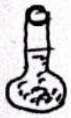
Exp-01

- Oxalic Acid dihyd. / primary std.

0.63 gm $H_2C_2O_4 \cdot 2H_2O$ + 100 mL H_2O

 Make up to 100 mark.

- Sodium Hydroxide / Secon. std.

Supp. Soln. / Sample Soln. + Add H_2O  Make up to 100 mark

Concentration → NaOH → Burette

→ $H_2C_2O_4$ → Conical fl

Exp-01

Strong Base Weak Acid Neutralization.

Accuracy

CamScanner

STANDARDIZATION OF SODIUM HYDROXIDE (NaOH) SOLUTION WITH STANDARD OXALIC ACID DIHYDRAT ($H_2C_2O_4 \cdot 2H_2O$) SOLUTION. (Normality)

ocedure

0 ml oxalic Acid dihyd
$_2C_2O_4 \cdot 2H_2O$) + 80 ml H_2O
2/3 drop. Indicator + Tit.
th Supp. Sodium hydroxide
NaOH) Samp. → Light pink

CHEMICALS and CHARACTER

- Sodium Hydroxide (NaOH) Second. Std
- Oxalic Acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) prim.std
- Phenolphthalein ($C_{20}H_{14}O_4$) Weak Organic Acid

MECHANISM OF INDICATOR

Phenolphthalein (HIn)

Acid Media: HIn $\underset{H^{\oplus}\,(Acid)}{\overset{OH^{\ominus}\,(base)}{\rightleftharpoons}}$ $H^{\oplus} + In^{\ominus}$: Basic Media

(Colorless) (Light pink)

Abstract

Solu.$H^{\oplus}$ + HIn $\xrightarrow{OH^{\ominus}}$ $H_2O + OH^{\ominus} + In^{\ominus}$

(Colorless) (light pink)

CALCULATION

$V_1S_1 = V_2S_2$

$S_2 = V_1S_1/V_2$

= Strg. of. NaOH

V_1 = vol of oxalic Acid

S_1 = Strg. of Oxalic Acid

$= \frac{\text{wt taken in gm}}{\text{wt to be taken}} \times \frac{N}{10}$

V_2 = Vol of NaOH

S_2 = ???

STANDARDIZATION OF SODIUM HYDROXIDE (NaOH) SOLUTION WITH STANDARD OXALIC ACID DIHYDRAT ($H_2C_2O_4 \cdot 2H_2O$) SOLUTION.

(Normality)

Procedure

10 ml oxalic Acid dihyd ($H_2C_2O_4 \cdot 2H_2O$) + 80 ml H_2O + 2/3 drp. Indicator + Tit. with Supp. Sodium hydroxide (NaOH) Soup. → Light pink

CHEMICALS and CHARACTER

- Sodium Hydroxide (NaOH) Second. Std
- Oxalic Acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) prim.Std
- Phenolphthalein ($C_{20}H_{14}O_4$) Weak Organic Acid

MECHANISM OF INDICATOR

Phenolphthalein (HIn)

Acid Media: HIn (Colorless) $\rightleftharpoons$ $H^{\oplus} + In^{\ominus}$ (Light pink) Basic Media

$OH^{\ominus}$ (base) ; $H^{\oplus}$ (Acid)

Abstract

Solu.$H^{\oplus}$ + HIn (Colorless) $\xrightarrow{OH^{\ominus}}$ $H_2O + OH^{\ominus} + In^{\ominus}$ (Light pink)

CALCULATION

$V_1S_1 = V_2S_2$

$S_2 = V_1S_1/V_2$

= Strg. of. NaOH

V_1 = vol of oxalic Acid

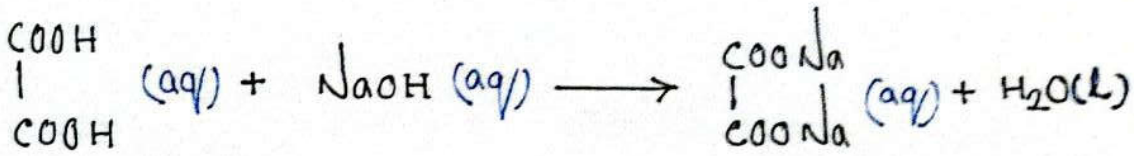
S_1 = Strg. of oxalic Acid

$= \frac{\text{wt taken in gm}}{\text{wt to be taken}} \times \frac{N}{10}$

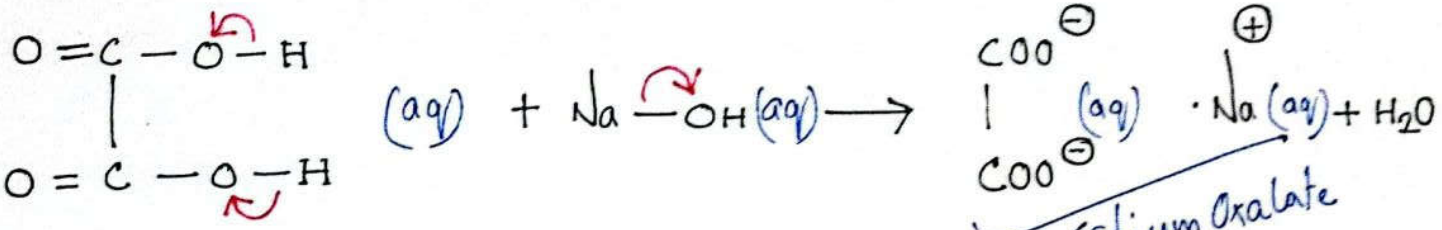
V_2 = Vol of NaOH

S_2 = ???

Reaction



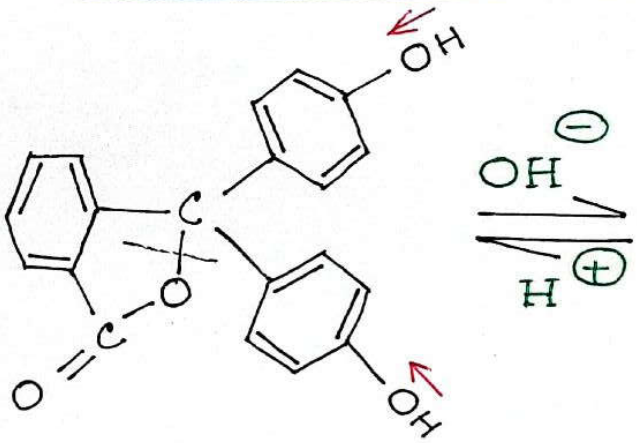
Reaction Mechanism / Molecular Equation



- The equivalent weight (or the number of Reacting unit's) depends on the chemical Reaction.
- The equivalent weight is that weight of a substance in grams that will Furnish one mole of the Reacting unit.

MECHANISM OF Phenolphthalein(HIn) Indicator

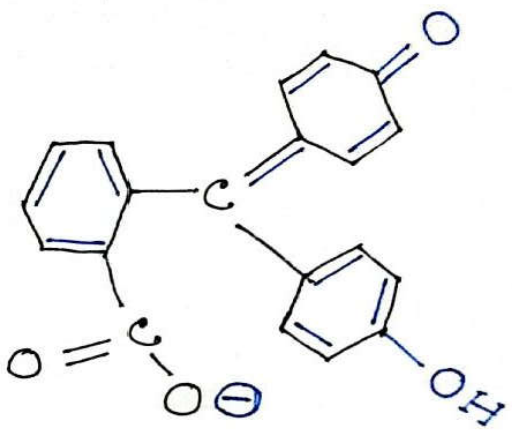
acid Media



HIn (clear)

