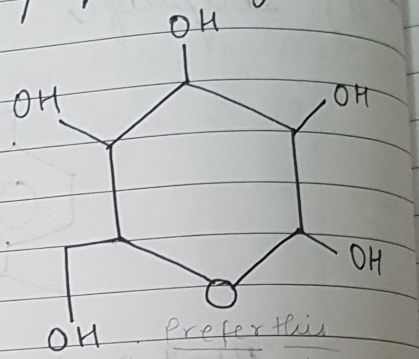
□ → dangerous compound

B) Greener Method

In Greener method, adipic acid is prepared by

D-Glucose.





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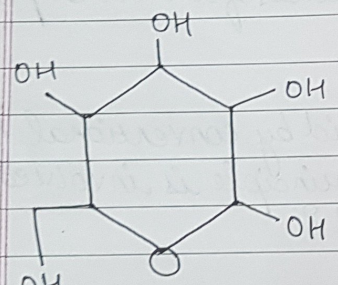

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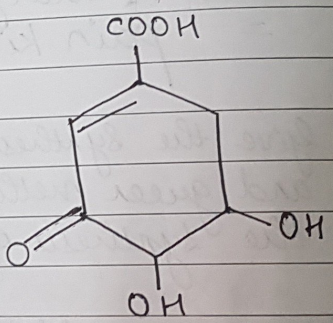
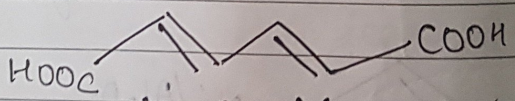


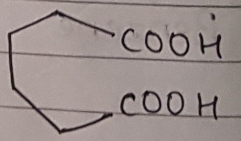
3-dehydrosikimate

↓ E. coli



cis, cis-Muconic acid

Pt ↓ H_2



In the synthesis of adipic acid, use of renewable feedstock (glucose) is used as a principle out of the 12 principles.

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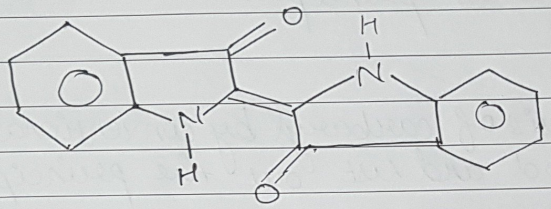
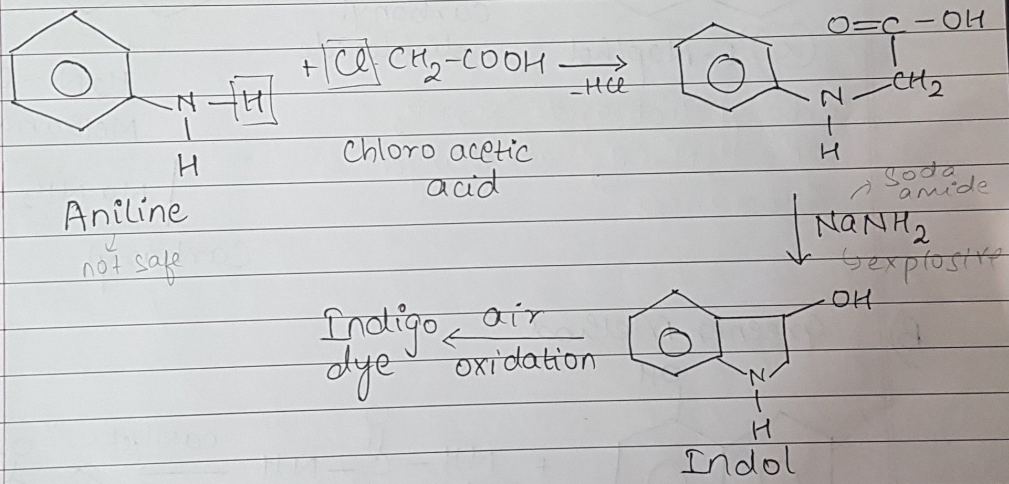
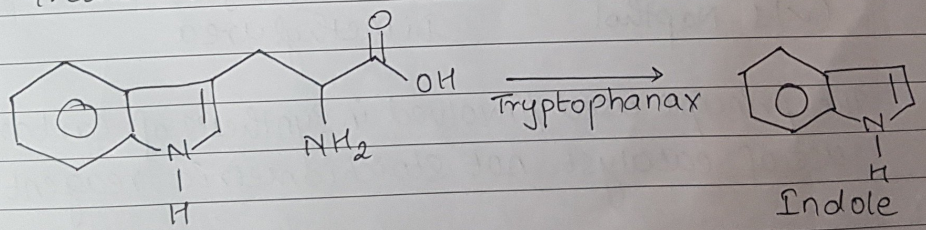
2) Give synthesis of Indigo Dye by conventional and greener method. list out the principle involved in it.



