

VANSH SRIVASTAVA

Applied Chemistry  
Rishi Gupta Titrimetric Analysis

TITRATION: used to determine strength of an unknown solution using a <sup>conc</sup> known solution and the normality equation

Types of indicators

→ internal → external → self indicator → redox adsorption  
 (MeOH, HIn) [we take out a drop from titrating mix] (KHNiO<sub>4</sub>)  
 [added in same flask in which titration is done]



Ans

ANALYSIS To identify the substance present and its quantity

↳ Quantitative &amp; Qualitative

Gravimetric (by mass) Volumetric aka Titrimetric (new and replaced version)  
 (by vol)

is the process of

estimation

\* Titrimetric analysis = quantitative analysis of ~~the~~ strength of an unknown solution whose fixed vol will react with a definite volume of known sol<sup>n</sup> and by applying normality eq<sup>n</sup>. Indicators are used to determine end point

KNOWN SOL<sup>n</sup> :- (Titrant)

Primary Standard 1° 2°

UNKNOWN SOL<sup>n</sup> :- (Titrand)

standard solution:-

whose conc is known

\* Primary Standard Substance are those subs that can be weighed accurately and directly and dissolved in a given solvent to get the desired conc<sup>n</sup> and this conc<sup>n</sup> does not vary over a period of investigation / or due to atmospheric cond<sup>n</sup>. The resulting sol<sup>n</sup> is called P.S. Solution

- Characteristic
- ① available in highly pure form
  - ② Does not decompose at ~~oven~~ temperatures
  - ③ Should not be deliquescent & efflorescent
  - ④ Must be easily soluble in water

high molecular weight  
insoluble  
no preservative



④ Must be easily soluble in water

⑤ Stable at oven / high / drying temp

⑥ Stable for long periods

e.g.

Substances which do not come under above cond are called Secondary Standard Subs.

RbCl, anhyd. Na<sub>2</sub>CO<sub>3</sub>

D.S. → Crystalline oxalic acid, AgNO<sub>3</sub> sol<sup>n</sup>, CuSO<sub>4</sub> · 5H<sub>2</sub>O, Mohr's salt

Sec. Stand. → all mineral acids, KMnO<sub>4</sub> (reduces to MnO<sub>2</sub>)

\* INDICATOR: any auxilliary subs that helps in visual detection of completion of the rxn either by undergoing a change in colour or forming ppt or causing turbidity.

\* Equivalence pt: rxn is just complete

\* End pt: when we can detect completion

Difference b/w end pt & equivalence pt is called titration error

EQUivalence PT CAN BE DETECTED USING CERTAIN INSTRUMENTS SUCH AS PH METER

• formula wt is used for ionic compounds as they exist in ions and molecular wt can't be used

\* TYPES OF TITRATION :

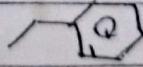
a) → Acid - Base      b) → Redox      c) → Complexometric      d) → Precipitation

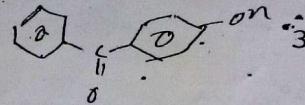
Acidimetry

Strength of acid is unknown

Alkalimetry

Strength of alkali is unknown



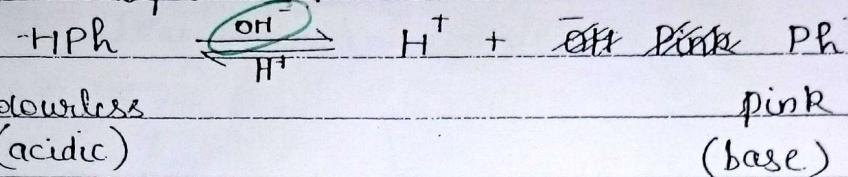


⇒ Theory of indicators ← → modern Benzenoid or Quinoneid

Ostwalds 1) Indicators are themselves WA or WB

2) They have different colours in ionised or un-ionised form

## Action of Phenolphthalein:

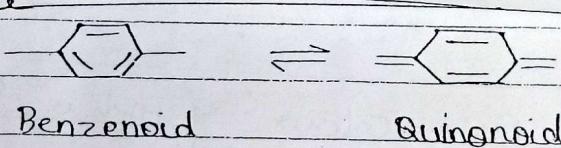


Disad: Did not explain structure of indicators

## Modern Benzenoid Theory:

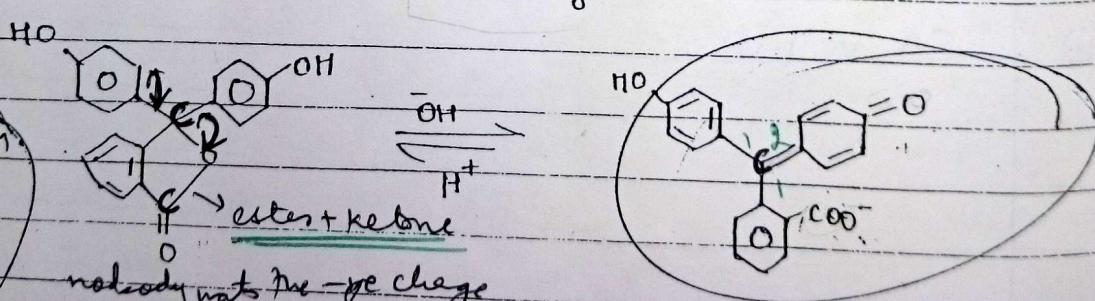
- 1) Indicators can exist in interconvertible tautomeric forms - benzenoid & quinonoid. One form predominates in one medium and other in other is medium.

2) Quinonoid is more deeper in colour than benzenoid ( $\alpha > \beta$ )



Interaction  
with  
acid / base

PHENOLPHTHALEIN: pH range 8.2 - 10



nobody wants me - we change

## Colours

St. acidic

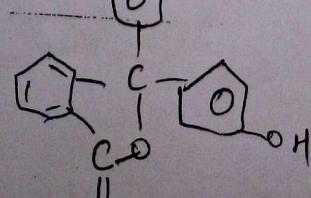
**basic**

- orange

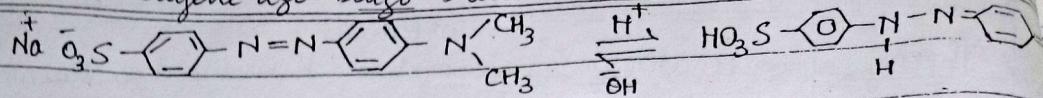
- colorless

- pink  
- colorless

transition



Salt benzene azo benz- $\beta$ -aniline

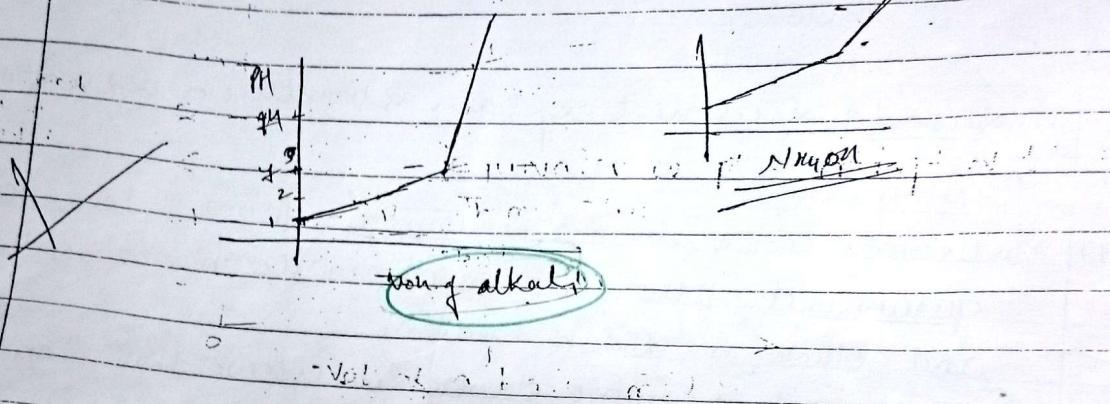


Yellow (Alkaline)

Red (acidic)

TITRATION CURVE: is a plot of pH vs. vol. of acid/alkal  
added.