$\overset{\ominus}{OH}$

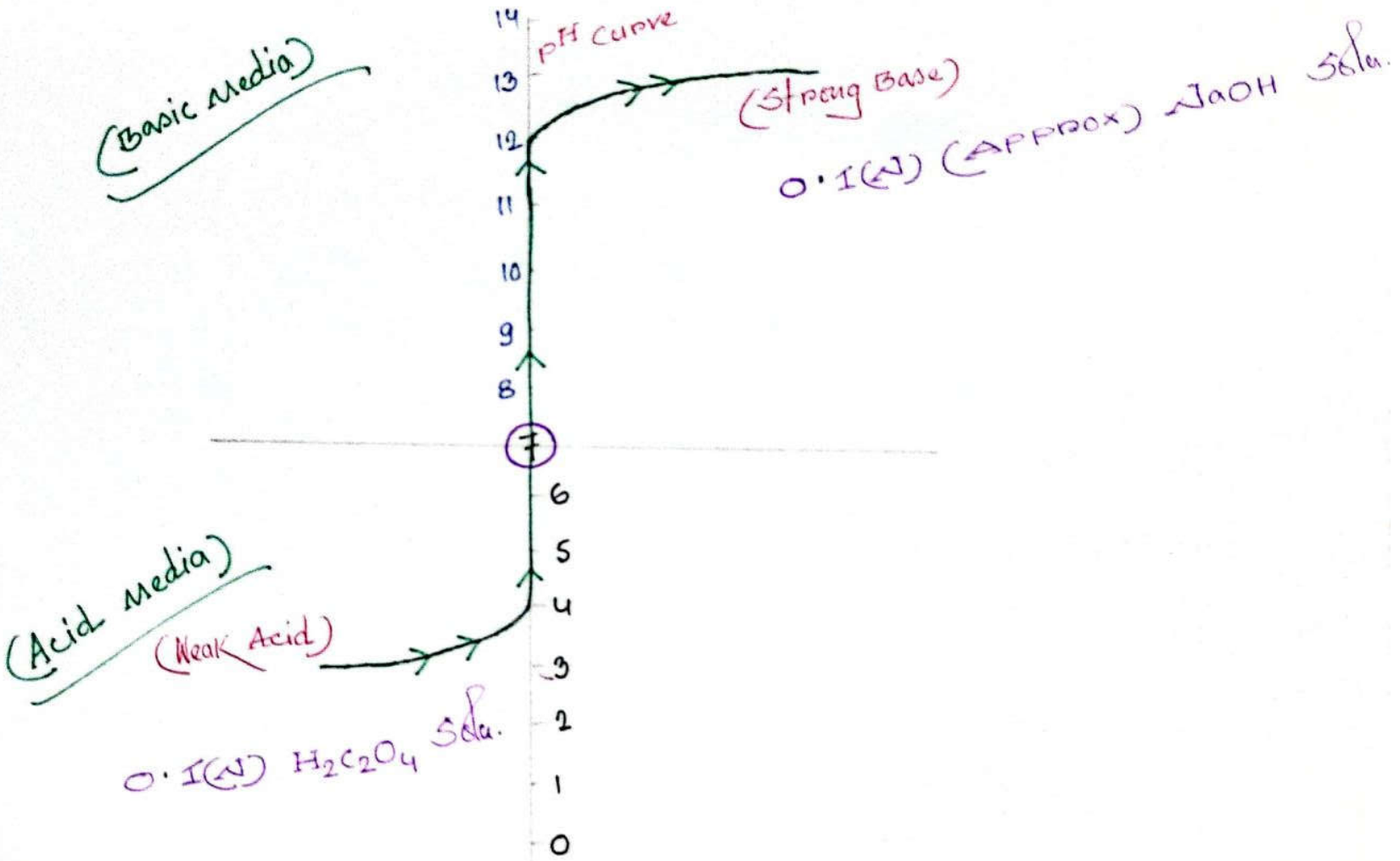
$H^{\oplus}$



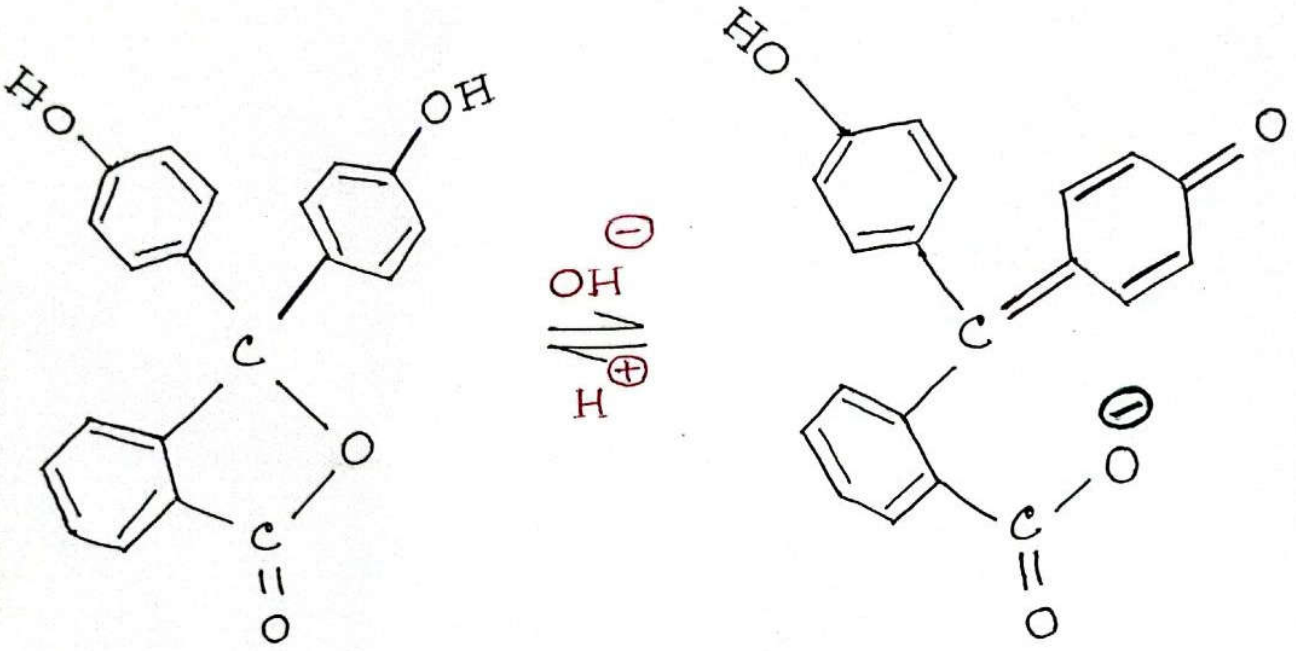
Basic Media

$In^{\ominus}$ (light pink)

STRONG BASE WEAK ACID NEUTRALIZATION



Quinonoid Theory



(Benzenoid structure) (Quinonoid structure)

Colorless — Light-pink

Exp-01

For student ONLY

- Oxalic Acid dihyd. Prop. ($H_2C_2O_4 \cdot 2H_2O$) Wt-126

  0.63 gm + 100 mL flask H_2O → 100 mL Mark → Known Conc. Soln.

- Sodium Hydroxide → Samp. Soln → Unknown Conc.

  + H_2O → Mark 100 ml

- NaOH / 0.1(N) Soln. Prep. → 0.40 gm NaOH

Exp-02 + H_2O make up to 100 mL.

- HCl / Soln. Prep. → Take the Supp.

Soln. + H_2O make up to 100 mL.

- Concentration
  - HCl → Unknown → Burette
  - NaOH → Known → Conical Flask

- In both
  - The H and - ions (Na and Cl)

Exp-

H_2O and the other

anged.

STANDARDIZATION OF HYDROCHLORIC ACID (HCl) SOLUTION WITH STANDARD SODIUM HYDROXIDE (NaOH) SOLUTION.

Normality

STRONG ACID STRONG BASE NEUTRALIZATION

Procedure

10 ml Sodium hydroxide Soln.
+ 80 ml H_2O + 2/3 drop. Ind.
+ Titration with Suppl. HCl
Soln. ⟶ Colorless

CHEMICALS and CHARACTER

- Hydrochloric Acid (HCl) Second. Std.
- Sodium Hydroxide (NaOH) Second. Std.
- Phenolphthalein ($C_{20}H_{14}O_4$) Weak. Org. Acid

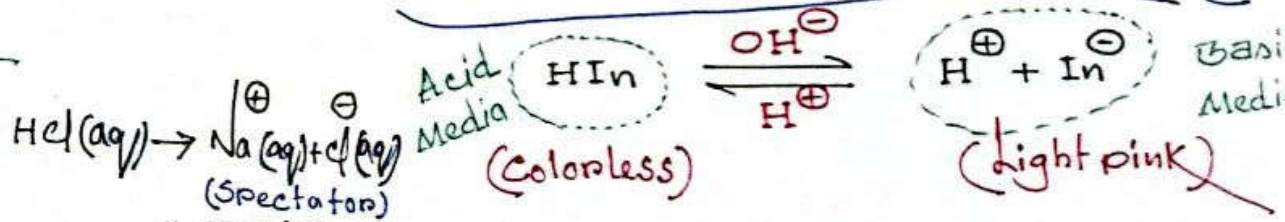
CALCULATION

$V_1S_1 = V_2S_2$

$S_2 = V_1S_1 / V_2$

= Strg. of HCl

MECHANISM OF PHENOLPHTHALEIN (HIn)



Reaction

$NaOH(aq) + HCl(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$

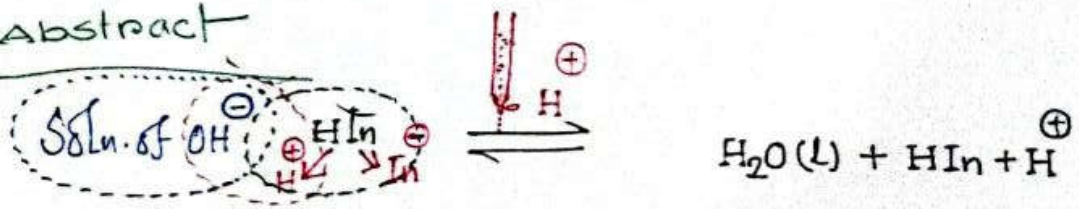
(Na^+ (Spectator))

Reaction Mechanism

$NaOH(aq) \rightleftharpoons Na^+(aq) + OH^-(aq)$

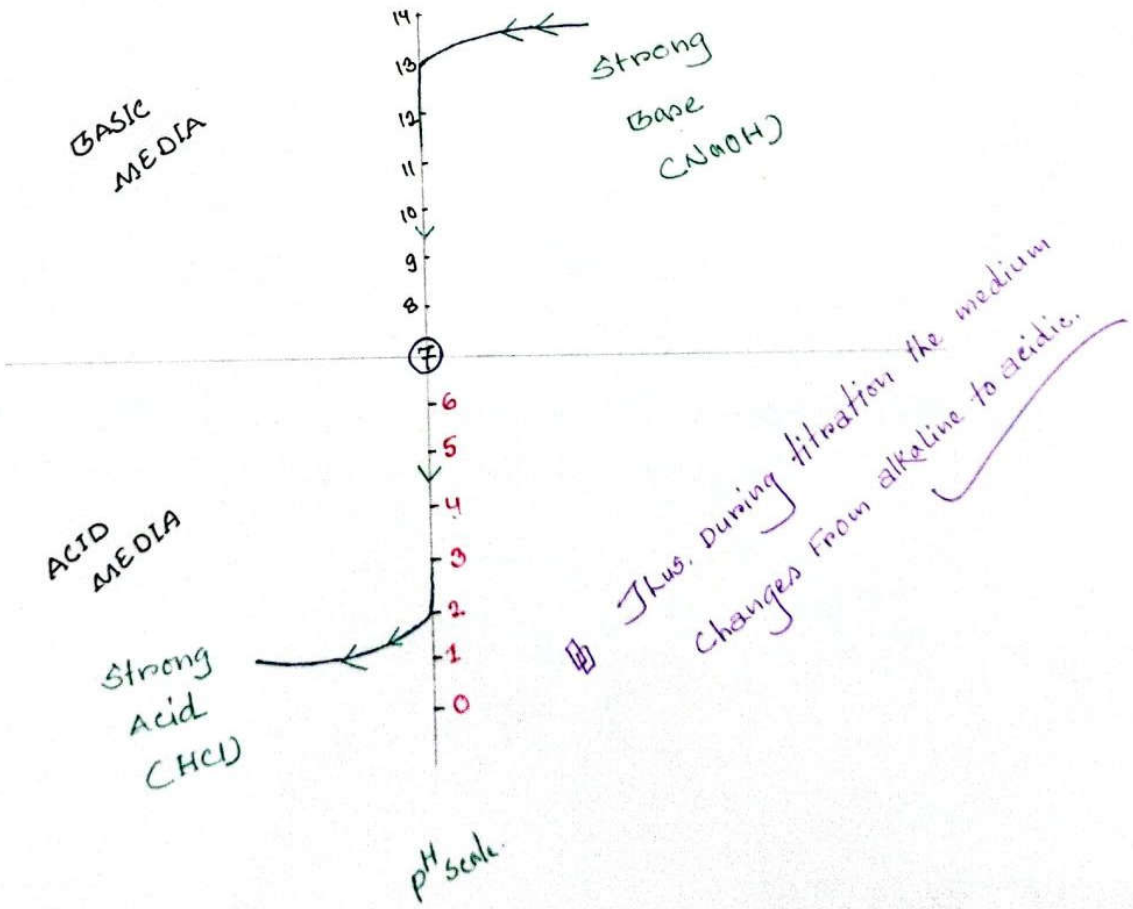
$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$

Abstract



STRONG ACID VS STRONG BASE Curve

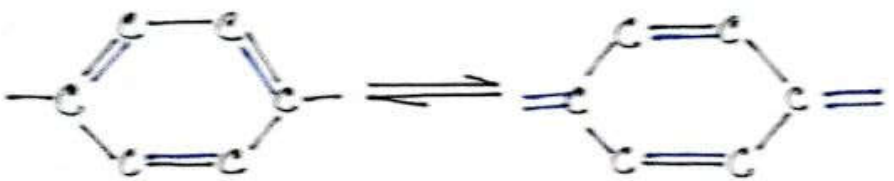
(pH Curve)



Thus, during titration the medium changes from alkaline to acidic.