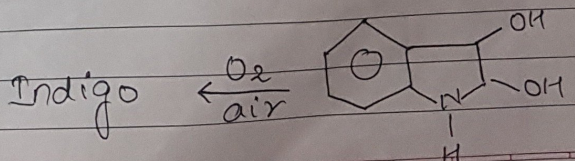
A) Conventional Method



B) Greener Method



Napthalade ↓ Deoxygenase



Carbonyl dichloride

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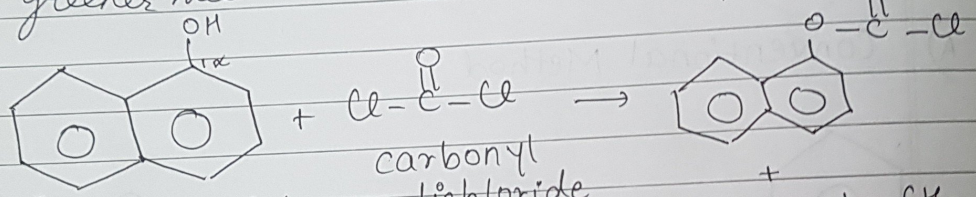
In the synthesis of Indigo dye, use of safer chemicals ~~principle~~ is used as principle.

3) CARBARYL

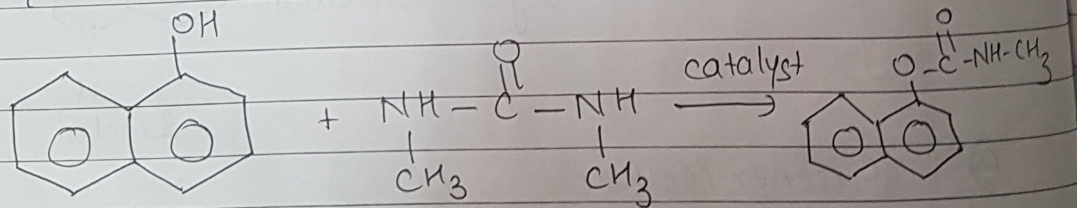
Give the synthesis of carbaryl by conventional, greener method and list out the principles.

A)



Carbonyl dichloride, $NaNH_2$, and H_2N-CH_3 are dangerous substances

B) Greener Method



The principle used/involved in Synthesis of Carbaryl is: use of catalyst not stoichiometric reagent.

Supercritical
1. Supercritical
2. Green reage

H_3C
3

Supercritic
inexpensive

MODULE 5

Ibuprofen

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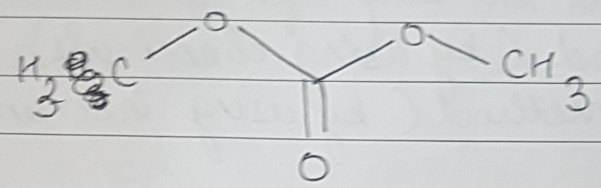
Supercritical fluid extraction (SFE)

1. Supercritical CO_2
2. Green reagent (Dimethyl carbonate)



Supercritical CO_2 is non-inflammable, non toxic and inexpensive.

MODULE 5:- SPECTROSCOPIC METHODS AND ITS APPLICATIONS

Ibuprofen:-

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MODULE: 5

SPECTROSCOPIC METHODS AND ITS APPLICATIONS

Various compounds like Ibuprofen can be analysed by
1) Chemical method (by using chemicals).
2) Instrumental method (by using instruments)

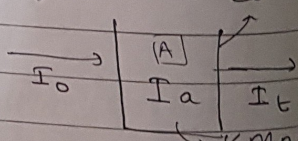
* Advantages of Instrumental method
→ Accuracy to analyse
→ Easy to operate
→ Small quantity of chemical required for analysis
→ Instrument can be reused. (∴ chemicals can be saved)

* Limitations of Instrumental Method
→ Expensive
→ Trained chemist required for operating the machine
→ It should have standard operating procedure.