100ml of 1M HCl is titrated with ~~1M NaOH~~



Since light pink colour of HPh is closer to equivalence  
there " " is preferred

ii)

SA vs WB

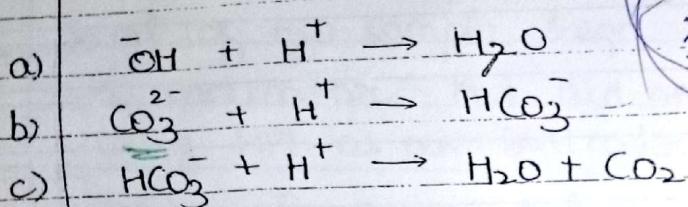
iii)

WA vs SB

P = M → C  
P > M →  
P < M →  
P = C  
M →

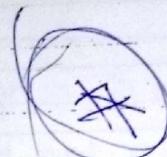
$$\begin{aligned}
 P = M &\rightarrow CO_3^{2-} \\
 P > M &\rightarrow OH^- \text{ & } CO_3^{2-} \\
 P < M &\rightarrow HCO_3^- \text{ & } CO_3^{2-} \\
 P = O &\rightarrow HCO_3^- \text{ (weak)} \\
 M = O &\rightarrow OH^- \\
 V_1 &= V_{OH^-} + V_{HCO_3^-} \\
 (M-O) &V_{CO_3^{2-}} = 2V_2 \\
 V_2 &= V_{1/2} CO_3^{2-} \\
 1) OH^- & 2) CO_3^{2-} \quad 3) HCO_3^- \quad 4) OH^- \& CO_3^{2-} \quad 5) CO_3^{2-} \& HCO_3^- \\
 \end{aligned}$$

ation, scales, insolubility  
 & the ability of  $H_2O$  to neutralize free  
 of 2 types: caustic & bicarbonate  
 alkalinity all cause hardness but ch  
 are. Following ions cause alkalinity.



Cases possible:

A)  $P = M$ , B)  $P > M$ , C)  $P < M$ , D)  $P = O$ , E)  $M = O$



] P. insol due to M-O

] M-O. sol due to H-O.

- If  $P = O$ ,  $HCO_3^-$  is only
- If  $M = O$ , only  $OH^-$  is
- also present,  $HCO_3^-$  will
- when  $P = M$ ,  $CO_3^{2-}$  is
- If  $P > M$ , (4) and (5)

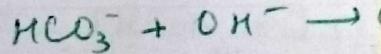
4

$$V_{CO_3^{2-}} = 2V_1$$

$$V_{HCO_3^-} = V_2 - V_1$$

$$f CO_3^{2-}$$

If  $HCO_3^-$  &  $OH^-$  are present  
 result in  $CO_3^{2-}$  [Don't do]



mately

Q 100 ml of  $H_2O$  sample reqd. 20ml of  $\frac{N}{50}$  HCl for neutralization to  $H_2O$  endpt. After this phenol indicator was added and further acid reqd was 20 ml. What is the type of alkalinity present and calculate the extent terms of  $CaCO_3$  equivalents.

Sol It is  $P = M$  case  $\rightarrow CO_3^{2-}$  present

Now,  $(NV)_{\text{water}}$   $(NV)_{\text{acid}}$

$$\frac{N_w \times 100}{50} = \frac{1}{(20+20)} = \frac{N_w}{20} = \frac{10}{50 \times 100}$$

$$\text{Strength} = \frac{40}{50} \times 50 \text{ g/L}$$

$$= \frac{40}{500} \times 50 \times 10^3 \text{ mg/L} = 400 \text{ ppm}$$

FOR PRACTICALS

In case of NaOH + Na<sub>2</sub>CO<sub>3</sub>

Q.

Sol.

Q.

200 ml of H<sub>2</sub>O sample reqd 20 ml of N HCl using M<sub>eq</sub>ON  
 Another 200 ml of sample & reqd <sup>some</sup> 40 8 ml of N HCl  
 using MPH as indicator. What is the type and calculate the extent

Sol.

Calculating total hardness: A' Noy

$$N \times (200) = \frac{1}{40} \times 20$$

$$M \equiv 20 \text{ ml} \Rightarrow N = \frac{1}{20} \times \frac{40 \times 200}{4}$$

$$\text{ppm Strength} = \frac{\frac{10}{20} \times 50 \times 1000}{40 \times 200} = \frac{500}{4} = 125 \text{ ppm}$$

NH <sub>3</sub>	OH <sup>-</sup>	8 ml
	CO <sub>3</sub> <sup>2-</sup>	
	HCO <sub>3</sub> <sup>-</sup>	= 12

20 ml

(Meth can indicate total hardness also)

Here we say that NH<sub>3</sub> &

> CO<sub>3</sub><sup>2-</sup> & HCO<sub>3</sub><sup>-</sup> are present

8 ml of soln for  $\frac{1}{2}$  neutralisation of  $\text{CO}_3^{2-} \Rightarrow 16 \text{ ml for full}$   
 $\therefore N \times 200 = \frac{1}{40} \times 16 \Rightarrow 100 \text{ ppm of } \text{CO}_3^{2-}$

Hence 25 ppm of  $\text{HCO}_3^-$ .  
[OR Total hardness due to  $\text{CO}_3^{2-}$  = hardness due to  
 $\text{HCO}_3^-$ ]

$$N \times 200 = \frac{1}{40}$$

Q. 50 ml of H<sub>2</sub>O sample reqd. 5 ml of N HCl using MeOH as indicator but did not give any colouration using HPh as an indicator. Calculate type & extent.

Sol. Since P = 0  $\Rightarrow$  only  $\text{HCO}_3^{2-}$  is present.

$$\text{Now, } N \times 50 = \frac{1 \times 5}{50}$$

$$\Rightarrow \text{Strength} = \frac{1}{10} \times 50 \times \frac{1000}{50} \text{ ppm}$$

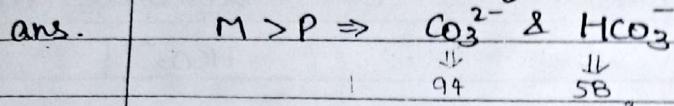
$$= 100 \text{ ppm}$$

Q. 100 ml of H<sub>2</sub>O sample on titration with N  $\text{H}_2\text{SO}_4$  reqd. 12.4 ml of acid upto HPh end pt.  $\overset{50}{\text{and}}$  15.2 ml acid upto MeOH end pt. calculate the type and extent of alkalinity.

$\frac{\text{Weight of solute}}{\text{Weight of sol}}$

Strength  
Equivalent wt.

a. A H<sub>2</sub>O sample is alkaline to both MeOH & HPh. 100 ml H<sub>2</sub>O sample with N HCl reqd. 4.7 ml acid upto H<sub>2</sub> when a few drops of MeOH are added to same sol<sup>t</sup>. titration continued, yellow colour just turned after 10.5 ml of acid. Express in CaCO<sub>3</sub> equivalents.



$\frac{4.7}{50} \text{ ml reqd. for } \frac{1}{2} \text{ neut. of CO}_3^{2-} \Rightarrow 9.4 \text{ ml for full}$

hardness due to  $\text{CO}_3^{2-}$ :

$$N \times 100 = \frac{1 \times 9.4}{50} \Rightarrow 94 \text{ ppm}$$

Now, out of 10.5 ml, 4.7 is used up by  $\text{CO}_3^{2-}$

So, remaining 5.8 ml was used by  $\text{HCO}_3^-$ .

$$\text{So, } N \times 100 = \frac{1 \times 5.8}{50} \Rightarrow 58 \text{ ppm}$$

\*

### REDOX TITRATION: those in which

- Sufficient difference in oxidising & reducing powers agents used.
- commonly used reducing agent:
  - Mohr Salt,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
  - Hypo ( $\text{Na}_2\text{S}_2\text{O}_3$ ) was originally called hyposulphite of sod hypo is the short form
  - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

### KRNOY titration:

acts in all medium

Strongest oxidising agent in acidic medium

only  $\text{H}_2\text{SO}_4$  can be used to acidify Krnoy sol<sup>t</sup>

HCl &  $\text{HNO}_3$  can't be used

self indicator ( $\text{K}_2\text{Cr}_2\text{O}_7$  is not a self indicator its different colours are not very distinct)

? redox indicators should have some R.P. which be lower than analyte system so that once it's work is to analyse.

Why?  
HCl can be  
oxidised to Cl<sub>2</sub>  
 $\text{HNO}_3$  can oxidise  
the reducing agent

R.P. →

Reducing  
power

analyte is consumed, then then this indicator is acted upon  
Drawback: not a primary standard ( $MnO_2$  is present as impurity).

In  $KMnO_4$  vs oxalic acid titration, we heat continuously  
So as to evolve  $CO_2$  gas from medium.