MECHANISM OF PHENOLPHTHALEIN (Basic change)

Note:



(benzenoid) (colorless)

(quinonoid) (light pink)

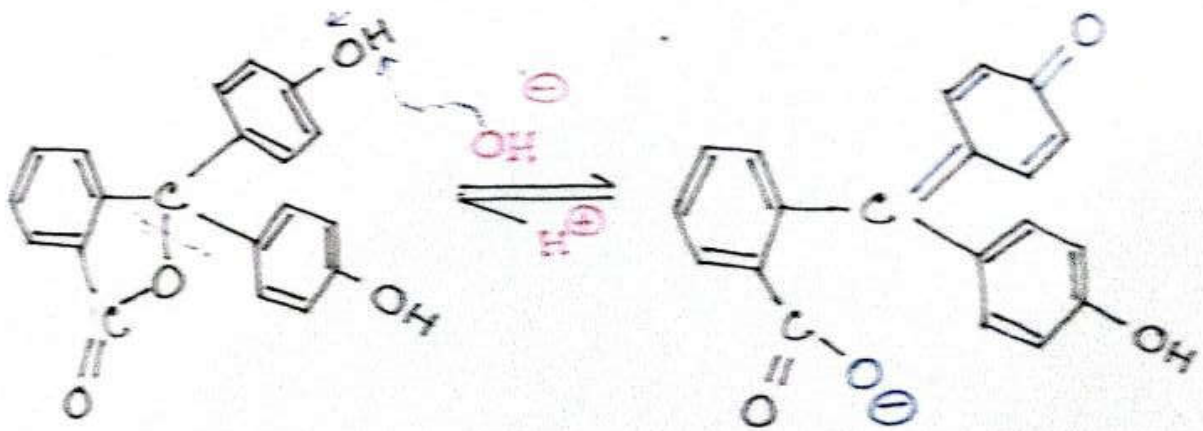
Resonance

e⁻ electr

The two forms have different colors. The color change is due to the interconversion of one tautomeric form into other.

Phenolphthalein

STRUCTURAL MECHANISM



(colorless) (light pink)

STRONG ACID STRONG BASE NEUTRALIZATION.

- In aqua Sol. $Na^{\oplus}$ and $Cl^{\ominus}$ does not participate in Reaction. Here $Na^{\oplus}$ and $Cl^{\ominus}$ is spectator Ion.
- There is no electron transition in this Reaction.
- In this Reaction $H^{\oplus}$ and $OH^{\ominus}$ Ion participate Reaction and product is Neutral water H_2O

$$H^{\oplus}(aq) + OH^{\ominus}(aq) \rightarrow H_2O(l)$$

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Exp-03

- HCl Soln. Prep. ⟶ Take Supp. Soln.
  + Add H_2O and make up to 100 mL.

- Slightly hygroscopic
  Na_2CO_3 Soln. Prep. ⟶ Take 1.06 gm
  Na_2CO_3 + H_2O and shake 10 min + Then Add H_2O and make up to 100 mL

Moderately Strong Base

Concentration

- HCl → Burette
- Na_2CO_3 → Conical flask.

মাহমুদ

$Na_2CO_3 \equiv 2\,NaOH \equiv 2\,HCl$

EXP-03

STRONG ACID

WEAK BASE

NEUTRALIZATION

Mahmud



- Slightly hygroscopic
- Moderately strong base

Sodium Carbonate can be titrated to give end point's corresponding to the step-wise addition's of Protons to form HCO_3^- and CO_2:

$$CO_3^{2-}{}_{(aq)} \xrightarrow{H^+_{(aq)}} HCO_3^-{}_{(aq)} \xrightarrow{H^+_{(aq)}} H_2CO_3 \downarrow$$

$$CO_2 + H_2O$$

Exp-03

STANDARDIZATION OF HYDROCHLORIC ACID (HCl) SOLUTION WITH STANDARD SODIUM CARBONATE (Na_2CO_3) SOLUTION. (molarity)

Procedure

10 ml Sodium Carbonate (Na_2CO_3) Sdn. + 80 ml H_2O + 2/3 drp. phenolphthalein indicator + Titration with supplied Hydrochloric Acid (HCl) Sdn ……→ Colorless

STRONG ACID WEAK BASE NEUTRALIZATION

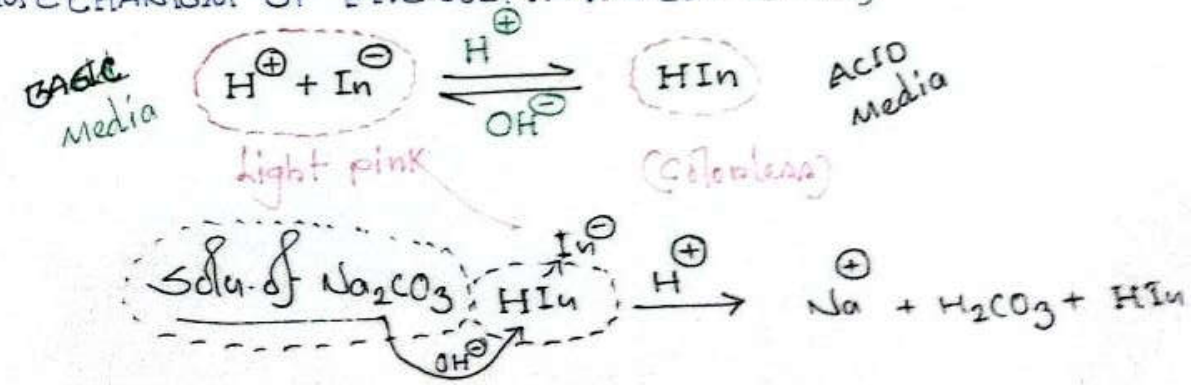
CHEMICALS and CHARACTER

- Hydrochloric Acid (HCl) (Second stand Subst)
- Sodium Carbonate (Na_2CO_3) (Prim Stand Subst)
- Phenolphthalein ($C_{20}H_{14}O_4$) (Indicator) (Weak Organic Acid)

Abstract

$$Na_2CO_3 \equiv 2NaOH \equiv 2HCl$$

MECHANISM OF PHENOLPHTHALEIN (HIn)



Sodium Carbonate (Na_2CO_3) is a moderately strong BASE

- Na_2CO_3 hydrolyzes in two step's

1. $Na_2CO_3 \underset{}{\overset{H_2O}{\rightleftharpoons}} NaHCO_3 + NaOH$
2. $NaHCO_3 \overset{H_2O}{\rightleftharpoons} H_2CO_3 + NaOH$

$H_2CO_3 \rightarrow CO_2 + H_2O$

- Buffer Soln.
- Basic buffer $Na_2CO_3/NaHCO_3$
- Acid buffer $H_2CO_3/NaHCO_3$

- Reaction

$$Na_2CO_3(aq) + HCl(aq) \longrightarrow Na^{\oplus}(aq) . Cl^{\ominus}(aq) + H_2CO_3$$

$H_2CO_3 \rightarrow CO_2 + H_2O$

- Reaction Mechanism

1. $Na_2CO_3(aq) + HCl(aq) \longrightarrow NaHCO_3(aq) + Na^{\oplus}(aq)\ldots Cl^{\ominus}(aq)$
2. $NaHCO_3(aq) + HCl(aq) \longrightarrow Na^{\oplus}(aq)\ldots Cl^{\ominus}(aq) + H_2CO_3$

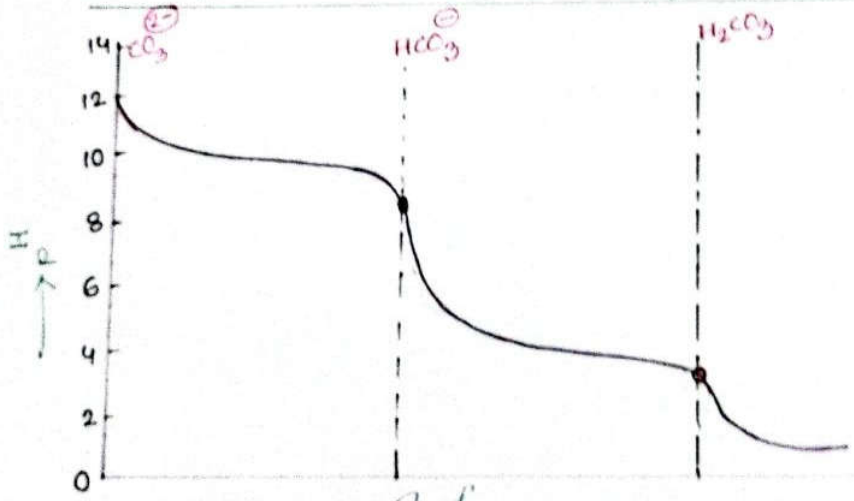
Spectator Ion

$H_2CO_3 \rightarrow CO_2 + H_2O$

Note

$HCO_3^{\ominus}$ is the conjugate acid of CO_3^{2-} and H_2CO_3 is the conjugate acid of $HCO_3^{\ominus}$

STRONG ACID (HCl) WEAK BASE (Na_2CO_3) NEUTRALISATION CURVE



1. $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

2. $HCO_3^- + H^+ \longrightarrow H_2CO_3$ ($CO_2 + H_2O$)

Two equivalence point's can be detected. one when all of the CO_3^{2-} has been converted to the amphiprotic HCO_3^- and second when all of the HCO_3^- has subsequently been converted to H_2CO_3 ($CO_2 + H_2O$)

- Abstract / Discussion

At the start of the titration, p^H is determined by the hydrolysis of the Bronsted base CO_3^{2-}. After the titration is begun, part of the CO_3^{2-} is converted to $HCO_3^{\ominus}$, and a $CO_3^{2-}/HCO_3^{\ominus}$ buffer region is established.

At the first equivalence point, there remain a solution of Beyond the first equivalence point, the $HCO_3^{\ominus}$ is partially converted to H_2CO_3 (CO_2) and a second buffer region is established, the p^H being established by $[HCO_3^{\ominus}] / [CO_2]$

The p^H at the second equivalence point is determined by the concentration of the weak acid CO_2.

- Always add the solution from the burette drop wise Constant shaking until color change is observed
- The weighing bottle should be free of moisture.

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$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$

1 mol | 2 mol

Na_2CO_3

$$\frac{V_1 \times S_1 \text{ (Strg. of } Na_2CO_3)}{V_2 \times S_2 \text{ (Strg. of } HCl)} = \frac{1 \text{ mol}}{2 \text{ mol}}$$

$Na_2CO_3 + 2HCl$

50.

$$N_0 - C \quad \frac{V_1 S_1}{V_2 S_2} = \frac{1}{2}$$

$$N_0 - O \quad V_2 S_2 = N_0 V_2 S_2$$

50 ml gel.

$$\Rightarrow V_1 S_1 \times 2$$

$$\Rightarrow S_2 = \frac{2 \times V_1 \times S_1}{V_2}$$

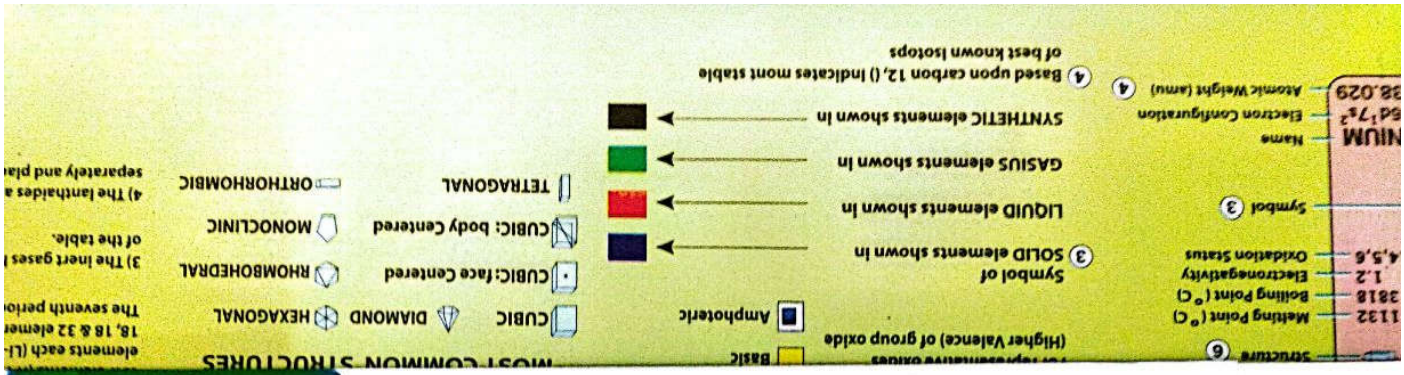
$\therefore$ Strg. of HCl Aqu.