Based on 3 Laws:-

1) → Beer's Law:- Molecules can be studied by its absorbance using calorimeter.
Calorimeter works in visible range

U.V → 200-400 nm
Visible → 400-800 nm
IR → 800-1200 nm



It states that the absorbance of light of colour compounds is directly proportional to concentration of solution

$A \propto C$

Unit of concentration (C) = $\frac{mol}{litre}$ = mol/Litre

2) Lambert's Law
It states tha
compound is
length of cu
Unit of path

3) Combined
It states th
compound i
of solution

A
A

Unit

Numerical
Case 1: B

Q A solution
shows abs
Coefficient

Soln:- Given:-

Ideal path length = 1

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2) Lambert's Law
It states that absorbance of light of colour compound is directly proportional to path length of cuvette. (path length :- b)
Unit of path length (b) = cm

3) Combined Beer Lambert Law.
It states that absorbance of light of colour compound is directly proportional to concentration of solution and path length of cuvette

$$A \propto bc$$

$$A = \epsilon bc$$

↓ Molar Ext. Coefficient

$$\epsilon = \frac{A}{bc}$$

$$\text{Unit} = \frac{1}{\frac{\text{mole}\ cm}{L}} = L^1\ mol^{-1}\ cm^{-1}$$

Numerical based on Case 1:-
Case 1 :. Beer Lambert Law

$$A = \epsilon bc$$

Q A solution of $KMnO_4$ of concentration 2.8×10^{-5} Molar shows absorbance 1.1. Find out its Molar Ext. Coefficient.

Soln:- Given :- ~~$\epsilon = 2.8 \times 10^{-5}$~~ concentration (c) $= 2.8 \times 10^{-5}$ M
~~A =~~ Absorbance (A) = 1.1
Ideal path length = 1
Path length (b) = 1

$$\Rightarrow A = \epsilon bc \qquad \therefore \epsilon = \frac{A}{bc}$$

ϵ :- Molar Ext. Coefficient
or
Molar Adsorbtivity

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$$\epsilon = \frac{1 \cdot 1}{1 \times 2 \cdot 8 \times 10^{-5}}$$

* case 2: Different absorbance with respective different concentration ratio.

a) Conc C_1 $\quad A_1 = \epsilon b C_1$

Conc C_2 $\quad A_2 = \epsilon b C_2$

$\therefore$ Ratio: $\quad \frac{A_1}{A_2} = \frac{C_1}{C_2}$

Eg/b) Ratio of absorbance w.r.t. path length.

$$A_1 = \epsilon b_1 C$$

$$A_2 = \epsilon b_2 C$$

$$\Rightarrow \frac{A_1}{A_2} = \frac{b_1}{b_2}$$

Eg A coloured solution of potassium dichromate ($K_2Cr_2O_7$) of concentration 2×10^{-4} Molar is placed in 4 cm path length of cell shows absorbance of 0.8. What will be the absorbance of solution if it is placed in 2 cm path length of a cell.

Given:- Concentration 1 (C_1) = 2×10^{-4} M

path length 1 (b) = 4 cm

Absorbence 1 (A_1) = 0.8

Path length 2 (b) = 2 cm

Absorbence 2 (A_2) = ?

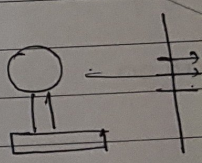
$\frac{A_1}{A_2}$

$\frac{0.8}{A_2}$

$\therefore$

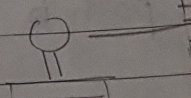
In this chapte
1) Calorime
2) Single be
3) Double

1) Calorimet



1) Principle
2) Compon

1) Calorim



1) Source (Tungsten Lamp)
1) Source

Source

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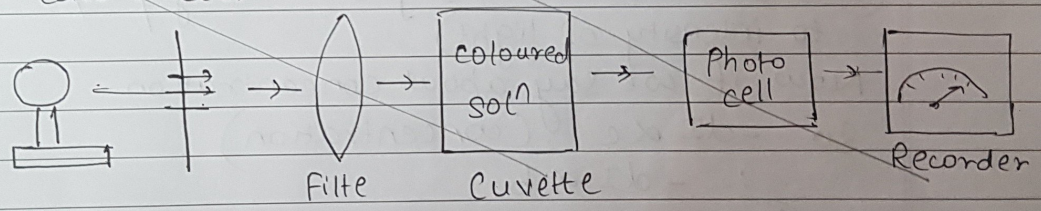
$$\frac{A_1}{A_2} = \frac{b_1}{b_2}$$