### $K_2Cr_2O_7$ titration:

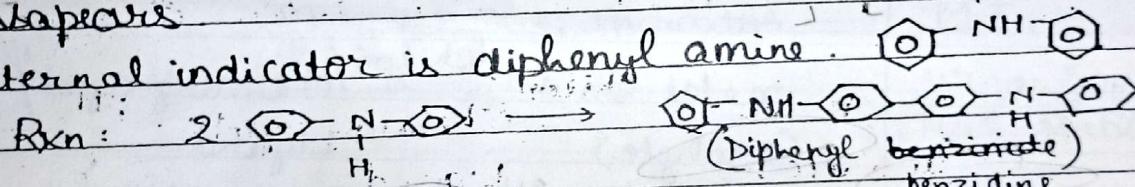
milder than  $KMnO_4$ , but the advantage is  
that it is primary std substance  
as both  $H_2SO_4$  &  $HCl$  can be used.

not a self indicator,  $K_3[Fe(CN)_6]$  is used as an external indicator (in titration of  $K_2Cr_2O_7$  with ferrous ammonium sulphate,  $Fe^{2+} \rightarrow Fe^{3+}$ )

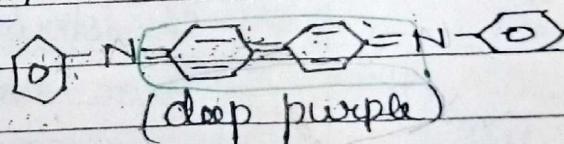
On a white tile, we put drops of ext indicator and at regular intervals, we put drops of titrating mixt. As soon as all  $Fe^{2+} \rightarrow Fe^{3+}$ , Prussian blue colour disappears.

→ check

Internal indicator is diphenyl amine.



(used in  $Fe^{(II)}$  vs  $K_2Cr_2O_7$ . After all  $Fe^{(II)}$  is consumed, addition of excess drop of  $K_2Cr_2O_7$  oxidises diphenylamine)



### Iodine titration

mild oxidizing agent  
in neutral aqueous medium

Iodometry

Iodometry

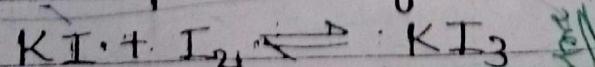
- when an analyte that is reducing agent is titrated directly with a standard iodine solution, the method is called "iodometry"
- when an analyte that is an oxidising agent is added to excess iodide to product iodine and the iodine produced is determined by

(comes  $\Rightarrow$  direct titration of  $I_2 \Rightarrow I_2 \text{ vs R.A.}$ )  
to determine the strength of R.A., sulphate = "iodometry"

In iodometry:  $I^- \text{ O.A.} \xrightarrow{\text{excess}} (I_2) \text{ vs. R.A.}$

Iodine titration

Always done in presence of K.I.



$I_2$  is very volatile

$KI_3$  salt reduces volatility

$I_2$  is very less soluble

reducing agent  
quantity

Iodometry is used to quantitatively determine the concentration of R.A.

- Starch is adsorption indicator and is polymer indicator. Added after 99% completion (I<sub>2</sub> indicators are added in beginning).

How to DETECT 99%?

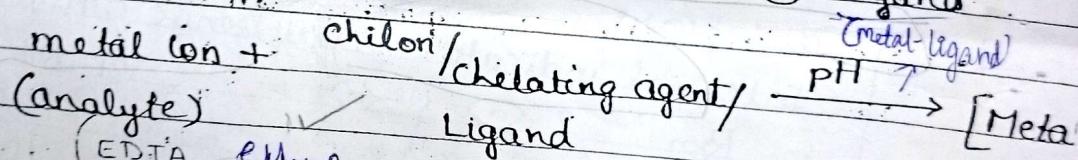
Sol<sup>n</sup> of I<sub>2</sub> is initially dark brown. As titration proceeds, sol<sup>n</sup> turns pale yellow. Here with starch.

Why add starch in the end?

- its temp sensitive

- Starch has helical structure  $\Rightarrow$  so I<sub>2</sub> may get trapped and may also get absorbed.

COMPLEXOMETRIC TITRATION: complex is getting formed  
The species shall be ① metal ion ② Ligand



(EDTA) Ethylene diamine tetra acetic acid  
 $\xrightarrow{6 \text{ binding sites}}$

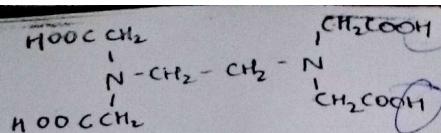
Sequestering agent: those agent (ligands) which form water soluble complexes with metal cations  
eg: EDTA

used to determine hardness of water (presence of Ca<sup>2+</sup>) Thus hard water is used as analyte disodium salt of EDTA is used which is primary standard (available in highly pure H<sub>2</sub>O soluble form) symbol: Na<sub>2</sub>E

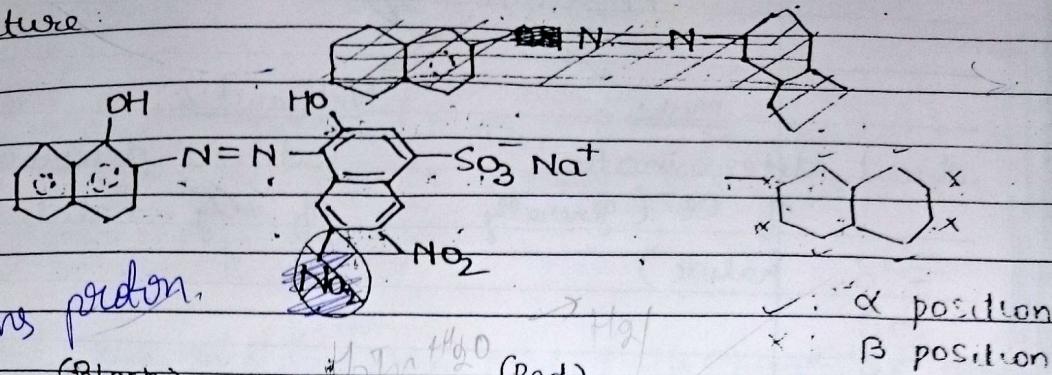
Symbols of EDTA  $\rightarrow$  H<sub>4</sub>Y, H<sub>3</sub>Y<sup>-</sup>, H<sub>2</sub>Y<sup>2-</sup>, HY<sup>3-</sup>, Y<sup>4-</sup>

These forms are pH dependent.

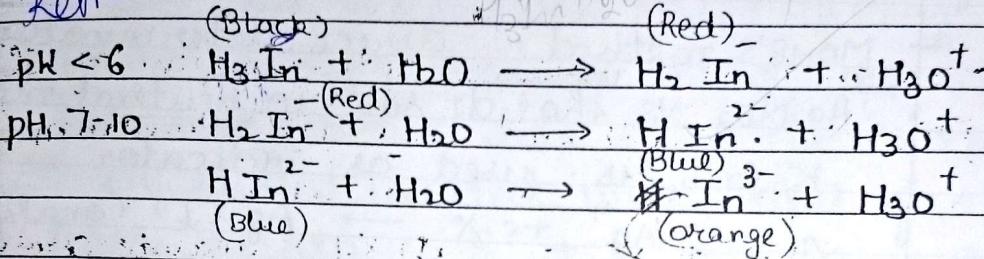
EBT (Eriochrome Black-T) is used as an indicator



## Structure



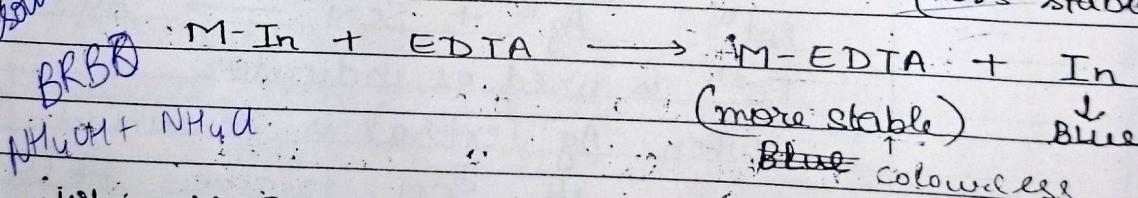
Remains proton



Ammoniacal buffer sol<sup>n</sup> is used to maintain pH b/w 8 to 10 ( $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ ) It is added b4 adding indicator

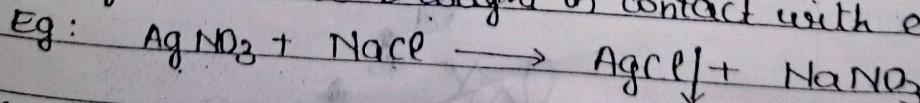
Process:  $\text{M} + \text{ABS} + \text{Indicator} \xrightarrow{\downarrow} \text{M-In}$  (drop)

Process:  $M + ABS + \text{Indicator} \rightarrow M-\text{In}$   
 buffer ↓ metal from analyte wine red.  
 (less stable)



When M-EDTA is added, Indicator is released and is free and in pH 8-10; it is blue in colour.