- Carbonate is a moderately strong base
- Slightly hygroscopic.

Sodium Carbonate can be titrated to give
end points corresponding to the stepwise
additions of protons to form HCO_3^- and CO_2.

$$CO_3^{2-}(aq) \xrightarrow{H^+(aq)} HCO_3^-(aq) \xrightarrow{H^+(aq)} H_2CO_3(aq) \rightarrow CO_2 + H_2O$$

Sodium Carbonate is a Bronsted base that is used
as a primary standard for the standardization
of strong acids.



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Exp-04

- $CaCl_2 \cdot 2H_2O$ Soln. Prep. → Supp. Soln.

  H_2O make up to 100 mL.

- Na_2-EDTA 0·1 (M) Soln. Prep. →

  Take 3·72 gm Na_2-EDTA + H_2O and shake + Add H_2O make up to 100 mL

- 1·25 (M) NaOH Prep. → Take 3·0 g. NaOH Solid + 60 mL H_2O in 100 mL Beaker

METAL INDICATOR

LIGAND

In^{3-} → $CaIn^{\ominus}$ (wine red)

$CaIn^{\ominus} + H_2Y^{2-} \rightarrow CaY^{2-} + H_2In^{\ominus}$

$HIn^{2-} + H^{\oplus}$ (Light blue)

FLOW SHEET

REDDISH → WINE RED → PURPLE → LIGHT BLUE

CamScanner

Mahmud

COMPLEXOMETRIC TITRATION

Exp-04

DETERMINATION OF CALCIUM (Ca)

Mahmud

Multidentate Ligand and Metal Complex

- The ligand provides both of the electrons for the bond that forms between itself and the central metal atom or ion.



Exp-04

DETERMINATION OF CALCIUM (Ca) CONTENT IN A CALCIUM CHLORIDE DIHYDRATE ($CaCl_2 \cdot 2H_2O$) SOLUTION WITH STANDARD DI-SODIUM ETHYLENE DIAMMINE TETRA ACETIC ACID (Na_2-EDTA) SOLUTION. (MOLARITY)

Working procedure

10 ml $CaCl_2 \cdot 2H_2O$ soln. + 80 ml H_2O + 2 drop. Eriochrome blue (calcon) Indicator + 10 ml 1·25 (M) NaOH soln. to increase the pH + Titration with Na_2-EDTA ⟶ Light blue

COMPLEXO METRIC TITRATION

CHELOMETRIC TITRATION

Metal Ligand Complex

* Metal ion is a Lewis Acids.
* The complexes is a Lewis base.
* Complex formation between the analyte and titrant.

CHEMICALS

- Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) // Alkaline earth metal. // Earth Base metal
- Di-Sodium EDTA (Na_2-EDTA) // Primary std (Ligand) (chelate)
- Sodium hydroxide (NaOH) // P^H Increasing agent
- Eriochrome blue ($C_{20}H_{13}N_2NaO_3S$) / CALCON // Indicator



Complexometric Titration / chelometric Titration

- Ligand (pair electron doner)
- Metal (pair electron accepter)
- Co-ordinate bond
- Complex Compound
- Show in Color Compound

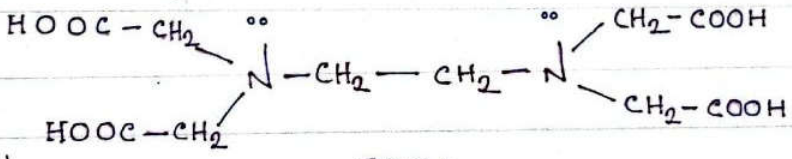
→ Crystal Field theory

L F T → Ligand Field Theory

- Verner →→ Lewis and Sidgwick
  - Complex Formation between the analyte and titrant.
  - Multidentate Ligand and Metal Complex.

- A compound in which molecules or ion's form coordinate bond's to a metal atom or ion.

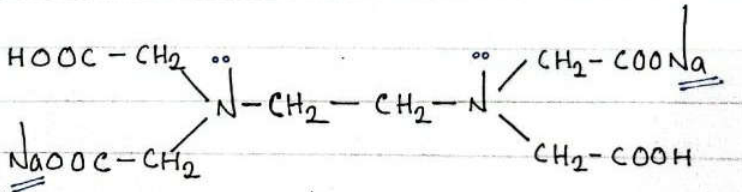
Ligand / Chelate



EDTA

Sharing of pair electrons

Coordinate bond



Na_2-EDTA

Complexometric titration is based on the fact that certain organic compounds form stable complexes with metal ions in solution.

$N_7 \rightarrow 1s^2 \boxed{2s^2} 2p_x^1 2p_y^1 2p_z^1$

$O_{(8)} \rightarrow 1s^2 \boxed{2s^2} \boxed{2p_x^2} 2p_y^1 2p_z^1$

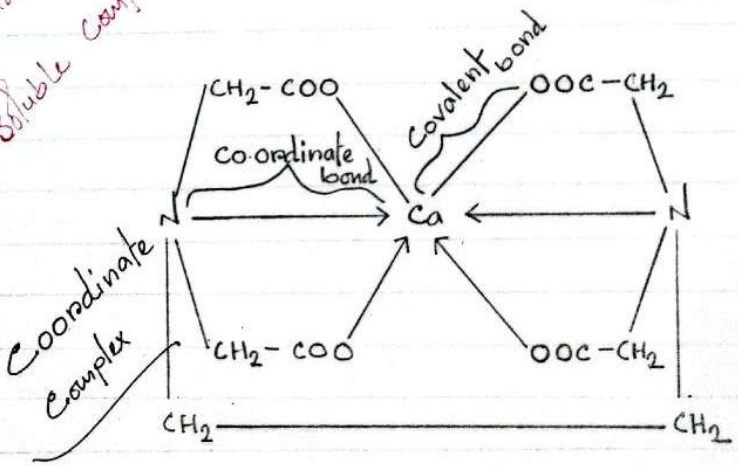
Pair electron

Reaction

Complexometric titrations involve reaction between metal ions and complexing agent (Ligand) to give a soluble complex.

$CaCl_2$ + $HOOC-CH_2$ $NaOOC-CH_2$ $N-CH_2-CH_2-N$ $CH_2-COONa$ CH_2-COOH

Na_2EDTA



Octahedral Type Geometry

Ca-EDTA Multidentate Ligand and Metal Complex.

COMPLEX COMPOUND

MECHANISM (metal - Indicator - Ligand)

$M + In \longrightarrow M\text{-}In$ (wine red)

$M\text{-}In + Ligand \longrightarrow M\text{-}Ligand + In$ (light blue)

Metal-Indicator complex (M-In) is less stable than Metal-EDTA complex.

$Na_2\text{-}EDTA \rightleftharpoons Na_2\text{-}H_2Y \rightleftharpoons H_2Y^{2-}$

Molecular equation

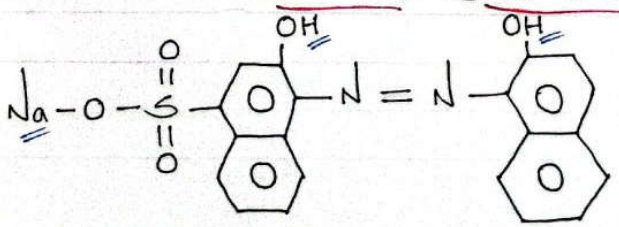
$Ca^{2+} + In^{3-} \longrightarrow CaIn^{-}$ (wine red)

$CaI^{-} + H_2Y^{2-} \longrightarrow CaY^{2-} + HIn^{2-} + H^{+}$

(wine red) (Colorless) (Colorless) (Light blue)

Eriochrome blue (CALCON) ($C_{20}H_{13}N_2NaO_5S$)

In^{3-}



Zwitterion / Amphoteric Electrolytes

A Neutral molecule with positive and negative charge

NH_2-CH_2-COOH (Glycine)

⇅

$H_3N-CH_2-COO^-$ (a dipolar Ion)

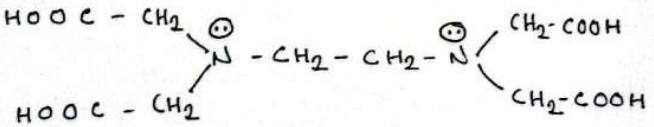
Internal proton transfer from the carboxylic acid group to amine group.

The result is a Zwitterion.

Zwitterions are sometimes called inner salt's.

Complexones

Amino poly carboxilic Acid



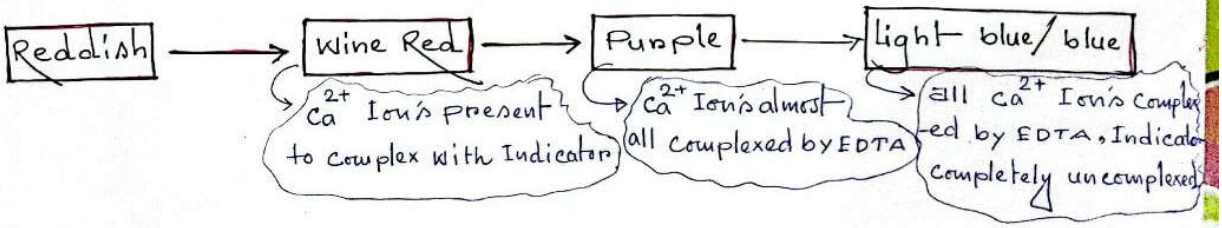
EDTA

1·25 (N) NaOH

60 ml Solu. Prepn. → pH → 11·5 ~ 12·5

$$\frac{40 \times 1{\cdot}25\,(N) \times 60\ ml}{1000} = 3{\cdot}0\ gm\ NaOH\ solid$$

Flow Sheet



Abstract

Calcium ion's react with EDTA to form a relatively stable complex. The value of equilibrium constant (called formation constant in complex forming reaction's) is high. The reaction is suitable to act as a basis of a titrametric method for the determination of Ca^{++} ion.

- The formation of complexes can also serve as the basis of accurate and convenient titrations for metal ions in which the titrate is a complexing agent.
- The protons in EDTA are displaced upon complexing with a metal ion.
- An organic agent that has two or more groups capable of complexing with a metal ion is called a chelating agent.