$$\frac{0.8}{A_2} = \frac{4}{2} \quad \Rightarrow \frac{0.8}{A_2} = 2$$

$$\therefore A_2 = 0.4$$

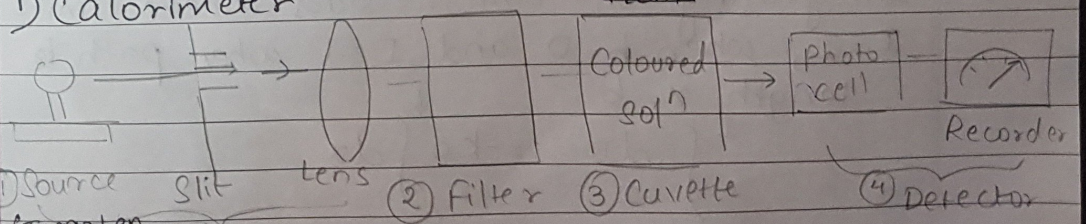
V. IMP
** In this chapter, there are 3 instruments
1) Calorimeter
2) Single beam spectrophotometer
3) Double beam spectrophotometer

1) Calorimeter



① Principle ③ Diagram ⑤ Application
② Components ④ Working

1) Calorimeter



① Source ② Filter ③ Cuvette ④ Detector

Source :- for visible light :- tungsten Lamp

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* λ_{max} :- Wavelength at which absorbance is maximum.

Calorimeter

Principle :- When a monochromatic ray of light passes through a coloured solution at constant path length, the absorbance of light is directly proportional to concentration of the given solution.

Derivation of Beer-Lambert Law

$A = \epsilon bc$ Abs Transmittance

So, we can write here, $-dI \propto I$ (Intensity)
(The decrease in intensity is directly proportional to intensity of light)
Now, if we say about concentration
So $-dI \propto c$ (concentration)
$\therefore -dI \propto b$

$$\frac{-dI}{dx} \propto cI$$

$$\therefore \frac{-dI}{dx} = kcI$$

Rearranging the equation $-dI/I = kc\,dx$
Integrating on both the sides where limits are $I = I_0$ when $b = 0$ and $I = I$ when path length $x = b$

$$\int_{I_0}^{I} \frac{dI}{I} = -kc \int_0^b dx$$

$$[\ln I]_{I_0}^{I} = -kc\,[x]_0^b$$

Q A solu
path
will
in 2
Conc
Po

$$\ln I - \ln I_0 = -kc[b-0]$$

$$\frac{\ln I}{I_0} = -kcb$$

$$\ln \frac{I_0}{I} = kcb$$

$$2.303 \log_{10} \frac{I_0}{I} = kcb$$

$$k = \frac{2.303}{bc} \log_{10} \frac{I_0}{I}$$

$$\frac{k}{2.303} = \frac{1}{bc} \log_{10} \frac{I_0}{I}$$

$$\therefore \epsilon = \frac{1}{bc} \log_{10} \frac{I_0}{I}$$

$$\epsilon bc = \log_{10} \frac{I_0}{I}$$

this is formula of absorbance $\leftarrow A = \log \frac{I_0}{I}$ $\quad \therefore A = \epsilon bc$

Q/ A solution of concentration 2×10^{-2} M is placed in 4cm path length cell shows an absorbance of 1.2. What will be the absorbance of solution if it is placed in 2cm path length of cell.

~~Concentration (1~~

Path length 1 $(b_1) = 4$cm

Absorbance 1 $(A_1) = 1.2$

Path length 2 $(b_2) = 2$cm

Absorbance 2 $(A_2) = ?$

$$\frac{A_1}{A_2} = \frac{b_1}{b_2} \Rightarrow A_2 = \frac{A_1 b_2}{b_1} = \frac{1.2 \times 2}{4} = 0.6$$

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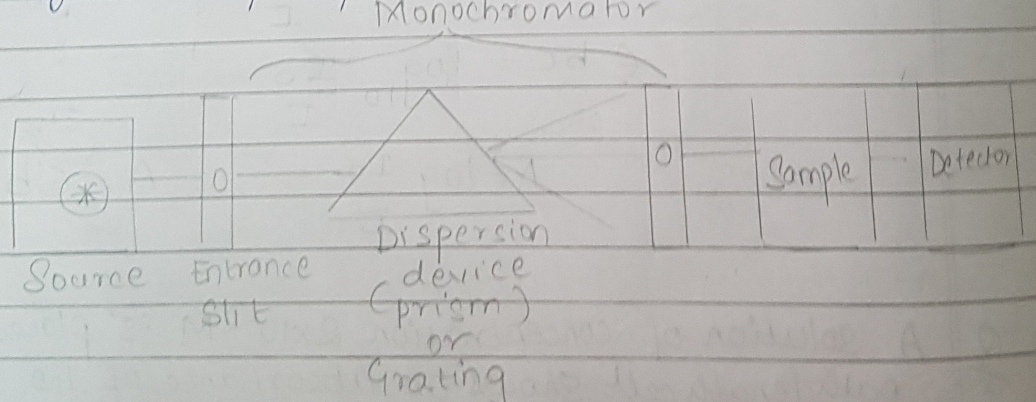
Drawbacks of colorimeter:-
→ Only works for visible range
→ It is time consuming.

