Redox Titration
Part 1

Dr. Mai Ramadan

Redox titration

Introduction

End point detection

Applications including pharmaceutical Examples

Problems

Redox reaction

Oxidizing Agent

Reducing Agent

Reducing agent loses electrons and be oxidized

Oxidizing agent gains electrons and be reduced

End point determination

Redox indicator

Iron (II) complex with 1,10-phenanthroline e.g Ferroin

Methylene blue

Diphenylamine

End point determination

Oxidation reduction indicators are substances that change in colour upon being oxidized or reduced.

$In_{ox} + n\,e^- \longleftrightarrow In_{red}$

color 1 color 2

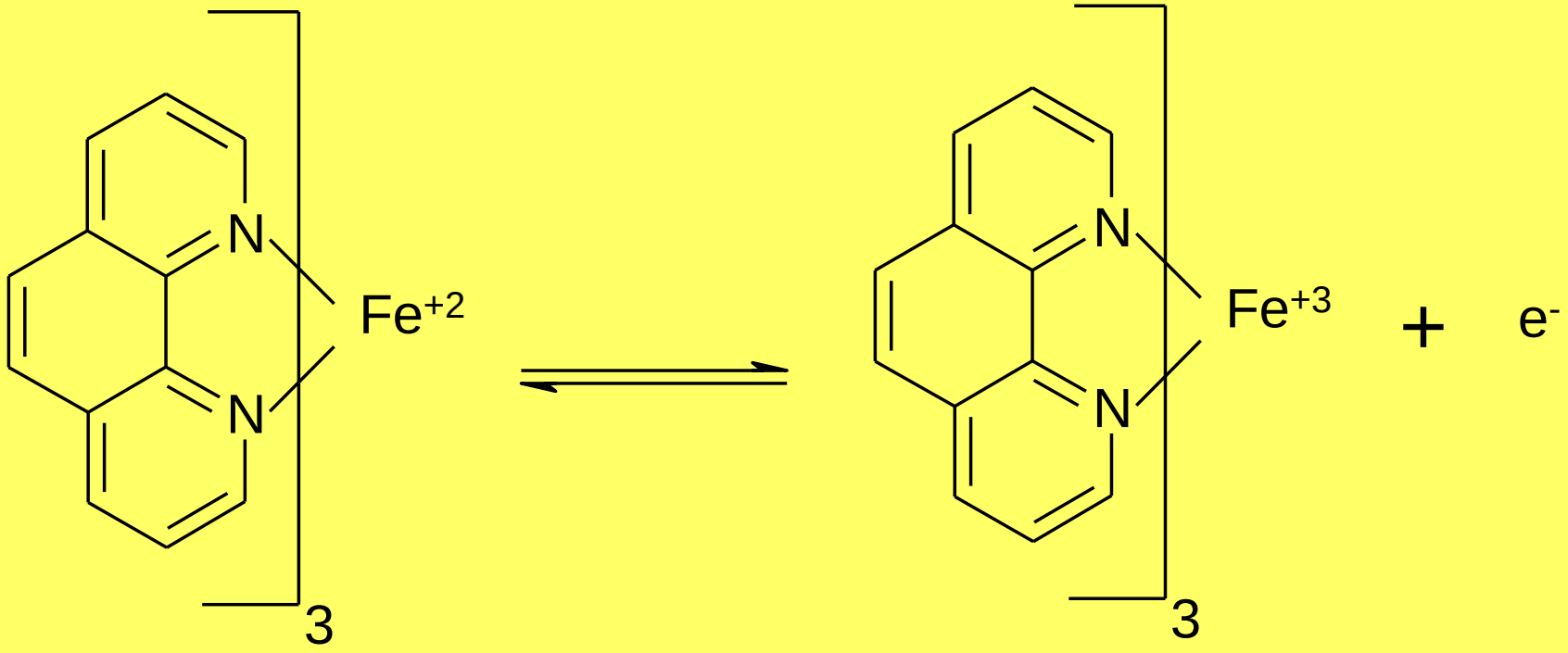
In_{ox} : oxidized form of indicator

In_{red} : reduced form of indicator

End point determination

Redox indicator: Example Ferroin

For further examples see chapter 16



$(Phen)_3Fe^{+2}$

Ferroin (Red)

$(Phen)_3Fe^{+3}$

Ferriin (blue)

End point determination

Self indicator

$KMnO_4$ is a strong oxidizing agent, has a purple colour when it reduced transformed to Mn^{+2}, which is colourless.