CamScanner

Standardization of $Na_2S_2O_3.5H_2O$



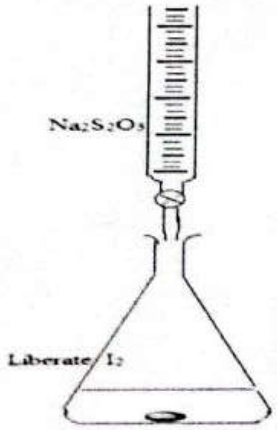
- ***Prep of Standard 0.1(N) $K_2Cr_2O_7$ Sol^n*** : Wt out **0.49** gm of $K_2Cr_2O_7$ and transfer into 100 mL + H_2O and make up to the mark.
- ***$Na_2S_2O_3.5H_2O$ Sol^n (Sample / Supplied)***

  Supplied Solution + H_2O and make up to 100 mL and then transfer to burettes
- ***Working Procedure***

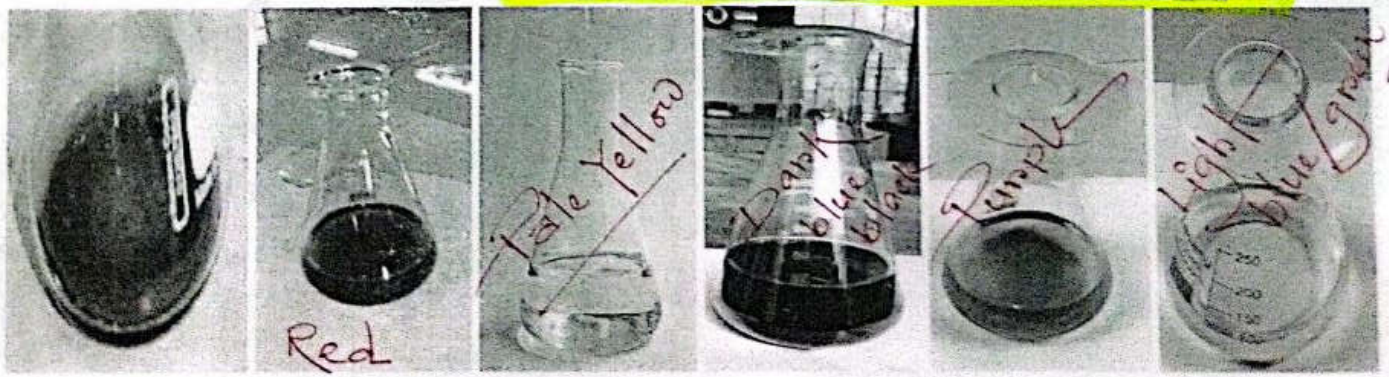
  Take 10mL KI Sol^n into a conical flask + 80 mL H_2O + 02 gm $NaHCO_3$ + 10 mL of 3N H_2SO_4 Sol^n + 10 mL $K_2Cr_2O_7$ Sol^n shake, cover with watch glass and keep in dark for 10minutes.

  Red or blood red colour appears, Titrate the liberated iodine with Sodium thio ($Na_2S_2O_3.5H_2O$) Sol^n.

  Light yellow color appears, Add Starch ***dark blue black*** color appears. Continue titration with $Na_2S_2O_3.5H_2O$ Sol^n ***Light green or light blue*** colour appears at the end point.



COLORS AND SIGNIFICANCE



IODOMETRIC METHOD

Iodometric Titration

Oxidation Number
Oxidizing agent
Reducing agent
Photolysis / Pyrolysis

Iodine solution should be kept in dark because it is highly photosensitive. Light accelerates a side reaction in which Iodine is converted to Free Radical. (Free Radical Iodine)

$I_2 \xrightarrow{h\nu} I \cdot$ (Free Radical)

In Iodometry, the analyte is oxidizing agent that react's with $I^{\ominus}$ to form I_2. The I_2 is titrated with sodium Thiosulphate.

$$K_2Cr_2O_7 \equiv I_2 \equiv Na_2S_2O_3$$

Exp-05

STANDARDIZATION OF SODIUMTHIOSULPHATE PENTA-HYDRATE ($Na_2S_2O_3 \cdot 5H_2O$) SOLUTION WITH STANDARD POTASSIUM DICHROMATE ($K_2Cr_2O_7$) SOLUTION

IODOMETRIC TITRATION

IODOMETRIC METHOD

Working Procedure

10 ml KI Sol^n. + 80 ml H_2O
+ 2 gm $NaHCO_3$ + 10 ml 3(N) H_2SO_4 Sol^n. + 10 ml $K_2Cr_2O_7$ Sol^n
+ Shake, Cover with watch glass and keep in dark For 10 min.
+ Titrate the Liberated iodine with supp. $Na_2S_2O_3 \cdot 5H_2O$ Sol^n.
----> Light yellow color appear
+ 2/3 drp. starch indicator
+ again Titration with Thio
----> Light green or blue.

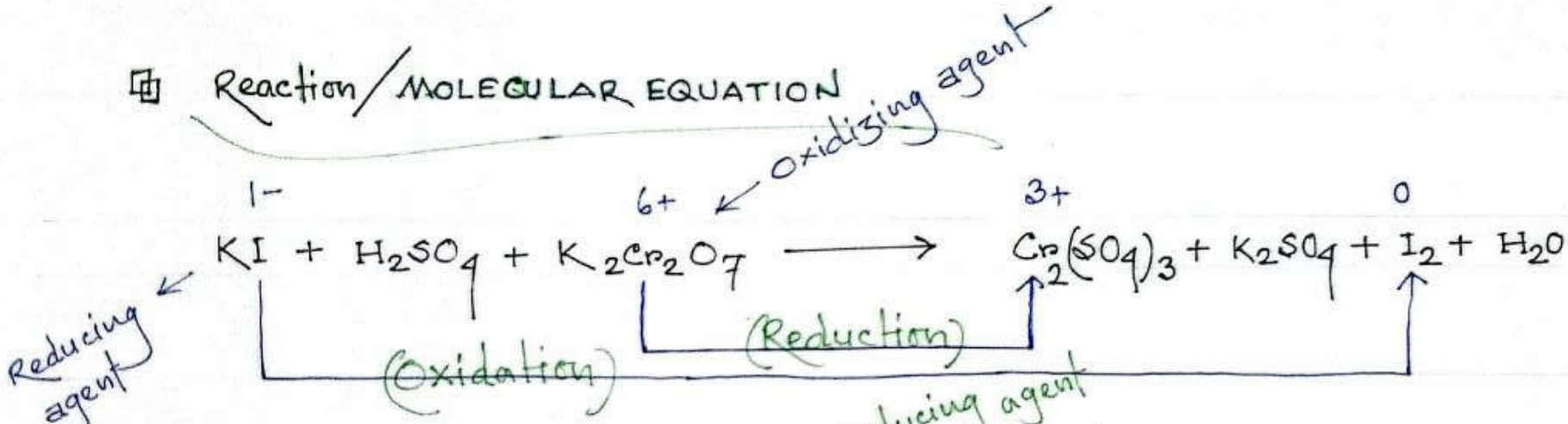
CHEMICALS

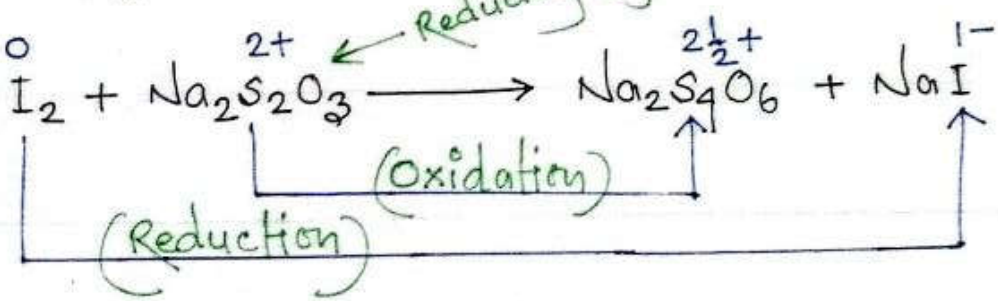
- $Na_2S_2O_3 \cdot 5H_2O$ Sample
- $K_2Cr_2O_7$ Solid
- 12% KI Sol^n.
- 3(N) H_2SO_4 Sol^n.
- $NaHCO_3$ Solid
- $(C_6(H_2O)_5)_n$ Indicator

Tech. Term.

- Free Radical
- Air Oxidation
- Adsorption
- Glycosidic bond
- Oxidizing agent
- Reducing agent

Reaction / MOLECULAR EQUATION





- Oxidation number
- Oxidizing agent
- Reducing agent

$$K_2Cr_2O_7 \equiv I_2 \equiv Na_2S_2O_3$$

mole equivalent Oxidizing agent ≡ mole equivalent I_2 ≡ mole equivalent Reducing agent.

Starch - Iodine Complex

Amylose in starch is responsible for the formation of a deep blue color in the presence of iodine. The iodine molecule slips inside of the amylose coil.

"amylose actually forms a spiral much like coiled spring."

"Iodine forms a coordinate complex between the helically coiled polysaccharide chain and iodine centrally located within the helix due to adsorption."

STARCH

- (amylose) → 10 to 20% → colloidal dispersion in hot water
- (amylopectin) → >80% → Completely insoluble.

Adsorption

Chemisorption

The formation of a layer of solid or Liquid on the surface.

COLORS AND SIGNIFICANCE

Note

1. Dilute triiodide Soln. are yellow.
2. More concentrated Soln. are brown.
3. Even more concentrated Soln. are Violet.
4. Iodide Soln. are colorless.
5. Strach Form's a dark blue adsorption complex with Iodine.

CHEMISORPTION is a kind of adsorption involves a chemical Reaction between the surface and the adsorbate. New chemical bond are generated at the adsorbant surface. The Formation of a layer of solid or Liquid on the surface ——— The result is ——— concept of Langmuir. / Chemisorption

MECHANISM

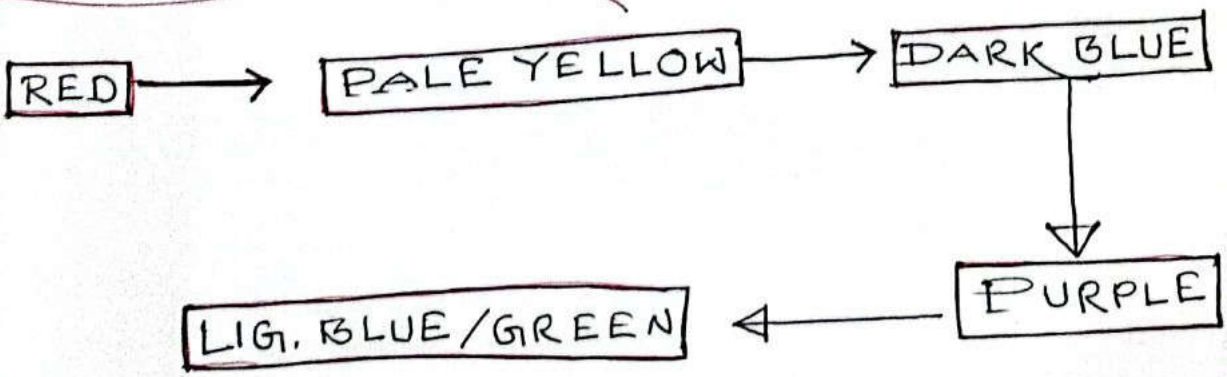
$$\text{Starch} + I_2 \longrightarrow \text{Starch}-I_2 \text{ (dark blue-blac}$$

(Adsorption Complex)

$$\text{Starch}-I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^{\ominus} + \text{Starch}$$