SPECTROPHOTOMETER

It is used to determine unknown concentration using ~~visible~~ UV as well as visible range.
(200-400nm) (400-800)

Spectrometer is of 2 types:-
(A) Single Beam
(B) Double Beam

(A) Single Beam Spectrophotometer.



Principle:- It is used to determine unknown concentration using monochromator at different range UV as well as infrared.

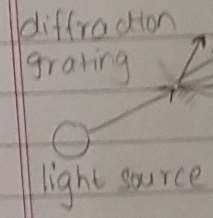
We have to take different reading for blank sample and coloured sample which is time consuming. So it can be replaced by Double beam Spectrophotometer

(B) Double Beam

* Cuvette having
or silica b
visible ligh

The detect
a) photo v
b) photon
c) Photo

Double



reference
sample

Visible
UV

Differen
Colori
→ uses
→ uses
→ used

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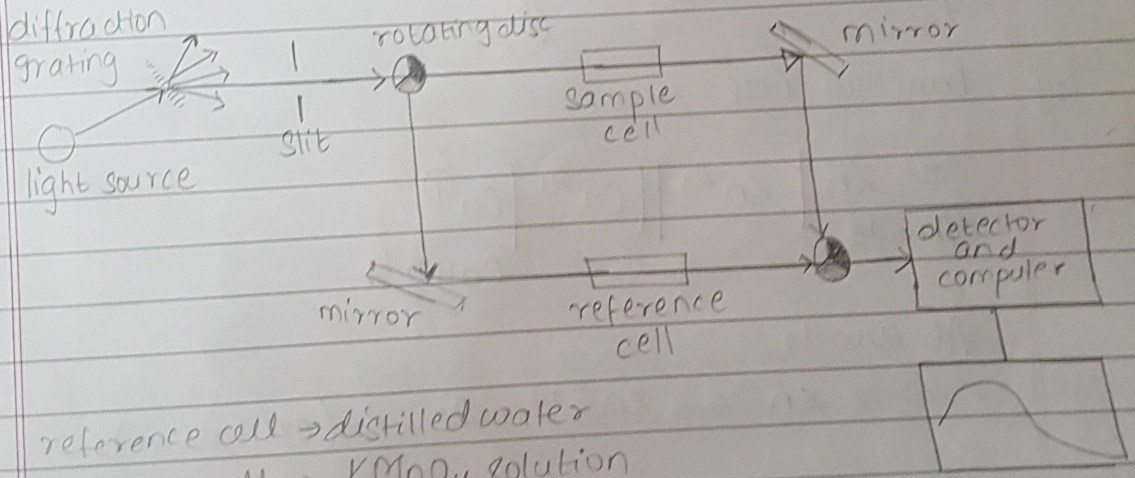
(2) ~~Double Beam~~

* Cuvette having a pathlength 1 cm which is made from quartz or silica because quartz does not absorb UV or visible light. (Quartz means 100% silica or pure silica)

The detectors used in spectrophotometer are as follows:
a) photovoltaic cell (used in single beam)
b) photomultiplier tube
c) Phototubes

Double Beam Spectrophotometer:



reference cell → distilled water
sample cell → $KMnO_4$ solution

Visible light :- source of light :- Tungsten lamp
UV :- Deuterium lamp.

Difference between Colorimeter and Spectrophotometer

Colorimeter	Spectrophotometer
→ uses filters	→ uses monochromators
→ uses narrow band of wavelengths	→ uses single wavelength
→ used only in visible region	→ used in UV & visible.

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MODULE-4

ELECTROCHEMISTRY AND ITS APPLICATION

(Th → Rxn, Definition, Description 8 Marks)

⇒ Electrochemistry:- Chemical energy is converted into electrical energy.

1) Oxidation:- At anode, oxidation takes place i.e. donation of electrons.
2) Reduction:- At cathode, reduction takes place (gain of electrons)

In Electrochemistry reactions are redox.

Redox reaction:- Oxidation and Reduction takes place simultaneously.