PRECIPITATION TITRATION: ppt is formed when 2 reacting subs are brought in contact with each other.



Mostly pptation rxn are carried with  $\text{AgNO}_3$  sol<sup>t</sup>, they are also termed Argentometric Titration  
Conditions for titration :  $Q > K_{sp}$

- 1)  $Q > K_{sp}$   
 2) Rapid pptation

- 3) PPT should nearly insoluble
  - 4) Proper indicator should be

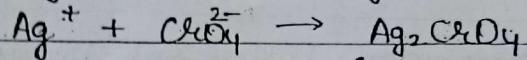
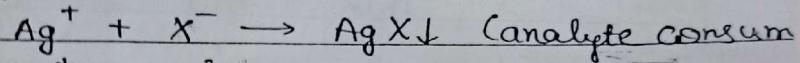
Pptation Rxn

Mohr'sVolhard's

direct determination

of  $\text{Cl}^-$  (generally  
halide)

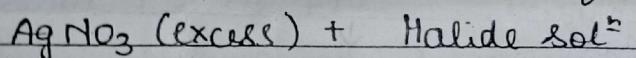
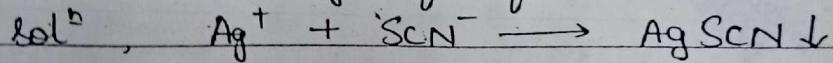
indirect determination

of ~~Ag<sup>+</sup>~~ halideMOHR'S method: direct determination of  $\text{Cl}^-$ Std.  $\text{AgNO}_3$  vs <sup>unknown</sup> halide sol<sup>b</sup> in neutral medium $\text{K}_2\text{CrO}_4$  is used as indicator

(Brick red ppt)

titration

Volhard's method: (an example of back titration)

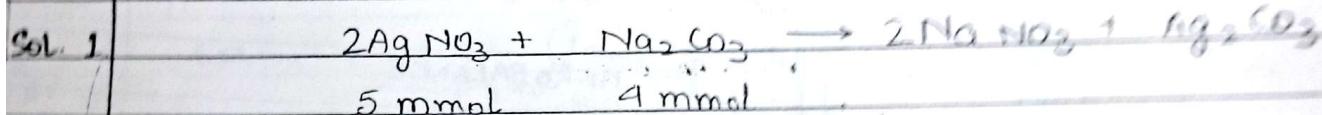
Extra  $\text{Ag}^+$  left after rxn with halide $\text{Fe}^{3+}$  is used as indicatorwhen  $\text{Ag}^+$  (extra) is consumed,  $\text{Fe}^{3+}$  reacts with  $\text{SCN}^-$  to give  $\text{Fe}(\text{SCN})_3^{3+}$  ↓

[blood red ppt].

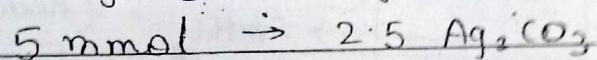
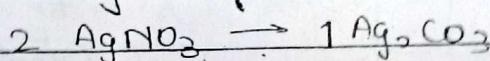
 $\text{SCN}^-$ : ammonium thiocyanate $\text{Fe}^{3+}$ : ferric ammonium sulphate

NUMERICALS

1. What mass of  $\text{Ag}_2\text{CO}_3$  (m.m. = 275.7 g/mol) will form when 25 ml of 0.2 M  $\text{AgNO}_3$  is mixed with 50 ml of 0.08 M  $\text{Na}_2\text{CO}_3$ .
2. A 30 l air sample was passed through an atomic absorption tower containing a soln. of  $\text{Cd}^{2+}$ , where  $\text{H}_2\text{S}$  was retained as  $\text{CdS}$ . The mixture was acidified and treated with 10 ml of 0.01070 M  $\text{I}_2$ . After the rxn:  $\text{S}^{2-} + \text{I}_2 \rightarrow \text{S}(\text{s}) + 2\text{I}^-$  was complete, the excess  $\text{I}_2$  was titrated with 12.85 ml of 0.01344 M thiosulphate. Calc'd. up.  $[\text{H}_2\text{S}]$  in ppm  
Density of gas stream = 1.20 g/l.



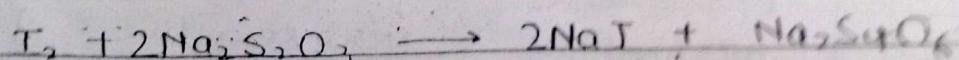
Limiting reagent =  $\text{AgNO}_3$



~~This mass. of  $\text{Ag}_2\text{CO}_3$  =~~   $\frac{2.5 \times 275.7}{1000}$

$$= 0.68925 \text{ g}$$

2. Total  $\text{I}_2$  =  $10 \times 0.01070 \text{ mmol}$   
 $= 0.1070 \text{ mmol}$

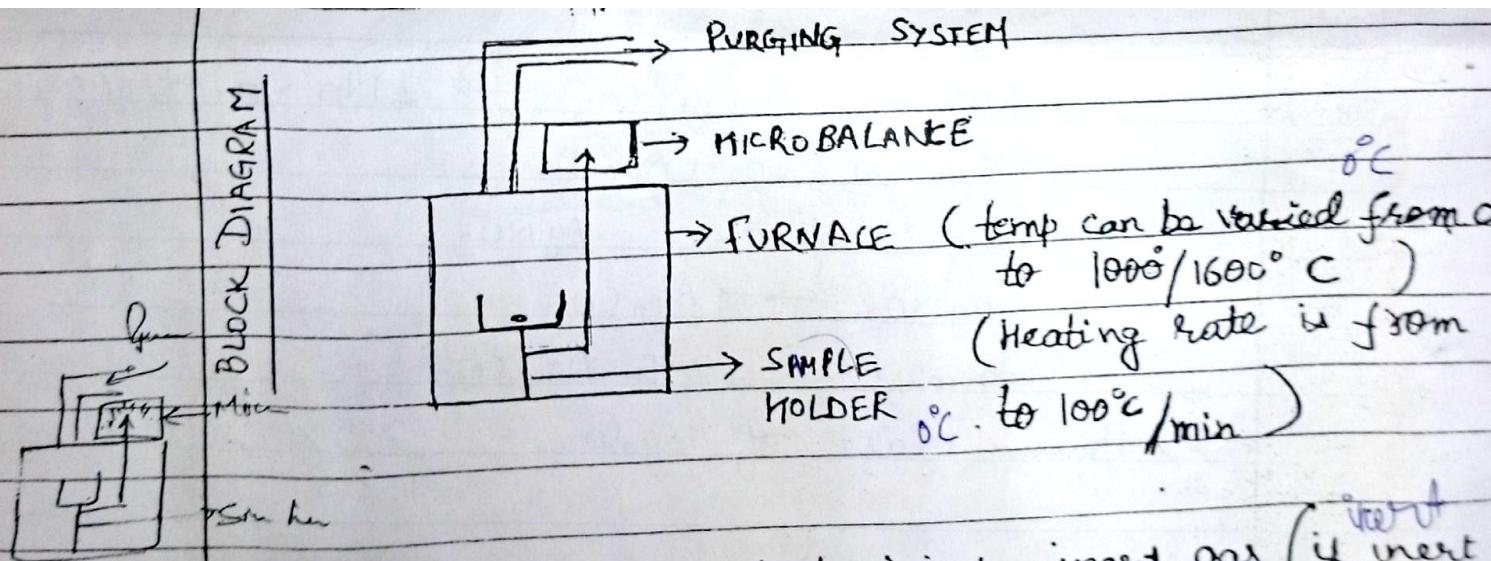


$$\text{mmol of " } =$$

$$\text{mmol of I}_2 \text{ used} =$$

$$\text{Used I}_2 = (0.1070 - \frac{1}{2}) \text{ mmol} = 0.02065 \text{ mmol}$$

$$\therefore [\text{H}_2\text{S}]_{\text{in ppm}} = \frac{0.02065 \times 10 \times (34)}{30 \times 1.2} \times 10^6 = 19.5 \text{ ppm}$$



Purging system : used to inject inert gas (if inert atmosphere is reqd) & used to cool the furnace <sup>inert</sup> <sub>cool</sub>

Simple holder made of inert substance like silicon <sup>silica</sup> or <sub>97%</sub> alumina <sub>250g</sub>

Microbalance = very sensitive = from 0.01 mg to

Based on null point balance. When there is a change in weight. The balance beam will deviate from its usual position. A sensor detects this deviation & initiates a force that will restore the balance to the null pt position. The restoring force  $\propto$  change in weight.