Light blue/gree

Flow Sheet



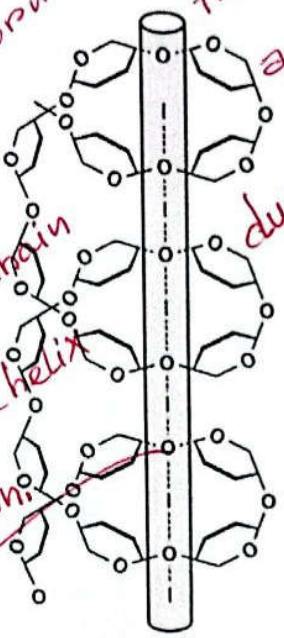
Main Two error of Iodometric Titratio

1. Vaporization or Evaporation of I_2 is so hig so, I_2 is chance to missing.
2. Air oxidation in Acid Media —

$$I^{\ominus} + O_2 + H^{\oplus} \longrightarrow I_2 + H_2O$$

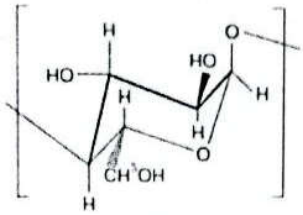
CamScanner

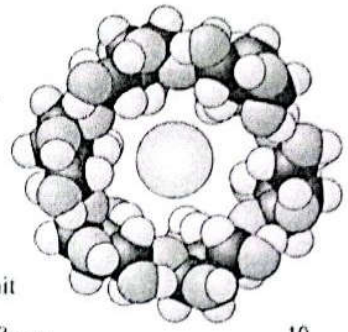
Starch-Iodine Complex



Starch is the indicator of choice for those procedures involving iodine because it forms an intense blue colour with iodine.

Starch is not a redox indicator;
it responds specifically to the presence of I_2,
not to a change in redox potential.





Structure of the repeating unit of the sugar amylose.

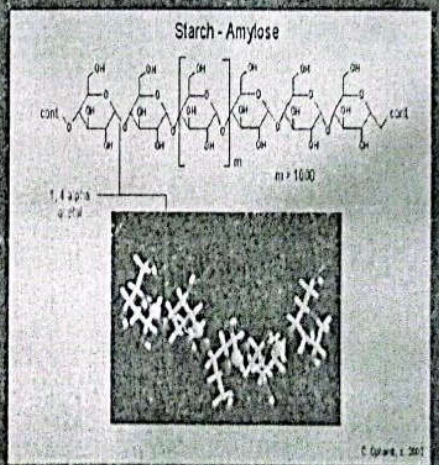
Figure 18-6(1)
Quantitative Chemical Analysis, Seventh Edition
© 2007 W. H. Freeman and Company

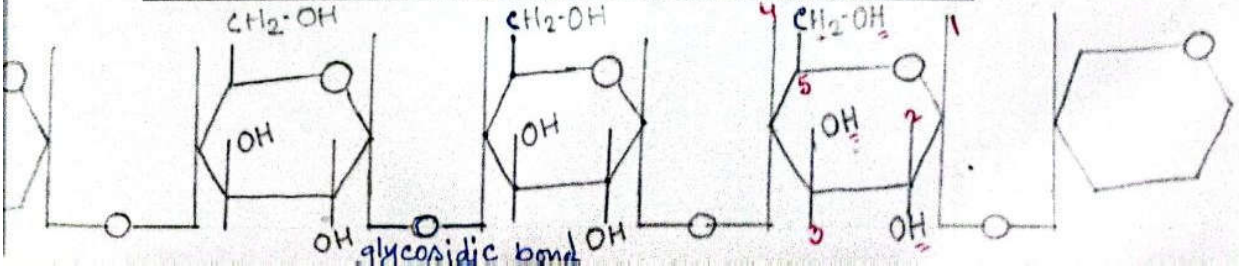
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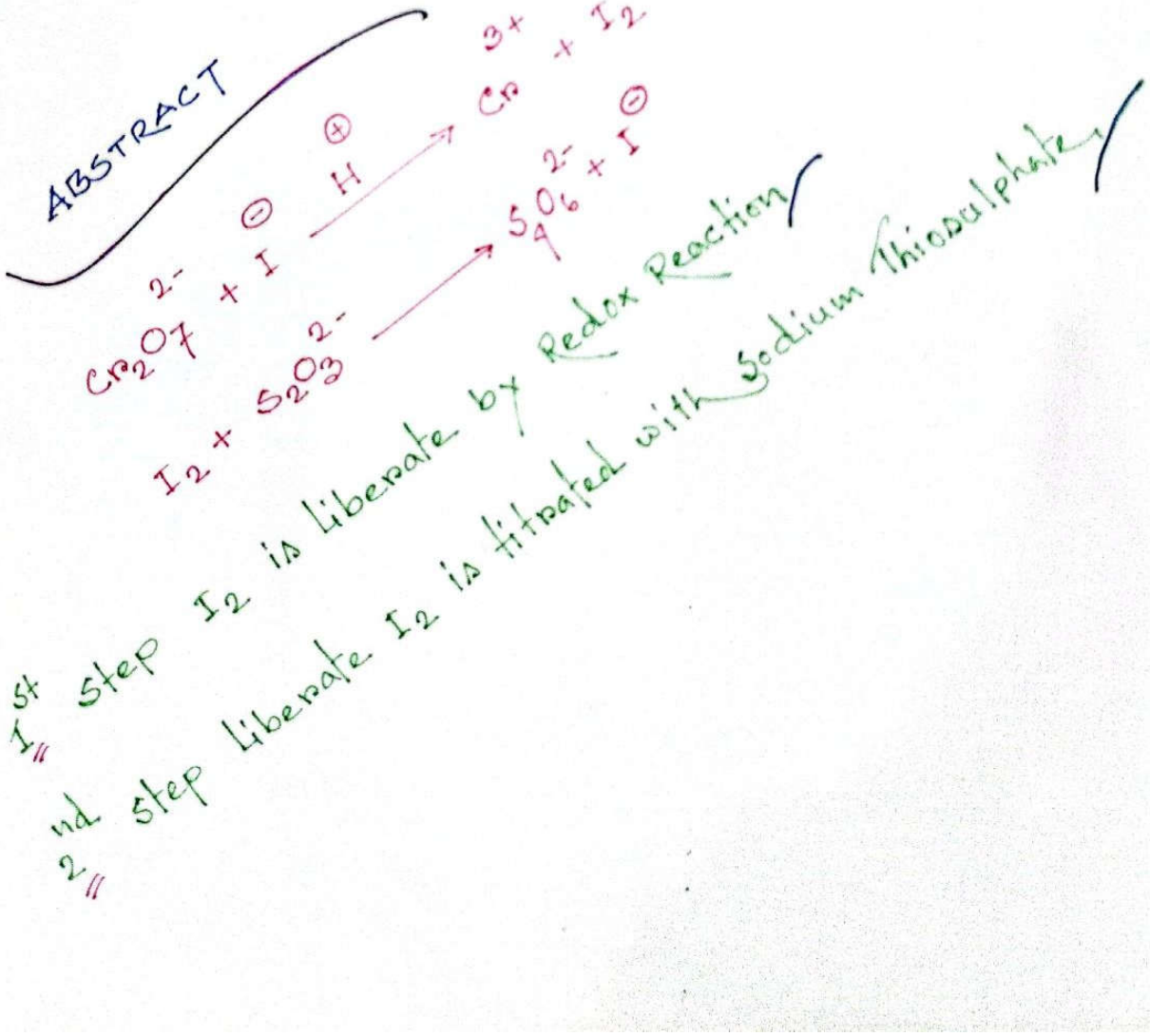
10

Amylose

- Linear component of starch
- Contains 1,4-alpha-glucosidic bonds
- Molecular weight: less than 0.5 million
- Can form coils which will trap iodine and turn blue






ABSTRACT
$Cr_2O_7^{2-} + I^- \xrightarrow{H^+} Cr^{3+} + I_2$
$I_2 + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + I^-$
1st step I_2 is liberate by Redox Reaction
2nd step Liberate I_2 is titrated with Sodium Thiosulphate
1st step I_2
2nd step

Error of Iodometric titration

- Vaporization of I_2 is so high. $I_2 \uparrow$
- Air oxidation in Acid media

$$I^{\ominus} + O_2 + H^{\oplus} \longrightarrow I_2 + H_2O$$

- Free Radicals can be produced by Photolysis or Pyrolysis. $\xrightarrow{h\nu} I^{\cdot}$
- Starch adsorbed some I_2

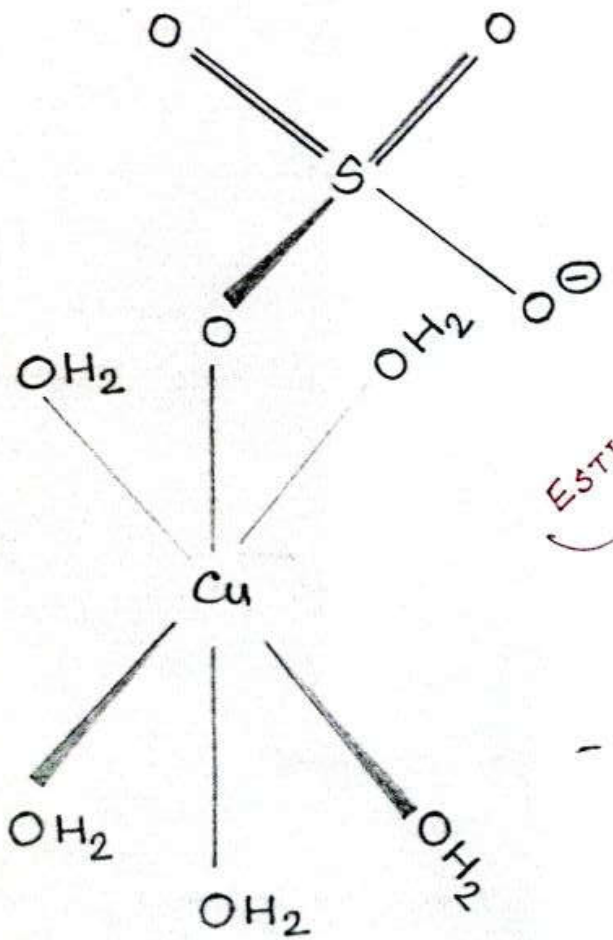
ABSTRACT

$$Cr_2O_7^{2-} + I^{\ominus} \xrightarrow{H^{\oplus}} Cr^{3+} + I_2$$

$$I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^{\ominus}$$

1st Step I_2 is liberate by Redox Reaction

2nd Step liberate I_2 is titrated with Sodium Thio.-



ESTIMATION OF COPPER (Cu) — Mahmud

$CuSO_4 \equiv I_2 \equiv Na_2S_2O_3$

mole equivalent — Oxidizing agent ≡ mole equivalent — I_2
≡ mole equivalent Reducing agent.