Eg. Danielle Cell:-

$$\ominus\ Zn \mid Zn^{2+} \,||\, Cu^{2+} \mid Cu\ \oplus$$

Anode — Cathode

At anode:-

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(oxidation)}$$

At cathode:

$$Cu^{2+} + 2e^- \longrightarrow Cu \quad \text{(Reduction}$$

Net cell reaction

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$Cu^{2+} + 2e^- \longrightarrow Cu$$
$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

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Emf can be calculated by Nernst Equation:-

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[C]\,[D]}{[A]\,[B]}$$

[C] [D] → Conc^n of products
[A], [B], → cond^n of reactants.

CORROSION:- The process in which metal undergoes deterioration or destruction due to reaction with the surrounding is called corrosion.
Corrosion is due to redox reaction.

CLASSIFICATION OF CORROSION:-
Depending on the medium there are 2 types of corrosion.

IMP 1) Dry / Direct / Atmospheric corrosion

IMP 2) Wet / Immersed / Electrochemical corrosion

A) Dry / Direct / Atmospheric corrosion
⇒ This type of corrosion is due to different gases present in the atmosphere.

Metal
$M + \frac{1}{2} O_2 \rightarrow$

Eg (1) O_2
gases that can corrode metals (2) X_2 (where X → Halogen)
(3) H_2S

M = Metal
$M + \frac{1}{2} O_2 \rightarrow MO$ (Metal oxide)
$M + \frac{1}{2} X_2 \rightarrow MX$ (Metal Halide)
$M + H_2S \rightarrow MS + H_2\uparrow$

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(B) ~~Wet~~ / Immersed / Electrochemical corrosion

⇒ Due to ~~medium~~ in liquid state. ~~Dep~~

① Absorption of O_2 gas

② Evolution of H_2 gas ~~gas~~

This type of corrosion is due to medium in liquid state. Depending on mechanism, there are 2 types of wet corrosion.

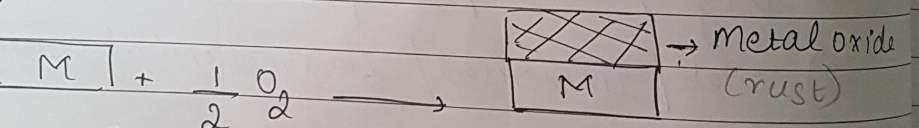
① Due to Absorption of O_2 gas

② Due to Evolution of H_2 gas

Corrosion due to Oxygen (O_2)

$$M + \frac{1}{2} O_2 \longrightarrow MO \text{ (Metal oxide)}$$

Metal on reacting with oxygen forms metal oxide layer.



The ~~reaction~~ process takes place by redox reaction

The reactions are as follows:-

At anode: (oxidation)

$$2M \longrightarrow 2M^{n+} + 2ne^-$$

At cathode: (Reduction)

$$\frac{1}{2} O_2 + 2ne^- \longrightarrow 2nO^{2-}$$

Net cell reaction

$$2M + \frac{1}{2} O_2 \longrightarrow 2M^{n+} + 2nO^{2-}$$

M_2O_n Metal oxide.

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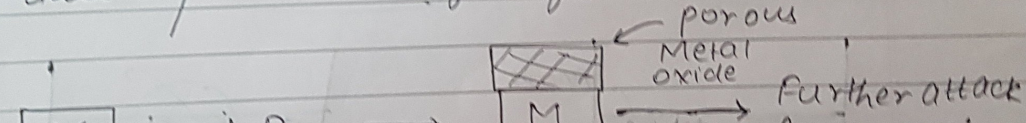
Depending on metal oxide, there are 3 types which are as follows:-

(I) Stable oxide Film
(II) Unstable oxide Film
(III) Volatile oxide film

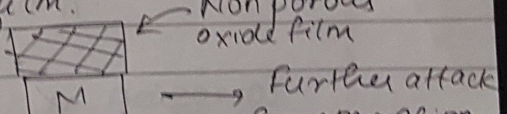
(I) Stable Oxide Film:- Metal when reacted with oxide, will form a stable oxide film. It is further classified as follows:-
(A) Porous oxide film (B) Non porous oxide film.