I2 is an oxidizing agent has a brown colour when reduced transformed to I^-, which is colourless.

End point determination

Specific indicator like strach

Forms a blue complex with tri-iodide, is widely used in redox reaction involving iodine as an oxidant or iodid ion as a reductant

When there is a large amount of I_2, starch should not be added. When the solution is pale yellow (amount of iodine is little) starch is added and titration continued until it is decolorized.

End point determination

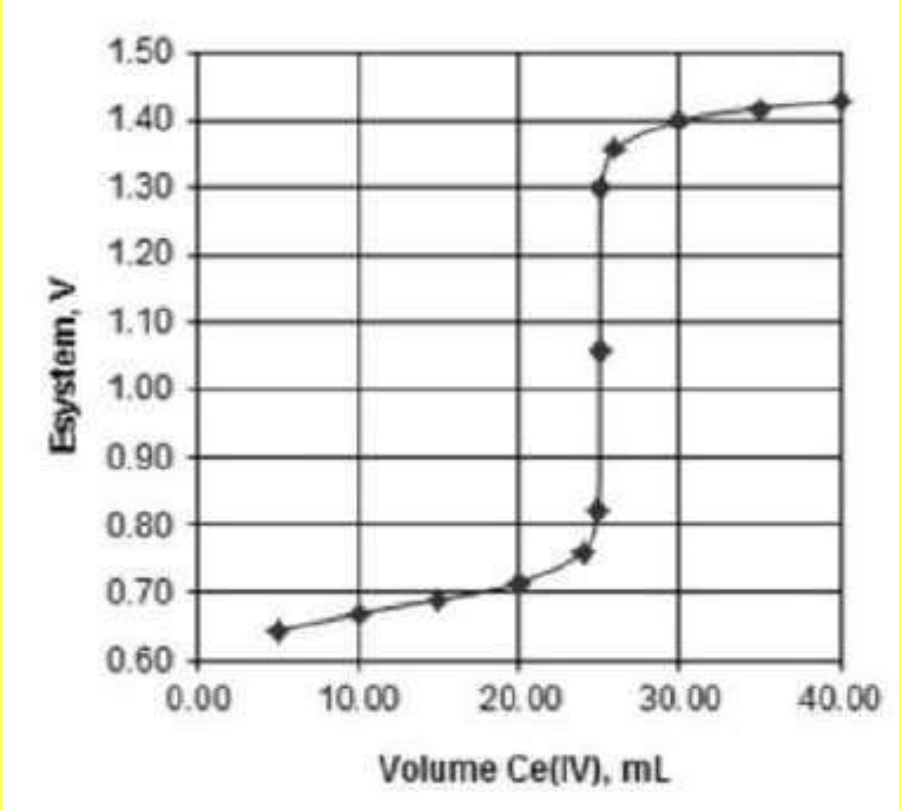
Instrumental end point like Potentiometry

The potential of the cell changes during the titration. The analyte solution is a part of a cell and the potential of a cell measured during the titration.

Sharp change in E the potential around equivalence point

Potentiometer record increases and remain at high value.

Titration curve is a plot of E (potential) against volume of titrant



Redox titration applications

Iodimetry

Iodometry

Permanganatometry

Bromatometry

Cerimetry

nitritometry

Iodimetry

Titrant: I_2 standard solution
Iodine is a weak oxidizing agent used for the determination of strong reducing agent.

Problems of I_2 -standard solution
solubility (dissolve as I_3^-)
lack of stability (volatile, attack of organic compound, air oxidation of I^- in solution)

$$4\,I^- + O_2\,(g) + 4\,H^+ \longrightarrow 2\,I_2 + 2\,H_2$$

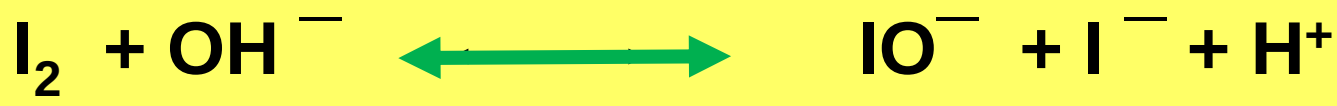
Analyte: Reducing agents

Iodimetry

Indicators: Self indicator
Starch
Extraction of I_2 with chloroform

Media: neutral or slightly acidic

Not basic to avoid dis-proportionation reaction



Iodimetry

Standarization of iodine solution:

Arsenious oxide

Barium thiosulfate monohydrate

Sodium thiosulfate anhydrous

Potassium antimony (III) tartarate

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

Iodimetry

Applications

Some Applications of Iodine Solutions

Substance Determined	Half-Reaction
As	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$
Sb	$H_3SbO_3 + H_2O \rightleftharpoons H_3SbO_4 + 2H^+ + 2e^-$
Sn	$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$
H_2S	$H_2S \rightleftharpoons S(s) + 2H^+ + 2e^-$
SO_2	$SO_3^{2-} + H_2O \rightleftharpoons SO_4^{2-} + 2H^+ + 2e^-$
$S_2O_3^{2-}$	$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$
N_2H_4	$N_2H_4 \rightleftharpoons N_2(g) + 4H^+ + 4e^-$
Ascorbic acid	$C_6H_8O_6 \rightleftharpoons C_6H_6O_6 + 2H^+ + 2e^-$

Iodimetry

Applications

$$AsO_3^{-3} + I_2 + H_2O \longrightarrow AsO_4^{-3} + 2\,I^- + 2\,H^+$$

$$SbO_3^{-3} + I_2 + H_2O \longrightarrow SbO_4^{-3} + 2\,I^- + 2\,H^+$$

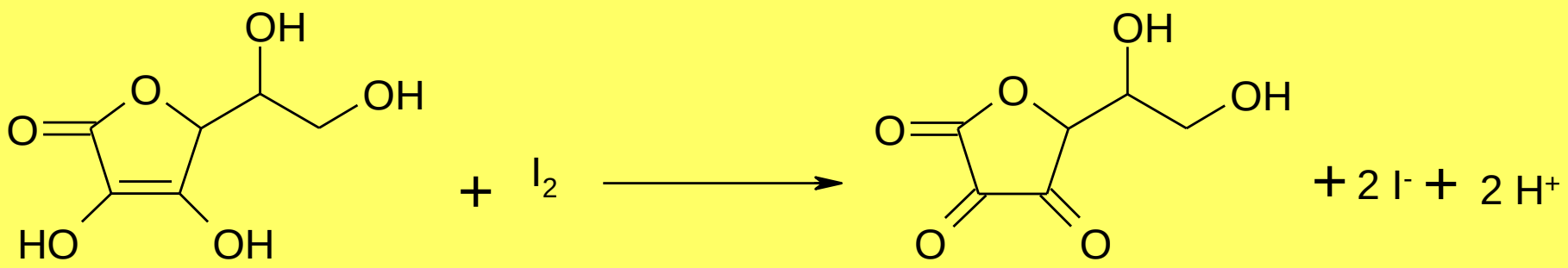
$$Sn^{+2} + I_2 \longrightarrow Sn^{+4} + 2\,I^-$$