ABSTRACT

$Cu^{2+} + I^{\ominus} \xrightarrow{H^{\oplus}} Cu_2I_2 + I_2$

$I_2 + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + I^{\ominus}$

1st step Cu^{2+} React with $I^{\ominus}$ and product Liberated I_2

2nd step, The Liberated I_2 is consume by $Na_2S_2O_3$

$CuSO_4 \cdot 5H_2O$ — Coordinate Compound

EXP-06

ESTIMATION OF COPPER (Cu) CONTENT IN A COPPER SULPHATE PENTAHYDRATE ($CuSO_4 \cdot 5H_2O$) SOLUTION BY IODOMETRIC METHOD (Liberate I_2) WITH STANDARD SODIUM THIOSULPHATE PENTAHYDRATE ($Na_2S_2O_3 \cdot 5H_2O$) SOLUTION.

Procedure

10 ml $CuSO_4 \cdot 5H_2O$ Soln. + 80 ml H_2O + 2 gm $NaHCO_3$ + 10 ml 3(N) H_2SO_4 Soln. + 10 ml KI Soln. + Keep dark for 10 min + Titration with Standard $Na_2S_2O_3 \cdot 5H_2O$ Soln. ……→ Light Yellow / Pale Yellow. + 3/4 drop. Starch Indicator + 5 ml NH_4SCN Soln. + Again titration with Thio. Soln. ……→ White / Off white.

Flow Sheet

REDISH → LIG. YELLOW → DARK BLUE → VIOLET/PURPLE → OFF-WHITE

Reaction

$$\overset{2+}{Cu}SO_4 + H_2SO_4 + \overset{1-}{K}I \rightarrow \overset{1+}{Cu_2}I_2 + \overset{0}{I_2} + K_2SO_4 + H_2O$$

(Reduction) (Oxidation)

$$I_2 + Na_2S_2O_3 \rightarrow Na_2S_4O_6 + NaI$$

$CuSO_4 \equiv I_2 \equiv Na_2S_2O_3$

mol equivalent Oxidizing agent ≡ mil equivalent I_2

IODOMETRIC TITRATION

PHASE-02

CHEMICALS

- $CuSO_4 \cdot 5H_2O$
- $Na_2S_2O_3 \cdot 5H_2O$
- KI
- 3(N) H_2SO_4
- $NaHCO_3$
- $(C_6(H_2O)_5)_n$
- NH_4SCN (Pseudo halogen)

Key point

- Iodometric Titration
- Iodimetric Titra.
- Diff. bet. Iodo and Iodi
- Why use $NaHCO_3$
- Why use NH_4SCN
- Why use starch indi.

COPPER ESTIMATION

$K_2Cr_2O_7$ → Phase-01 → $Na_2S_2O_3 \cdot 5H_2O$ → Phase-02 → $CuSO_4 \cdot 5H_2O$ → …. Cu^{++}

Back Reaction

* Air Oxidation $I^- + H^+ + O_2 \rightarrow I_2 + H_2O$
* Weak Vand. force

Over all Reaction / with out acid

$$2CuSO_4 + 4KI + 2Na_2S_2O_3 \longrightarrow Cu_2I_2 + Na_2S_4O_6 + 2K_2SO_4 + 2NaI$$

Note
The solution of $CuSO_4$ is acidic.

Iodimetry

No-1. In Iodimetry. the titrant is I_2.

No-2. In Iodimetry. I_2 is oxidizing agent.

No-3. In Iodimetry. the end point appear-
-ance of the dark blue (starch-I_2 Complex)

No-4. Reaction Example

$$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + NaI$$

Starch add acidl

- Large amount of Iodine were adsorbed on starch.
- The starch has a tendency to hyd-rolyze in acid solution.
- H_2SO_4 as a dehydrating agent.

TECHNICAL TERM

- Vigorous shaking
- Free radical
- Light sensitive reaction
- photolysis / pyrolysis
- Pseudo halogen

Cu_2I_2 ⟶ Precipitate bind some liberate I_2

When Titration end this bind I_2 release in solution then color back.

Cu_2I_2 ----- I_2 → Weak Vand. force

(White precipitate)

H_2SO_4 as a dehydrating agent

⊙ When some starch added to H_2SO_4 sol^n. it decompose the starch to carbon and H_2O. the latter being absorbed by H_2SO_4.

$$(C_6(H_2O)_5)_n + H_2SO_4 \longrightarrow C + H_2SO_4 \cdot H_2O$$

hydrated H_2SO_4

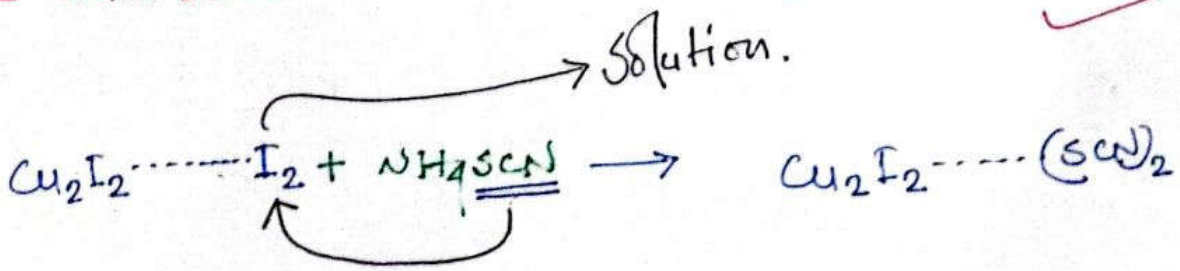
$$CuSO_4 + KI \longrightarrow Cu_2I_2 + I_2 + K_2SO_4$$

$$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + NaI$$

$$CuSO_4 + KI + Na_2S_2O_3 \longrightarrow Cu_2I_2 + Na_2S_4O_6 + K_2SO_4 + No$$

Pseudo halogen

The precipitate of Cu_2I_2 absorbs I_2 From th solution and releases it slowly making the detecti of sharp end point difficult. So a small amount of NH_4SCN is added near the end point to displac the absorbed Iodine From Cu_2I_2 precipitate.



11.03.17

ABSTRACT

Reactant's $\xrightarrow[\text{absorbing thermal energy}]{\text{Sufficient Activation Energy}}$ Product's



- Translational motion (স্থানান্তর গতি)
- Rotational motion (আবর্তন গতি)
- Vibrational motion. (কম্পন গতি)

Exp-07 Mahmud

In a Reaction, the reactant molecules come together and chemical bond are stretched, broken and formed in product's.

- Period of Induction → Mix করার পর যতক্ষন বিক্রিয়া শুরু থাকে।
- Initiation.
- Propagation.
- Termination.

CamScanner

10 ml $H_2C_2O_4 \cdot 2H_2O$ Soln. + 80 ml H_2O
+ 10 ml 3(N) H_2SO_4 + heat the solution
(60 ~ 70)°c + Slowly titration with suppl.
$KMnO_4$ Soln. ⋯⋯→ light pink.

Reaction

$$\overset{3+}{H_2C_2O_4} + H_2SO_4 + \overset{7+}{KMnO_4} \xrightarrow{75^\circ C} K_2SO_4 + \overset{2+}{MnSO_4} + \overset{4+}{CO_2} + H_2O$$

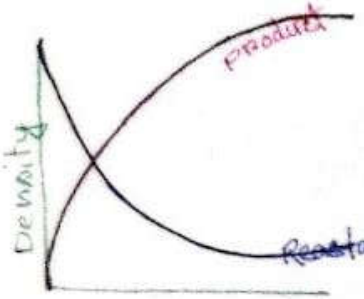
(Oxidation) (Reduction)

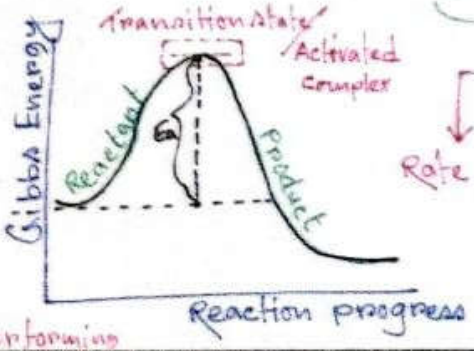
Reaction Mechanism / Molecular Equation

$$KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + H_2O + [O]$$

$$H_2C_2O_4 + [O] \longrightarrow CO_2 + H_2O$$

Reactant's → Sufficient Activation En → Product's





STANDARDIZATION OF potassium permanganate ($KMnO_4$) SOLUTION WITH STANDARD Oxalic Acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) SOLUTION. OXIDATION & REDUCTION

TEMPERATURE EFFECT TITRATION

CHEMICALS

- $KMnO_4$ Soln.
- $H_2C_2O_4 \cdot 2H_2O$ Solid
- 3(N) H_2SO_4 Soln.

REACTION STEP

- Period of Induction
- Initiation
- Propagation
- Termination

Reaction rate / Speed of Reaction

= Collision frequency x Activitated molecular Fraction

Technical Term

- Energy barrier
- Energy hill
- collision theory
- Transition state
- Activation Energy
- Auto catalyst

Arrhenius Equation

$$K = P \cdot Z \cdot e^{-E_a/RT}$$

K: Rate Const. P: Steric factor Z: collision rate

Influence of Temp. on Reaction Rate / Effect of Temp.

- No-1. The rise of temperature the velocity of reactant increase.
- No-2. The Number of collisions among the molecules increase.
- No-3. More molecules receive sufficient activation energy for the reacti

REACTION RATE / SPEED OF REACTION

= Collision Frequency x Activitated molecular Fraction.

Arrhenius Equation

$$K = P \cdot Z \cdot e^{-Ea/RT}$$

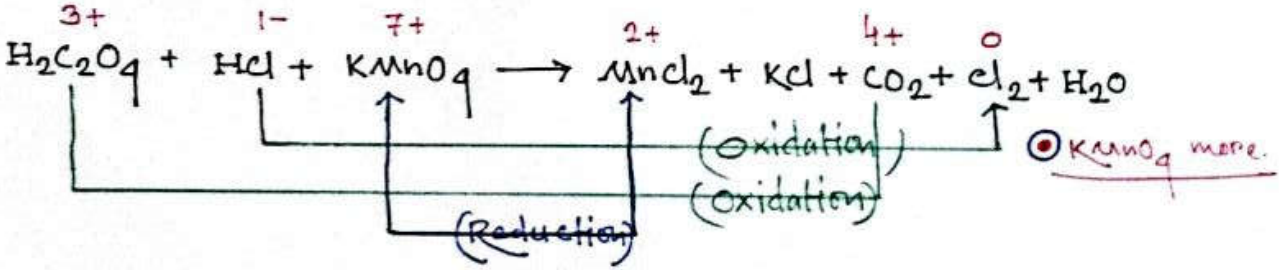
- K → Rate Const.
- P → Steric factor (ফিক ফ্যাক্টর)
- Z → Collision rate
- $e^{-Ea/RT}$

CamScanner

Collision theory

- must collide / jostle with each other (atom, molecul, ion)
- collision must occur with sufficient energy.
- collision must occur in a definite direction.

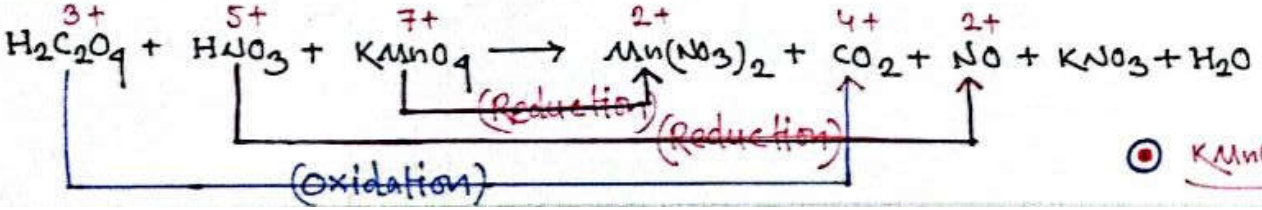
If use HCl



⊙ $KMnO_4$ more.