(A) Porous oxide film :- Generally alkaline (Na) and alkaline Earth metals (Mg) undergoes corrosion due to porous oxide film formation.



$$\underset{\text{Eg: Na, Mg}}{M} + \frac{1}{2}O_2 \longrightarrow$$

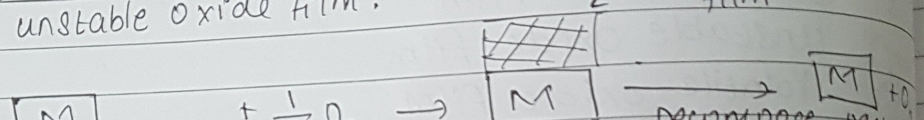
(B) Non Porous oxide film:- Aluminium and Chromium form non porous oxide film.



$$M + \frac{1}{2}O_2 \longrightarrow$$

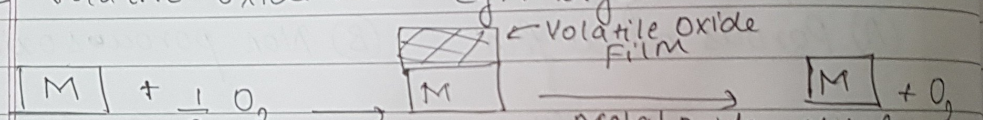
Eg:- $Al \rightarrow Al_2O_3$
$Cr \rightarrow Cr_2O_7 / Cr_2O_3$

II unstable Oxide film :- Generally noble metals ~~undergo~~ form unstable oxide film.

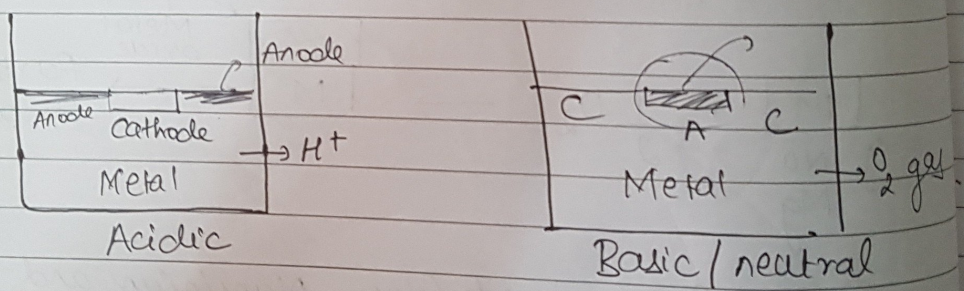


Eg:- Noble metal
Ag, Au, Pt

III Volatile Oxide Film : Eg:- Molybdenum



~~Eg:- Mo~~
Eg: Mo



~~Anode gets~~ gets corroded

Corrosion $\propto \frac{C}{A}$

C:- Cathodic area
A:- Anodic area

Corrosion $\propto$ temp

pH:- Acidic > Basic > Neutral

Corrosion more in acidic followed by basic followed by Neutral

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*** Factors affecting the corrosion:

1) Nature of metal:

a) Position of metal in galvanic series

The metals above H_2 in the galvanic series undergo corrosion as they are highly reactive due to high oxidation potential and the below metals vice versa.

b) Potential difference:- More the potential difference, more will be the corrosion as electron transfer will be more.

ii) Oxidation potential

iii) H_2 over voltage

iv) Relative areas of anode and cathode

v) Purity of metal:-

More the impurity, more reactive and more corrosion

(vi) Physical state of metal (Powder or rod form)

Powder has more surface area. Hence powder form gets more corroded

(vii) Nature of oxide film.

(viii) Solubility of corrosion products

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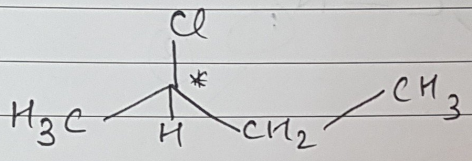
COMPUTATIONAL CHEMISTRY

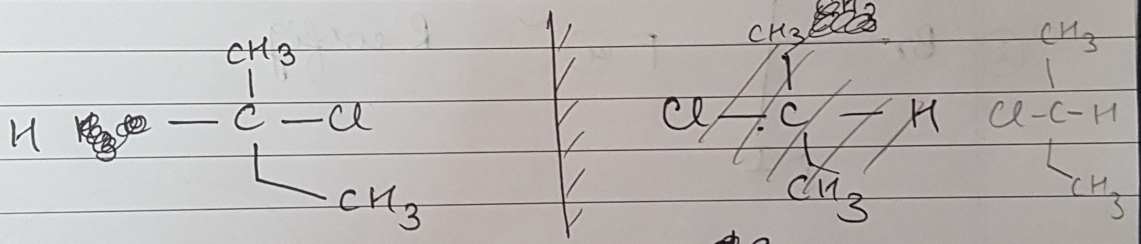
Stereochemistry:-

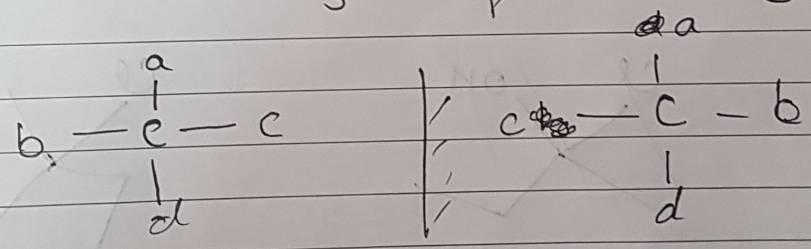
Chiral compounds:- These are the compounds in which all substituted groups are different and the mirror image of the compound is non super imposable.