$$H_2S + I_2 \longrightarrow S^\circ + 2\,I^- + 2\,H^+$$

$$SO_3^{-2} + I_2 + H_2O \longrightarrow SO_4^{-2} + 2\,I^- + 2\,H^+$$

Iodimetry

Applications



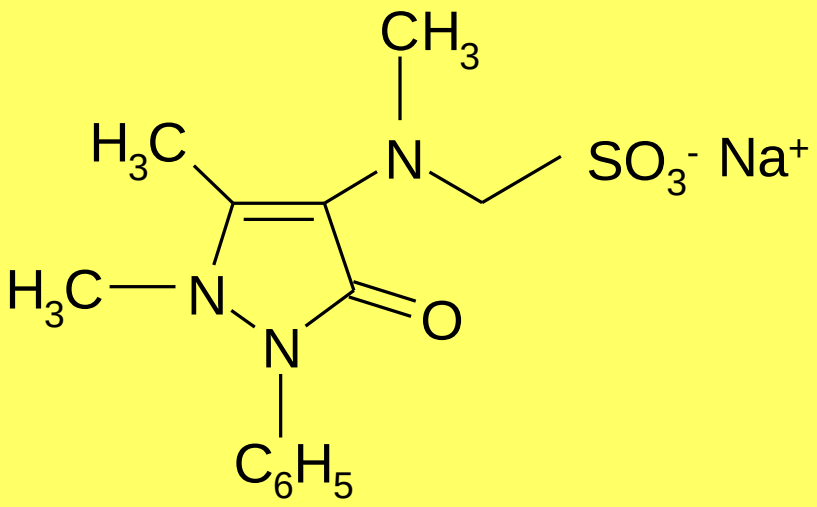
Ascorbic acid dehydroascorbic acid

Karl Fischer method: *to determine water content in solid*

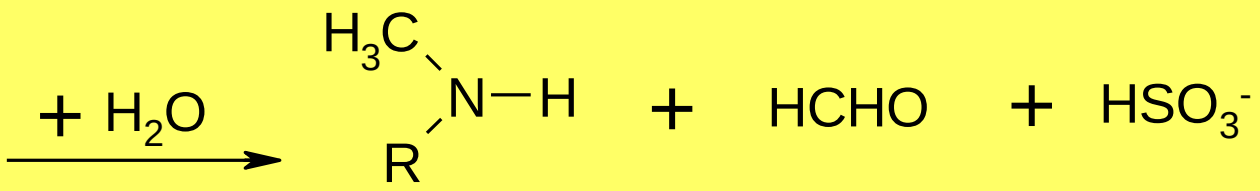
$$SO_2 + + I_2 + 2\,H_2O \longrightarrow 4\,H^+ + 2\ I^- + SO_4^{-2}$$

Iodimetry

Applications



Metamizol Na



$$HSO_3^- + I_2 + H_2O \longrightarrow HSO_4^- + 2\,I^- + 2\,H^+$$

Redox Titration Problems (Iodimetry)

Dr. Mai Ramadan

Problems

For determination of H_2S in a solution 50.0 ml of a 0.0196 N iodine solution was added to 25.0 ml of the H_2S solution. The excess iodine took 11.0 ml of 0.0204 N thiosulfate solution. Find the H_2S content of the solution in g per L?

$$H_2S + I_2 \longrightarrow S^\circ + 2\,I^- + 2\,H^+$$

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

Normality = No. Of equivalents/Volume (L)

N = M * a

a: according to the present reaction, in redox reaction (a) is No. of electrons

Problems

$I_2 + 2e^- \longrightarrow 2I^-$

I_2 solution $M = \frac{N}{a} = \frac{N}{2}$

$2\ S_2O_3^{-2} \longrightarrow S_4O_6^{-2} + 2e^-$

$S_2O_3^{-2}$ solution is each mole give only one e^-,

Conc (M) $S_2O_3^{-2} = \frac{N}{a} = \frac{N}{1}$

Problems

Solution :

No mmol I_2 (total) = 50 (mL) * 0.0098 (M) = 0.49 (mmol)

$$\text{No mmol } I_2 \text{ (excess)} = \frac{1 \text{ mol } I_2}{2 \text{ mol } S_2O_3^{-2}} * \text{no mmol} S_2O_3^{-2} =$$

$$= \frac{1}{2} * 11 \text{ (mL)} * 0.0204 \text{ (M)} = 0.1122 \text{ (mmol)}$$

No mmol I_2 (reacted)= Total – excess= 0.3778 (mmol)

No mmol H2S = no mmol I_2 reacted = 0.3778 (mmol)

$$\text{H2S content (g/L)} = \frac{0.3778 * 10^{-3} \text{ (mol)} * 34.08 \text{ (g/mol)}}{25 * 10^{-3} \text{ (L)}} = \mathbf{0.514 \text{ (g/L)}}$$

Problems

An 8.13-g sample of an ant-control preparation was decomposed by wet-ashing with H_2SO_4 and HNO_3. The As in the residue was reduced to the trivalent state with hydrazine. After removal of the excess reducing agent, the As(III) required a 31.46-mL titration with 0.03142 M I_2 in a faintly alkaline medium. **Express** the results of this analysis in terms of percentage of As_2O_3 in the original Sample.