### STANDARD THERMOGRAMS

15.1

- ① No change  
 ② Initial def. (% of loss of  $H_2O$ )

③ Single stage decomposition.

④ multi stage  
 (intermediate can be isolated)

⑤ multi stage  
 (intermediate can't be isolated)

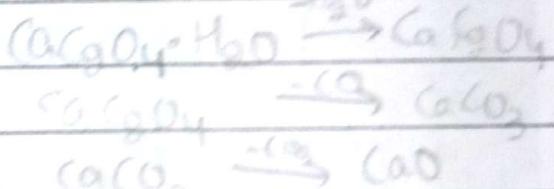
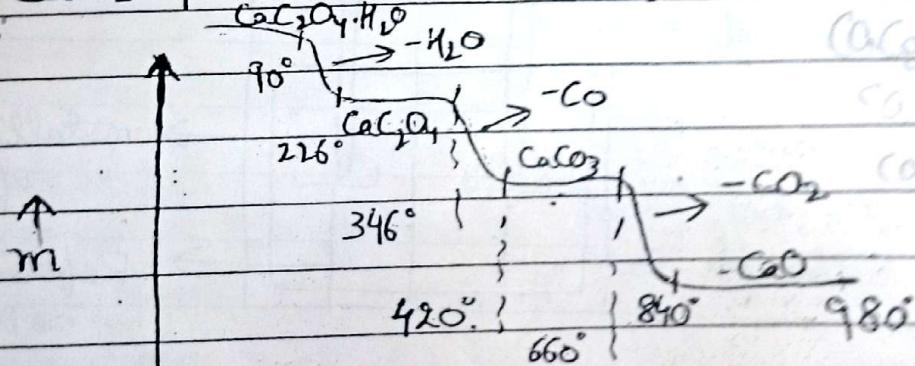
Temp ( $^{\circ}C$ ) →

⑥ oxidation

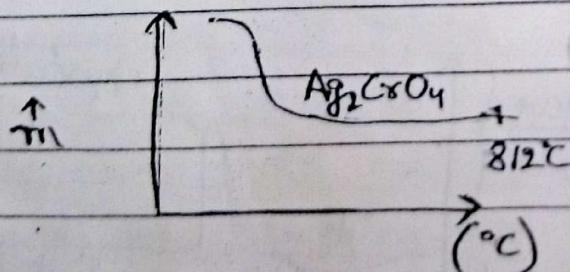
⑦ oxidation & then decomposition  
 (% of addition of oxygen)

Temp ( $^{\circ}C$ ) →

$CaC_2O_4 \cdot H_2O$  (In absence of air)



Temp ( $^{\circ}C$ )

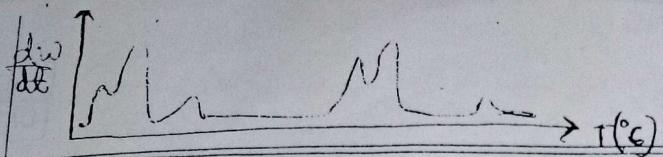


### APPLICATION:

- moisture content can be found

- composition - decomposition profile

- Thermal stability range



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- most suitable drying temperature of analytical

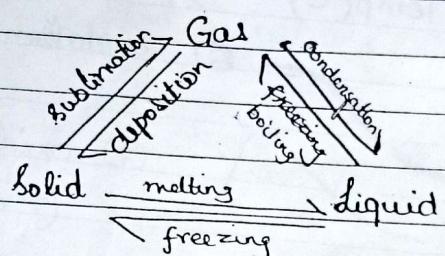
• (DTG): derivative thermogravimetry

Rate of change of mass ( $dw/dt$ ) with temperature plotted along temp.

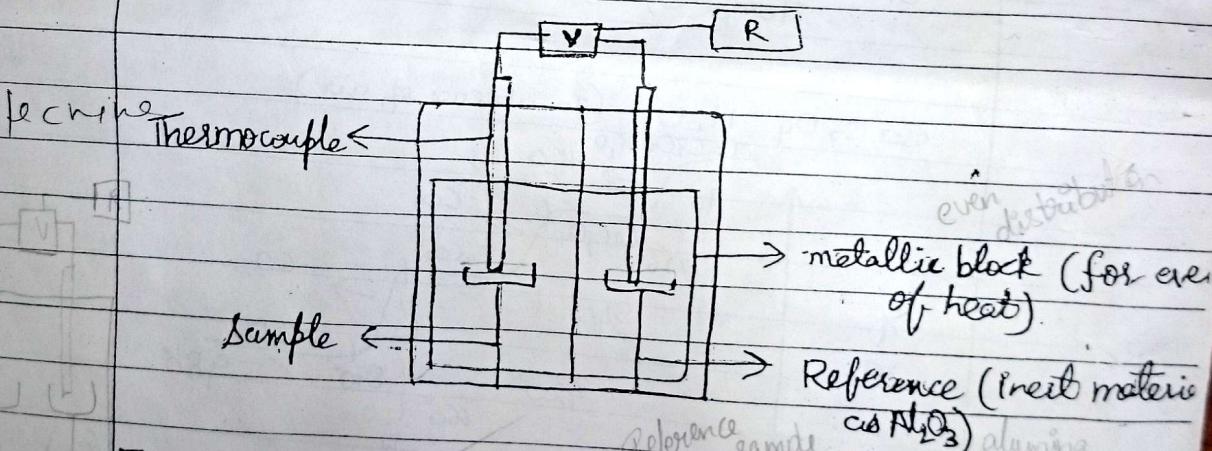
$dw/dt$

• DTA :  $\Delta T (= T_{\text{reference}} - T_{\text{sample}})$

Reference is an inert substance eg. Pt/alumina / SiC, which undergo any physical or chemical change.

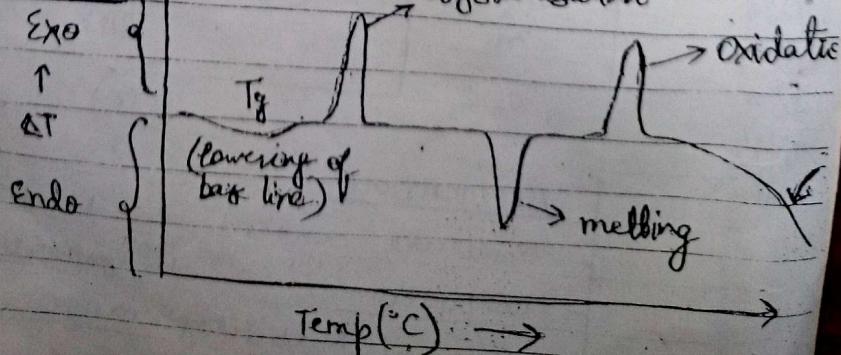


Block diagram



Thermocouple: this wire used to detect the temp of reference sample.

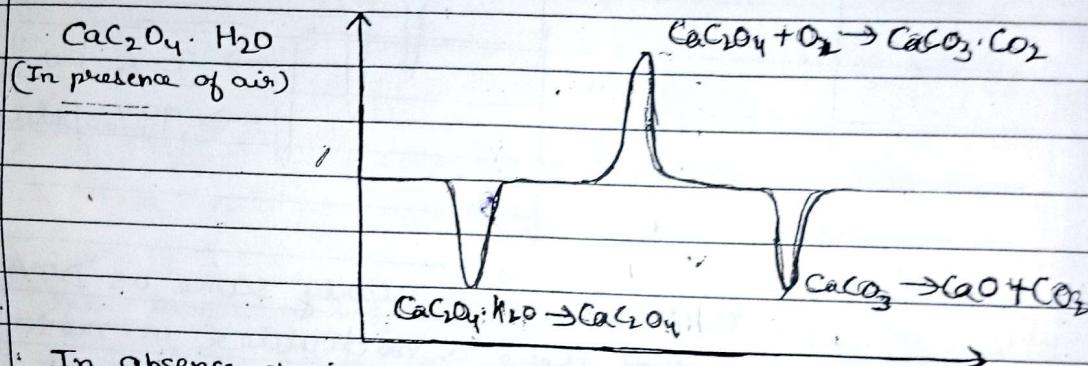
Standard curve



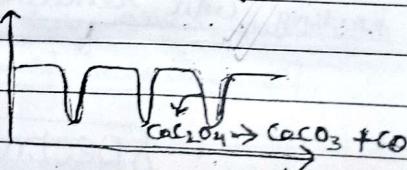
Analytical  
Reagent  
featureCrystallisation - exothermic  
Melting - endothermic

(only for polymeric substance, that too in beginning and we either see  $T_g$  or maxima or minima)

(Glass transition temperature at which glass-like amorphous polymers are converted to flexible rubber-like substance and concerted motion of large segment of polymeric molecules start. Then they try to get arranged into crystal structure)



In absence of air it will get 3 minima.