Eg:-



2-chloro butane

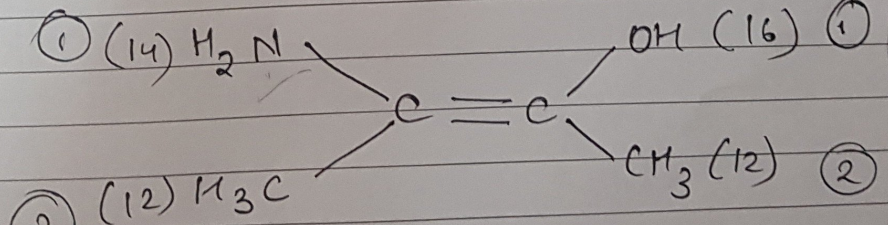


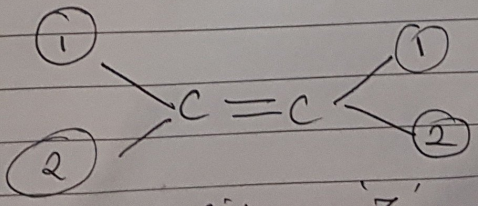


Z - E configuration

Atomic no. more ⇒ (1) Less ⇒ (2) Apply for both left & right side

You can consider At wt or not wt





cis → 'Z'

R → clockwise

S → anticlockwise

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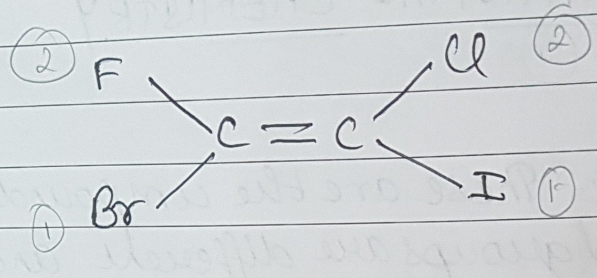
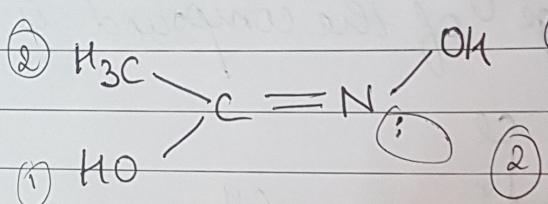
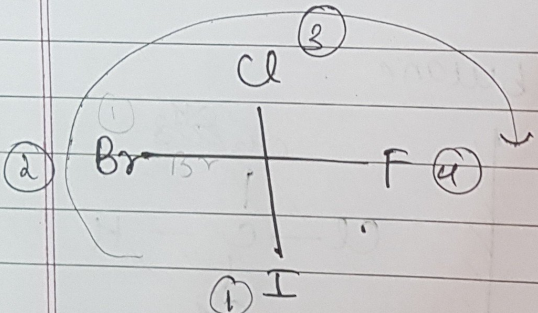


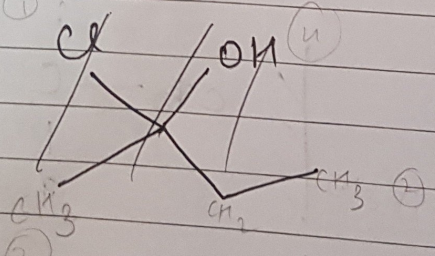
Z config

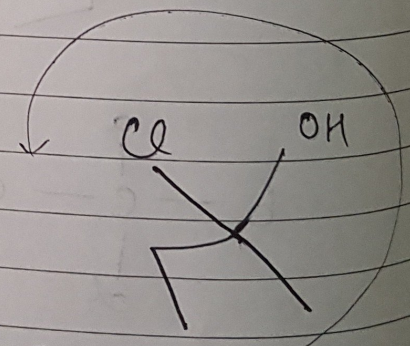


E config



R config





S config