Solution: 1.2%

Problems

$$AsO_3^{-3} + I_2 + H_2O \longrightarrow AsO_4^{-3} + 2\,I^- + 2\,H^+$$

No mmol I_2 = no mmol AsO_3^{-3} = Conc (M) * Vol (mL) =

= **0.9885 (mmol)**

$$\text{No mmol } As_2O_3 = \frac{1 \text{ mol } As_2O_3}{2 \text{ mol } AsO_3^{-3}} * \text{ no mmol } AsO_3^{-3} =$$

= 0.4943 (mmol)

$$\%\ As_2O_3 = \frac{\text{Wt } As_2O_3 \text{ (g)}}{\text{Wt sample (g)}} * 100 =$$

$$= \frac{0.4943*10^{-3} \text{ (mol)} * 197.85 \text{ (g/ mol)}}{8.13 \text{ (g)}} * 100 =$$

= 1.2%

Redox Titration

Part 2

Dr. Mai Ramadan

Iodometry

Titrant: Thiosulfate standard solution

Thiosulfate determine iodine formed during the reaction. This procedure avoids direct use of I_2 standard solution.

Analyte: An excess of KI is added to analyte. As a result I_2 should be formed. Analytes are oxidizing agent

End point: starch (decolorization of blue colour)
self indicator

Standarization: Iodate and iodide generates I_2

Iodometry

KI excess
H^+

Analyte

Analyte oxidizes iodide to iodine

$Na_2S_2O_3$ Titrant

I_2 Generated

I_2 Conc. ↑
Brown color

Starch indicator

I_2 Conc. ↓
Pale yellow color

$Na_2S_2O_3$ Titrant

Decolorization of starch

Iodometry

Applications

Determination of iodate

$$IO_3^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_2 + 3\,H_2O$$

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

Determination of Cu^{+2}, Co (III), Cr (VI)

$$2\,Cu^{+2} + 4\,I^- \longrightarrow I_2 + 2\,CuI\,(s)$$

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

Iodometry

Applications

Determination of bromate BrO_3^-, chlorate ClO_3^-

KBr is added in excess

$$BrO_3^- + 5\,Br^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$$

$$ClO_3^- + 6\,Br^- + 6\,H^+ \longrightarrow 3\,Br_2 + Cl^- + 3\,H_2O$$

Then KI is added in excess to generate iodine which should be titrated with thiosulfate

$$Br_2 + 2\,I^- \longrightarrow I_2 + 2\,Br^-$$

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

Iodometry

Applications

Determination of metal oxides:

MnO_2 (brown stone determination by Bunsen method)

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + 2\,H_2O + Cl_2$$

$$Cl_2 + 2\,I^- \longrightarrow 2\,Cl^- + I_2$$

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

Determination of hydrogen peroxide:

$$H_2O_2 + 2\,H^+ + 2\,I^- \longrightarrow I_2 + 2\,H_2O$$

The reaction is slow and need a catalyst.

Problems

A solution of sodium thiosulfate was standarized by dissolving 0.121 g of potassium iodate (MW = 214) in water adding a large excess of potassium iodide and acidified with HCl . the liberated iodine required 41.6 ml of thiosulfate to **decolorize** the blue colour.

Calculate the molarity of thiosulfate solution?

$$IO_3^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_{2\ \text{liberated}} + 3\,H_2O$$

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

Problems

Solution:

No mol I_2 (generated) = $\frac{3 \text{ mol } I_2}{1 \text{ mol } KIO_3}$ * no mol KIO_3

$= \frac{3}{1} * \frac{0.121 \text{ (g)}}{214 \text{ (g/mol)}} = 1.6963*10^{-3}$ (mol)

No mol $S_2O_3^{-2}$ = $\frac{2 \text{ mol } S_2O_3^{-2}}{1 \text{ mol } I_2}$ * no mol I_2

Conc (M) * 41.6 $*10^{-3}$ (L) = $\frac{2}{1}$ * $1.6963*10^{-3}$ (mol) =

Conc (M) = 0.082 (M)

Problems

a 5.3 g powder contains $C_6H_8O_6$ Ascorbic acid (Mw = 176) was analysed as follows, 0.5 g powder was dissolved 100 ml water. To 40 ml of the solution an excess of KI was added then 23 ml (0.25 N) KIO_3 solution and was allowed to stand for 15 min. in dark place. The unreacted I_2 has required 35 ml of (0.16 N) $Na_2S_2O_3$ standard solution.

Write the balanced chemical equation involved in this process.

Calculate the percentage of ascorbic acid in the original powder.