- Definition: that analysis in which difference in temp of sample & reference is recorded as a function of temp. When both are subjected to a controlled temperature program

#### Application:

- Qualitative technique (DSC is quantitative)

- able to measure the temperature at which various phase transitions take place.

~~but it does not give any info regarding the amt of energy associated with each event. This is provided by DSC.~~

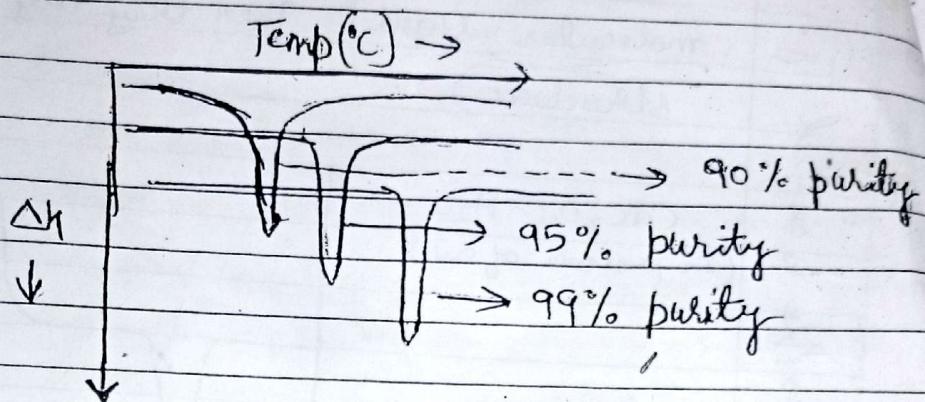
- used for studying and categorising characterizing polymer tells the phase transitions taking place.

- helps in generation of phase diagrams.

- used in metallic & ceramic industry.

DSC : analysis in which energy associated of energy involved) in maintaining a zero temperature difference b/w sample & reference is recorded (Basically used to check purity of a sample)

Block diagram :



Block diagram is nearly same as DTA. (only diff is that there is no divider in metallic block) & heating unit remains same

## • Spectroscopy •

Definition method to determine the structure of any compound by its study of interaction of EMR with matter.

- very less time consuming
- highly reliable
- reproducible (observations are very same)
- less amt of substance reqd & that too can be reused

EMR - they are form of energy which does not require any medium to travel & travel at enormous speed

CHARACTERISTICS: Wavelength, Frequency, Wave number, Energy.

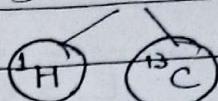
Cosmic X UV Visible I.R. Microwave Radiation

$\lambda$  decreases increases →

$\nu$  decreases →

### Types of Spectroscopy :-

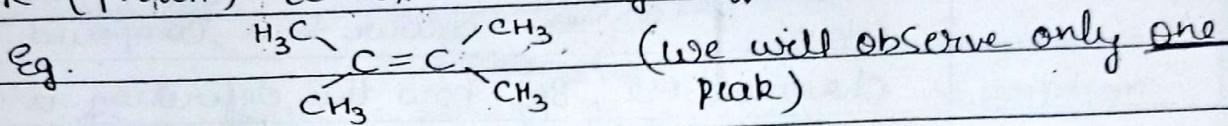
- 1) UV-vis
- 2) IR
- 3) NMR
- 4) Mass Spectroscopy method



UV-vis tells us where conjugation is present

IR tells abt function groups

NMR (proton) tells no. of chemically different protons present.



$^{13}\text{C}$  tells no. of chemically different carbons

[one peak for each chemically different]

When sample is subjected to IR, molecules can vibrate & rotate. Thus aka vibration & rotation spectroscopy.

When UV-vis is given, molecules can undergo electronic transition, thus also called electronic spectroscopy.

**UV Visible Spectroscopy** : deal with interaction b/w electromagnetic & matter.

UV  $\rightarrow$  200 - 400 nm, Vis  $\rightarrow$  400 - 800 nm.

#### Types of electronic transition

i. ①  $\sigma \rightarrow \sigma^*$  (possible in all kinds of molecules)

In any saturated compd. such as alkanes, without heteroatom, ONLY

$\sigma \rightarrow \sigma^*$  transition is possible. They absorb light in 120 - 200 nm (Far UV/vacuum)

ii. ②  $n \rightarrow \sigma^*$  (non bonding to  $\sigma$  antibonding)

any saturated compd with heteroatom, both ① & ② are possible

Energy reqd in ① > Energy reqd for ②

Since saturated compd absorb in 120 - 200 nm, they can't be used as solvent for UV-vis spectroscopy. (as not in uv region)

iii. ③  $\pi \rightarrow \pi^*$  (possible in any unsaturated compound,

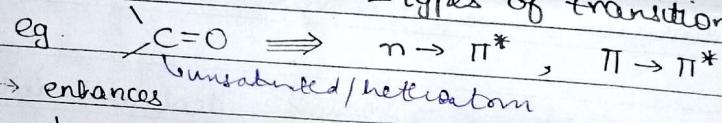
without heteroatom.)

E<sub>4</sub> (4)  $n \rightarrow \pi^*$  (possible for unsaturated compd with lone pairs)  
If some compd shows (4), it will also show 1, 2 & 3.

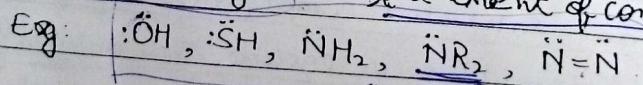
$$E_1 > E_2 > E_3 > E_4$$

Terms associated with UV-VIS:

- chromophore :- initially, any group capable of imparting colour to a compound was considered chromophore. But now this definition is modified. Now, any isolated, covalently bonded, <sup>(to C)</sup> unsaturated group of atoms shows absorption in UV-VIS region irrespective of the fact whether colour is produced or not. It is called chromophore. If it absorbs in  $\text{vis}$  region, no colour is produced and if it absorbs in  $\text{vis} \rightarrow \text{uv}$  region, no colour will be seen. Example:  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$ ,  $\text{C}\equiv\text{N}$ . Chromophores show 2 types of transition:



- auxochrome :- those grp. which themselves do not absorb in UV-VIS region but when present in conjugation with a chromophoric part, they shift  $\lambda_{\text{max}}$  towards higher wavelength OR They cause bathochromic shift / Red shift.  $\Delta \propto \text{extent of conjugation}$



Present in auxochrome

- ↳ lone pair takes part in conjugation  $260 \text{ nm} \rightarrow 280 \text{ nm}$
- p-extended conjugation causes lowering of energy and  $\lambda_{\text{max}}$  increases

Bathochromic shift: Shifting of  $\lambda_{\text{max}}$  to higher wave occurs due to presence of auxochrome  
 If  $\pi \rightarrow \pi^*$  transitions take place, we increase solvent polarity towards  $\text{red}$ .

Amr is the mass absolute

X.P. Hyperpolarisability  
 $\pi \rightarrow \pi^*$  bond  
 non bond

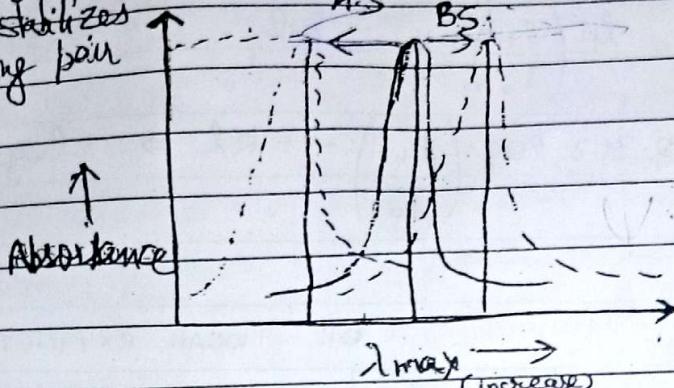
style  
 white  
 red  
 up  
 down

$\lambda_{max}$  is the wavelength at which compound shows maximum absorbance.

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- **Hypsochromic shift / Blue shift:** occurs due to removal of conjugation. Increase in solvent polarity stabilizes non bonding pair.



Intensity of absorption is same in all.