(disproportion)

If use HNO_3



⊙ $KMnO_4$ less

REACTION STEPS

- Period of Induction
  - Its the moment the reaction neither Athaf yet
- Initiation
  - The moment when the reaction Starts. The auto catalyst Atarfa working at this Point.
- Propagation
  - Also in the moment while the reaction is moving on till the end.
- Termination
  - The moment when the reaction ends as well as the auto catalyst

Autocatalyst

In some instance one of the product's of a Reaction acts as a catalyst. this phenomenon is known as autocatalyst.

Activation Energy

The minimum energy required for a chemical Reaction to take place.

In a Reaction, the Reactant molecule come together and chemical bond's are stretched, broken and formed in producing the product's.

CamScanner

EXP-08

DETERMINATION OF Fe CONTENT.

ABSTRACT

$MnO_4^- + H^+ + 5e \rightarrow Mn^{2+}$

MnO_4^- (purple) → Oxidized Form

Mn^{2+} (Colorless) → Reduced Form

Fe Determination

PHASE-1: $H_2C_2O_4 \cdot 2H_2O$ (Prim)

PHASE-2: $KMnO_4$ (Second. std)

$[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$

↓

Fe^{++} Qty =

Exp-08 DETERMINATION OF FERROUS (Iron) CONTENT IN A MOHR'S SALT SOLUTION WITH STANDARD POTASSIUM PER MANGANATE ($KMnO_4$) SOLUTION.

(REDOX TITRATION)

OXIDATION AND REDUCTION TITRATION

Light green crystals

Mohr's salt $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$

- It is classified as a double salt
- Containing Two different cations Fe^{++}, NH_4^+
- Double sulfates salt. (Tutton salt)

CHEMICALS and CHARACTER

- Mohr's Salt $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$
- Oxalic Acid dihydrate $(H_2C_2O_4 \cdot 2H_2O)$
- Potassium permanganate $(KMnO_4)$
- Sulphuric Acid (H_2SO_4)

Ferrous (Fe) Determi

PHASE-1: $H_2C_2O_4 \cdot 2H_2O$ → $KMnO_4$

PHASE-2: $KMnO_4$ → $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$

ABSTRACT

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

MnO_4^- (Purple) → Oxidized form

Mn^{2+} (Colorless) → Reduced for

Exp-08

DETERMINATION OF FERROUS (Iron) CONTENT IN A MOHR'S SALT SOLUTION WITH STANDARD POTASSIUM PERMANGANATE ($KMnO_4$) SOLUTION.

(REDOX TITRATION)

OXIDATION AND REDUCTION TITRATION

Light green crystals

Mohr's salt $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$

- It is classified as a double salt
- Containing Two different cations Fe^{++}, NH_4^+
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CHEMICALS and CHARACTER

- Mohr's Salt $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$
- Oxalic Acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$)
- Potassium permanganate ($KMnO_4$)
- Sulphuric Acid (H_2SO_4)

Ferrous (Fe) Determi

PHASE-1: $H_2C_2O_4 \cdot 2H_2O$ → $KMnO_4$

PHASE-2: $KMnO_4$ → $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2$

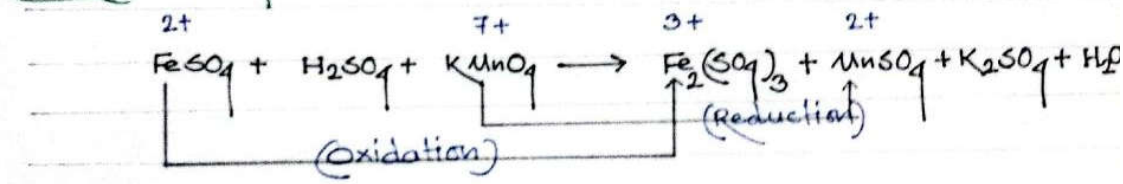
ABSTRACT

$$MnO_4^{7+} + H^{\oplus} + 5e^{\ominus} \longrightarrow Mn^{2+} + H_2O$$

(Purple) → Oxidized form

(Colorless) → Reduced for

Reaction

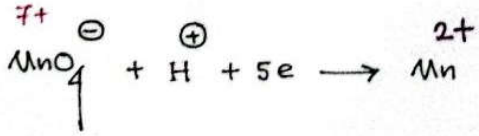


Reaction Mechanism / Molecular Equation

$$KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + H_2O + [O]$$

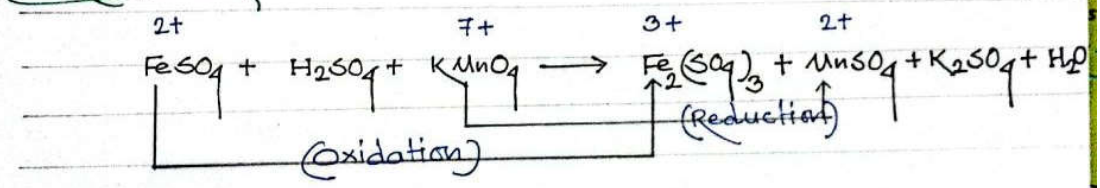
$$FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

Half Reduction



CamScanner

Reaction



Reaction Mechanism / Molecular Equation

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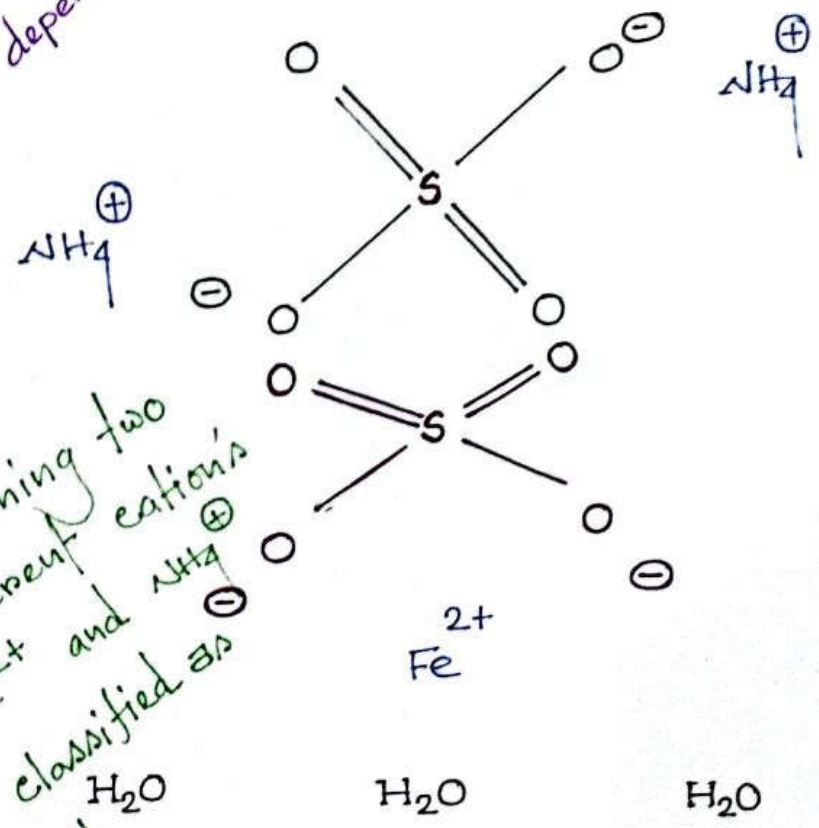
Half Reduction

$$\overset{7+}{MnO_4}^{\ominus} + \overset{\oplus}{H} + 5e \longrightarrow \overset{2+}{Mn}$$

Molecular geometry of Mohr's Salt

$[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$

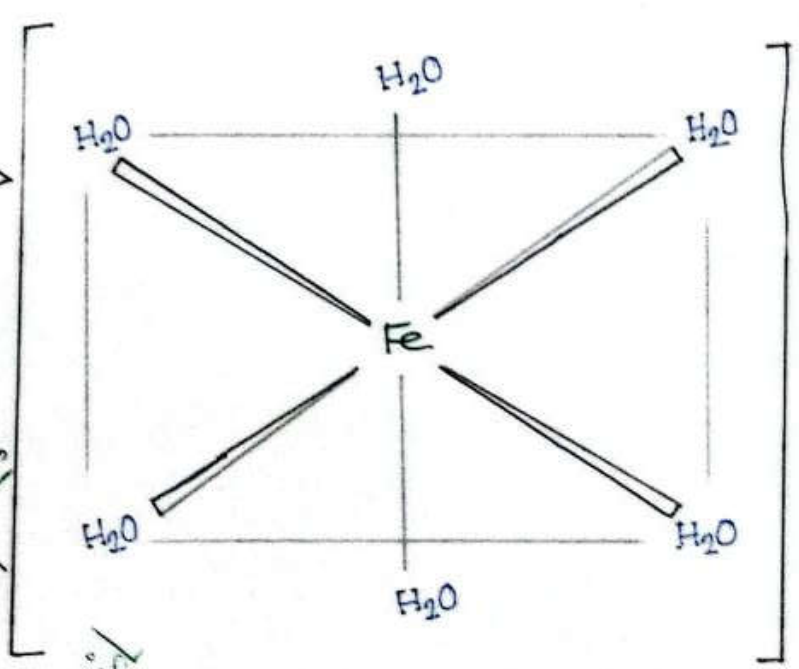
- The oxidation of solution's of Iron (II) is very p^H dependent.
- containing two different cation's Fe^{2+} and NH_4^+
- It is classified as a double salt



Octahedral Molecular geometry.

Mohr's salt $[FeSO_4(NH_4)_2SO_4 \cdot 6H_2O]$ —— when this salt dissolves in water to give aquo complex

$[Fe(H_2O)_6]^{2+}$



octahedral molecular geometry

The oxidation of solution of Iron (II) is very pH dependent occuring much more readily at high pH.

The ammonium ions make solu. of Mohr's salt slightly acidic, which slows this oxidation process.

⊕ NH_4^+ Lewis Acid

Discussion

1. Potassium permanganate ($KMnO_4$) is a strong oxidizing agent in acid medium. Sulphuric acid is the most suitable acid

2. With dilute HCl, there is a probability that some amount of permangana-te may be consumed in the formation of Cl_2 gas thus interfere estimati

$$2MnO_4^{\ominus} + Cl^{\ominus} + H^{\oplus} \longrightarrow Mn^{2+} + Cl_2 + H_2O$$

3. HNO_3 Can ~~act~~ Work's as oxidizing agent

$$HNO_3^{5+} + 3e \longrightarrow NO^{2+}$$

Self indicator

As the titration proceeds, the MnO_4^- will converted to Mn^{2+} and simultaneously Fe^{2+} will converted to Fe^{3+}. When whole of the reducing agent (Fe^{++}) will consumed, the oxidizing agent (MnO_4^-) cannot be reduced, then the addition even one drop of $KMnO_4$ solution given its colour to the solution. This indicates the end point of the titration.

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

(Purple) (Colourless)