Problems

$$IO_3^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_{2\ total} + 3\,H_2O$$

$$C_6H_8O_6 \text{ (Ascorbic acid, vit C)} + I_{2\ reacted} \longrightarrow C_6H_6O_6 + 2\,I^- + 2\,H^+$$

$$I_{2\ unreacted} + 2\ S_2O_3^{-2} \longrightarrow S_4O_6^{-2} + 2\,I^-$$

Solution:

$$\text{Conc (M) } KIO_3 = \frac{N}{a} = \frac{0.25}{5} = 0.05 \text{ (M)}$$

$$\text{Conc (M) } S_2O_3^{-2} = \text{Conc (N)} = 0.16 \text{ (M)}$$

Problems

Solution:

No mmol I_2 (generated) = $\frac{3 \text{ mol } I_2}{1 \text{ mol } KIO_3}$ * no mmol KIO_3 =

$= \frac{3}{1}$ * 23 (mL) * 0.05 (M)= 3.45 (mmol)

No mmol I_2 (excess) = $\frac{1 \text{ mol } I_2}{2 \text{ mol } S_2O_3^{-2}}$ * no mmol $S_2O_3^{-2}$

$= \frac{1}{2}$ * 35 (mL) * 0.16 (M) = 2.8 (mmol)

No mmol I_2 (reacted) = Total - excess = 0.65 (mmol)

Problems

Solution:

No mmol Ascorbic acid = no mmol No mmol I_2 (reacted) = 0.65 (mmol)

No mmol ascorbic acid (100 mL) = 1.625 (mmol)

No mmol ascorbic acid in (0.5 g powder) = 1.625 (mmol)

$$\text{\% ascorbic acid} = \frac{\text{Wt ascorbic acid (g)}}{\text{Wt sample (g)}} * 100 =$$

$$\text{\% ascorbic acid} = \frac{1.625*10^{-3}\ \text{(mol)} * 176\ \text{(g/mol)}}{0.5\ \text{(g)}} * 100 = \mathbf{57.2\%}$$

Redox Titration

Part 3

Dr. Mai Ramadan

Permanganatometry

$KMnO_4$ is a strong oxidizing agent. It is pH dependent

In acidic media:

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

In neutral or slightly acidic:

$$MnO_4^- + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O$$

In basic media:

$$MnO_4^- + e^- \longrightarrow MnO_4^{-2}$$

Permanganatometry

$KMnO_4$ Titrant

H^+

Analyte

Volume is measured

Color of excess permangante

Permanganatometry

$KMnO_4$ Standard solution (Read in chapter 17)

The prepared solution should be kept 7-10 days then filtered by glass crucible to remove MnO2 (Why?). The solution is put in dark bottles .

Media: should be acidic. **Do not use HCl.**

Standarization: $Na_2C_2O_4$, $H_2C_2O_4$. 2 H_2O, As_2O_3

$$2\ MnO_4^- + 5\ H_2C_2O_4 + 6\ H^+ \longrightarrow 10\ CO_2 + 2\ Mn^{+2} + 8\ H_2O$$

Mn^{+2} is a catalyst (Autocatalyst).

End Point: Self indicator

Permanganatometry

Applications

Determination of iron (II): pretreatment of sample

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

Determination of H_2O_2

$$5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ \longrightarrow 5\,O_2\,(g) + 2\,Mn^{+2} + 8\,H_2O$$

Determination of nitrite:

The analyte solution is put in the burett and known amount of $KMnO_4$ in conical flask, acidified, titrated until the purple colour disappears.