- **Hyperchromic shift:** change in intensity of absorption without change in  $\lambda_{max}$ .

B.S. & H.S. generally occur simultaneously. But if we want only H.S., increase the conc.

Related with Hypsochromic shift

**Hypochemical shift:** decrease in  $\lambda_{max}$  without change in intensity.  $\lambda_{max}$

$$T = \frac{I_t}{I_0}, A = -\log T = -\log \left( \frac{I_t}{I_0} \right)$$

$I_t$  = intensity of transmitted light

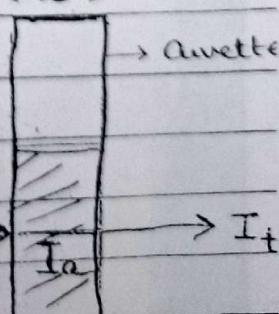
$I_0$  = " " incident light

Absorbance is additive property & Transmittance is a multiplicative property.

### Law of Absorbance:

**Lambert's law:** when a beam of monochromatic radiation is passed through homogeneous absorbing medium, then the rate of decrease in intensity of radiation with the thickness of the solution is  $\propto$  intensity of incident radiation.

$$\text{Mathematically, } -\frac{dI}{dx} \propto I$$



$$\int_{I_0}^{I_t} \frac{dI}{I} = -k \int_0^l dx$$

$$\Rightarrow \ln\left(\frac{I_t}{I_0}\right) = -kl$$

$$\Rightarrow 2.303 \log\left(\frac{I_t}{I_0}\right) = -kl \Rightarrow -\log\left(\frac{I_t}{I_0}\right) = \frac{k \cdot l}{2.303}$$

$\downarrow$   
E = MOLAR ABSORPTIVITY  
OR. MOLAR EXTINCTION COEFFICIENT.

$$\Rightarrow A = El$$

- Lambert Beer's law: When a beam of .... intensity of incident radiation as well as concentration of solut  
 $\therefore$  final expression is

$$A = E \cdot C \cdot l$$

A is unit less, C = moles/l, l = cm

CCH

#### LIMITATIONS:

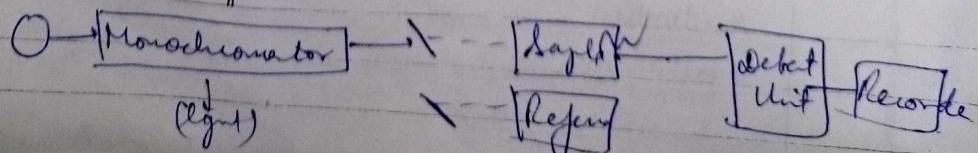
- Not valid for polychromatic beam of light.
  - Not valid for highly concentrated soln.
  - When different forms of compound (e.g. keto, enol) exist in the solution. not homogeneous
  - When some sort of complex formation is taking place.
  - When fluorescent compounds are used.
  - When medium is heterogeneous
- ~~\* valid~~

- Spectrophotometer: device used to measure amt. of light absorbed when U.V. - Some kind of radiations passed.

UV-VIS spectrophotometer - { Single beam

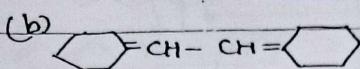
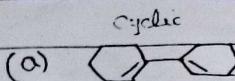
Double beam.

Block diagram:-



IV IMP

Woodward-Fieser Rule for calculating  $\lambda_{max}$



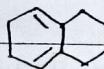
These  
substituents  
are present

present  
only if  
rings are  
fused

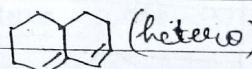
Basic System	Base value (nm)	Increment value for each Substituent
Acyclic / cyclic (Conjugated diene)	217 / 214	• Alkyl gp.
Homoannular	253	• Ring residue } 5 • Exocyclic d.b.
Heteroannular	217	• d.b. extending - 30 , gty. eg. conjugation • $\text{NH}_2$ - 30   • $\text{NR}_2$ - 60 of 2 • halogens - 5 extra

- If both double bonds are present in the same ring  
it is ~~hetero~~ homoannular.

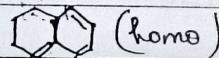
- Homoannular is preferred over heteroannular



(homo)



(hetero)



(homo)

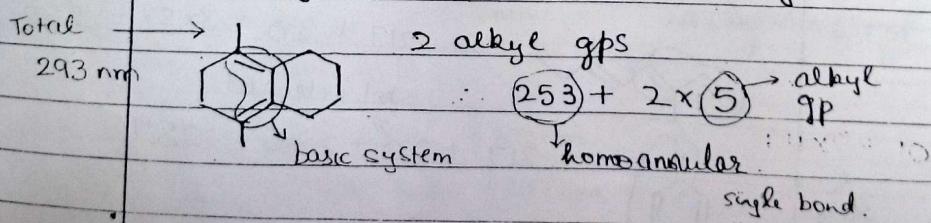
o not

not in

cyclic

$18 + 5 \times 2$

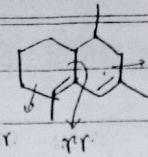
- Consider only those substituents which are directly attached to the basic system.



317 nm

- Calculating ring residue  $\downarrow$  part of conjugated system as well as ring is called ring residue (e.g.)

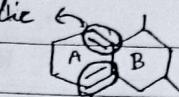
$\text{C} - \text{C} \rightarrow$  part of a ring  
from system



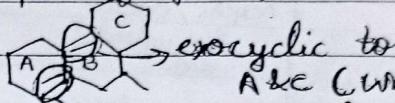
3 ring residues.

- Exocyclic double bond : any d.b. pointing outside a ring. (It can also be a part of system)

exocyclic

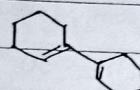


exocyclic  
Ring B

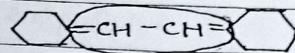


exocyclic to  
A & C (will be  
exocyclic to B  
considered twice)

Q)



$$217 + 4 \times 5 = 237 \text{ nm}$$



$$217 + 5 \times 4 + 2 \times 5 = 247 \text{ nm}$$

Q.

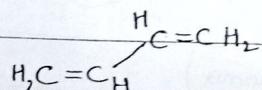


$$217 + 1 \times 5 = 222$$

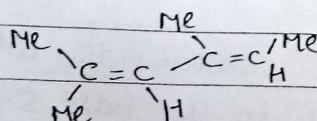


$$217 + 2 \times 5 = 222$$

valid

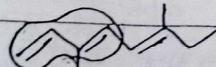


217



$$237 = 217 + 4 \times 5$$

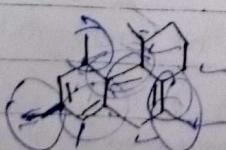
DOUBT



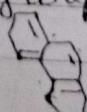
$$217 + 30 + 3 \times 5 = 262$$

not extended.

$$217 + 30 + 2 \times 5 = 257$$

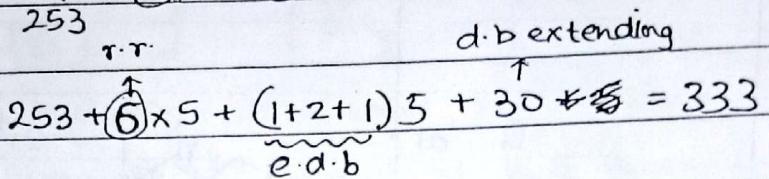
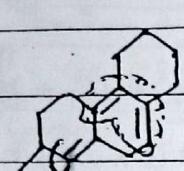
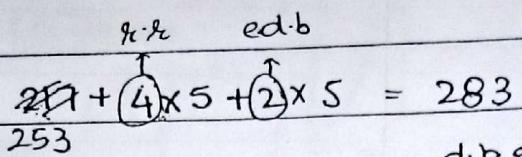
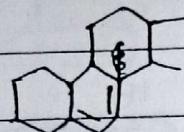
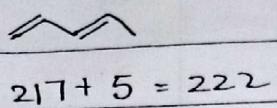
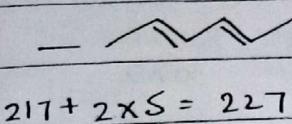


253 + (30 + 30) + 6 Ring residue  
+ 2 alkyl groups + 4 exocyclic



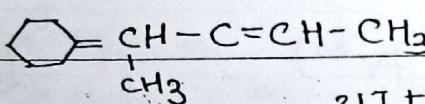
1  
Topic + Soln  
solvent

2,4-hexadiene → 1,3-Pentadiene.



eg. no.  
gty eg.

auto anti-X.



$217 + 5 +$

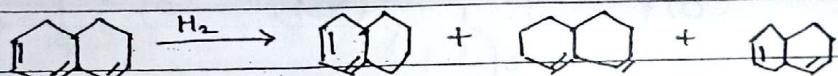
ans 242

of 2

rectra

o not

Q.



the products are separated by using gas chromatography. How to identify the products using UV-VIS?

not in

exocyclic

→  $\alpha$ - $\beta$  unsaturated aldehyde or ketone

$18 + 5 \times 2$

A

Base  
Solvent

Acyclic

Cyclic 6 membered  
, ald or ket

cyclic 5 membered ketone

" " " aldehyde

$215 \text{ nm}$

see the ring  
having carbonyl

$317 \text{ nm}$

INCREMENT values:  $\alpha$   $\beta$   $\gamma$  or higher

alkyl gp → ~~18~~ } 10 12 18 w.r.t.  $\text{C=O}$

Ring residue

Exocyclic → 5 at any position  
double

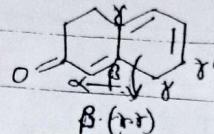
Tack  
Arrangement  
 $\beta$ s pendant  
groups &  
spac.

OH at a position  $\rightarrow 35$ , at B  $\rightarrow 30$

double bond extending. cong  $\rightarrow 30$

homoannular component  $\rightarrow 39$ .

Eg:



(2 bonds are counted as

215

$30 \times 2$

39

12

18

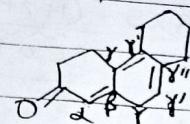
18

$5 \times 2$

~~double~~ exocyclic

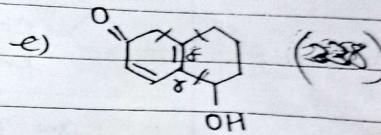
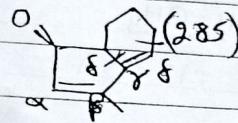
double bond

Q. a)

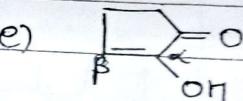
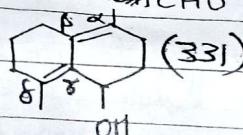


$$215 + (12 + 18 + \cancel{18} + 18 \times 2) + (4 \times 5 + (2 \times 30) + 39 = 418$$

b)



d)



Sol

b)

$$-RatB \quad \gamma \text{, } \alpha \text{, } \beta \quad d \text{, } b \text{, } c \quad e \text{, } c \text{, } d \text{, } b \\ 202 + 12 + 2 \times 18 + 30 + 5 = 285$$

c)

$$217 + 18 \times 3 + 39 + 30 = 338$$

d)

$$215 + 18 + \cancel{10+12+36} + 5 \times 2 + 30 = 331$$

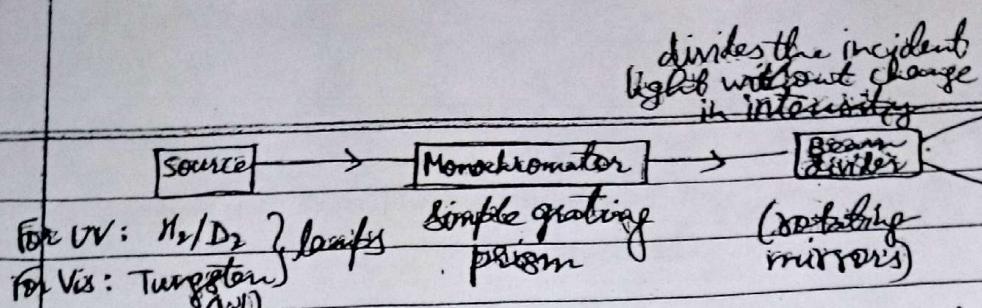
e)

$$202 + 12 + 35 = 249$$

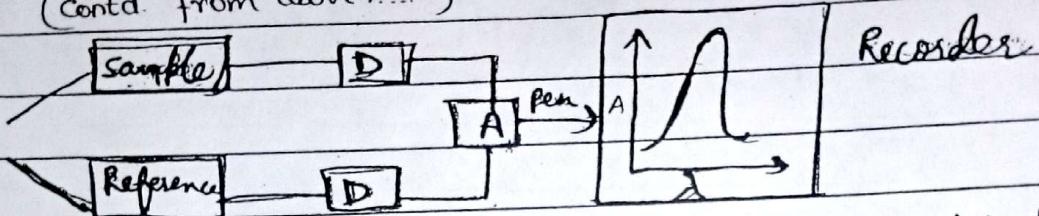
{ not valid

DS

Sample | Compd + Soln



The rotating mirrors move very fast and divide the incident light.  
(Contd. from above....)



D (detector) is a photo-voltaic cells, which detects the signal in terms of quanta and converts it to a measurable qty. e.g. voltage or current)

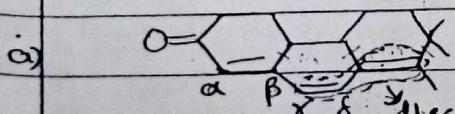
Al amplifier amplifies the signal, does subtraction of 2 Spectras (Compd + solvent) - (solvent) and produces the spectra

Sample & reference cells should be such that they do not absorb in the reqd. region.

Quartz does not absorb in UV & glass does not in Visible.

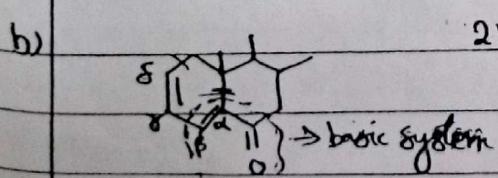
Q. (Woodward Fieser cont....)

exocyclic



$$215 + 30 \times 2 + 12 + 18 \times 2 + 18 + 5 \times 2 = 351$$

K-T. no dbec



$$215 + \overbrace{18+16}^{\text{K-T.}} + \overbrace{5}^{\text{no dbec}} + 30 + 39 = 317 \text{ nm}$$

In exam write like:

215 ... Base

18 ...

16 ...

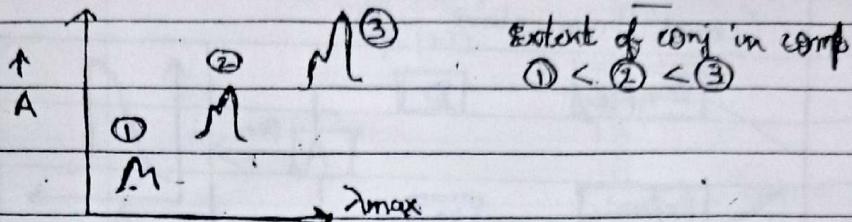
5 ... exocyclic

30 ... dbec

39 ... homannular

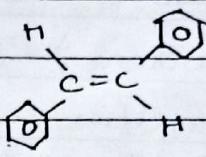
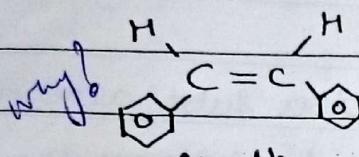
317

1. Detection of conjugation: compds without conjugation will absorb in  $\lambda$  range below 200 nm.
2. Extent of conjugation: more the double bond, more will be  $\lambda_{max}$ .

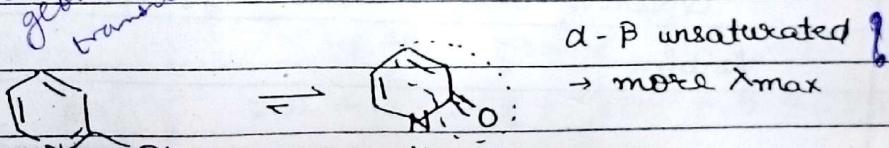


3. Detection of presence of chromophore or auxochrome

4. It can differentiate b/w the geometric isomers



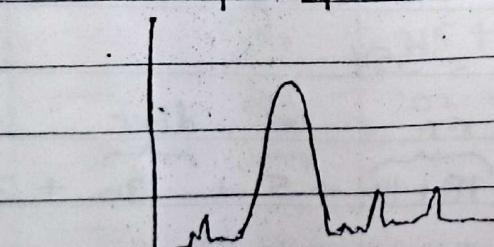
energy reqd absorbs at shorter wavelength than  
cis :- loss of coplanarity; steric hindrance; energy  
reqd for most favourable transition is more and  $\lambda_{max}$   
is less *e transition* *geometric transition*?



(more preferred tautomer)

5. Can be used for qualitative analysis

If compound is more pure  
we get a single well resolved  
peak.



Impure compd

6. Can be used for quantitative analysis  
(Lambert - Beer's law)

A polyene having more than 2 conjugated double bonds  
will show absorbance in UV-VIS region