Permanganatometry

Applications

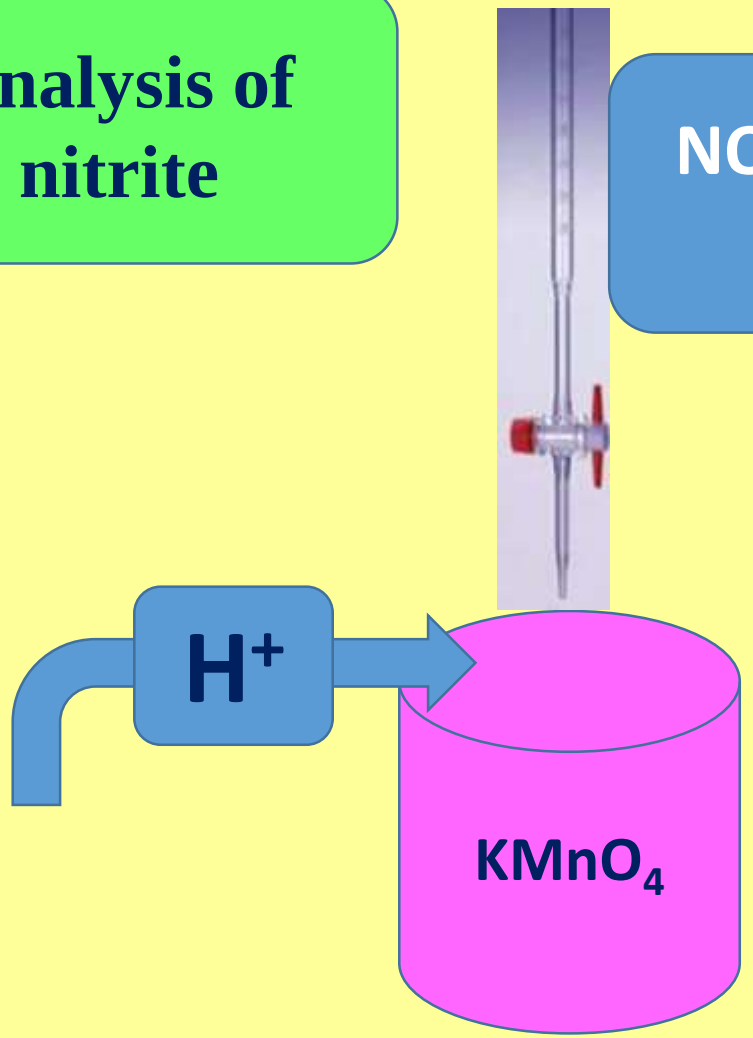
Determination of nitrite

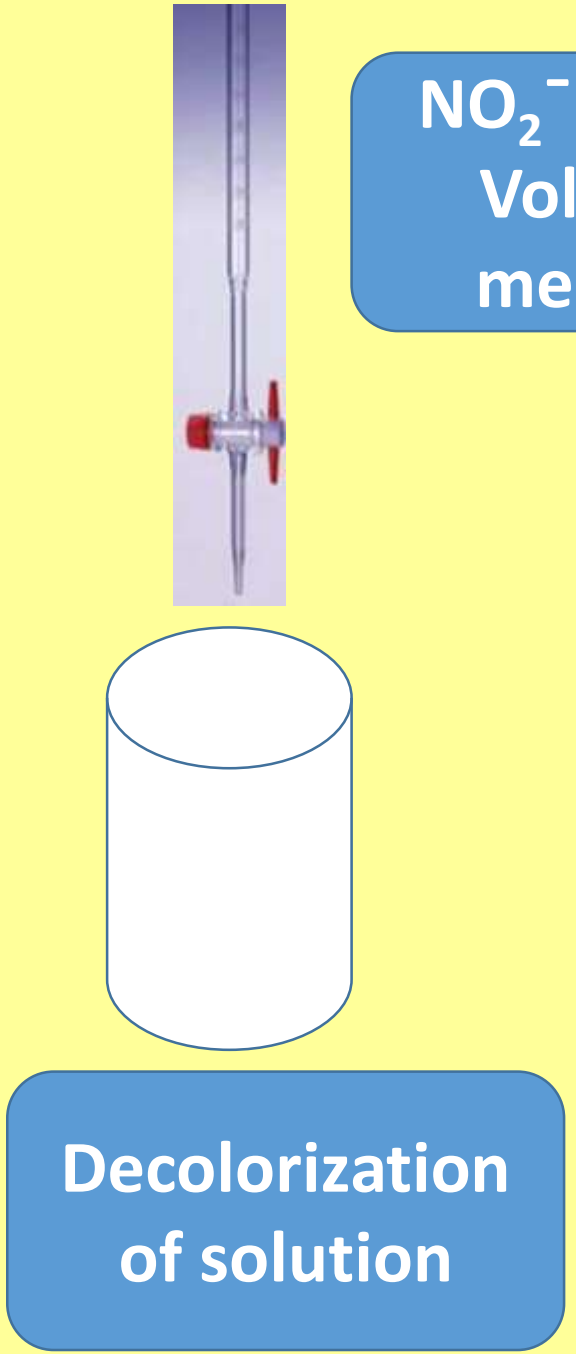
$$5\ NO_2^- + 2\ MnO_4^- + 6\ H^+ \longrightarrow 5\ NO_3^- + 2\ Mn^{+2} + 3\ H_2O$$

Nitrite in acidic media transformed to nitrogen gases.

$$2\ NO_2^- + 2\ H^+ \longrightarrow 2\ HNO_2 \longrightarrow NO_2 + NO + 2\ H_2O$$

Analysis of nitrite





Problems

You wish to standardize the permanganate solution (0.01 M) against primary $Na_2C_2O_4$ (134.00 g/mol). If you want to use between 30 and 45 mL of the reagent for the standardization, what range of masses of the primary standard should you weigh out?

$$2\ MnO_4^- + 5\ H_2C_2O_4 + 6\ H^+ \longrightarrow 10\ CO_2 + 2\ Mn^{+2} + 8\ H_2O$$

You should weigh between 0.101 to 0.151 g of the primary standard

$Na_2C_2O_4$ to consume 30 to 45 mL of the permanganate solution

Solution

When 30 mL is required for titration:

$$\text{No mol } KMnO_4 = \frac{2 \text{ mol } MnO_4^-}{5 \text{ mol } C_2O_4^{-2}} * \text{ no mol } Na_2C_2O_4 =$$

$$30*10^{-3} \text{ (L)} * 0.01 \text{ (M)} = \frac{2}{5} * \frac{X \text{ (g)}}{134 \text{ (g/mol)}}$$

X (g) = 0.101 (g)

Solution

When 45 mL is required for titration:

$$\text{No mol } KMnO_4 = \frac{2 \text{ mol } MnO_4^-}{5 \text{ mol } C_2O_4^{-2}} * \text{ no mol } Na_2C_2O_4 =$$

$$45*10^{-3} \text{ (L)} * 0.01 \text{ (M)} = \frac{2}{5} * \frac{X \text{ (g)}}{134 \text{ (g/mol)}}$$

X (g) = 0.151 (g)

Problems

A 0.1278-g sample of primary-standard $Na_2C_2O_4$ required exactly 33.31 mL of the permanganate solution in Example 20-2 to reach the end point. What was the molar concentration of the $KMnO_4$ reagent?

$$\text{No mol } KMnO_4 = \frac{2 \text{ mol } MnO_4^-}{5 \text{ mol } C_2O_4^{-2}} * \text{ no mol } Na_2C_2O_4 =$$

$$= \frac{2}{5} * \frac{0.1278 \text{ (g)}}{134 \text{ (g/mol)}} = 3.81*10^{-4} \text{ (mol)}$$

$$33.31*10^{-3} \text{ (L)} * \text{Conc (M)} = 3.81*10^{-4} \text{ (mol)}$$

Conc (M) of $KMnO_4$ = 0.01144 (M)

Redox Titration

Part 4

Dr. Mai Ramadan

Nitritometry (Diazotitration)

Analyte : primary aromatic amine

Media: acidic

Conditions: add KBr to analyte solution, the analyte solution is put in ice bath

Titrant: $NaNO_2$

End point: Use starch / iodide paper. Blue color produced on paper when titrated solution is applied.

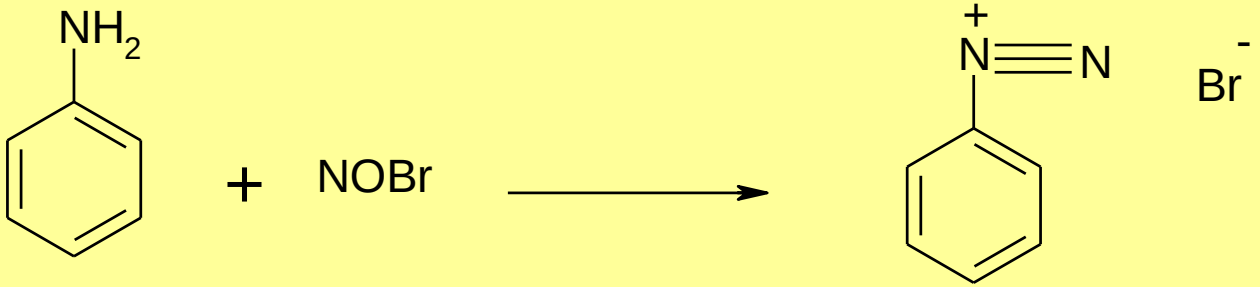
Example: Benzocaine

Nitritometry (Diazotitration)

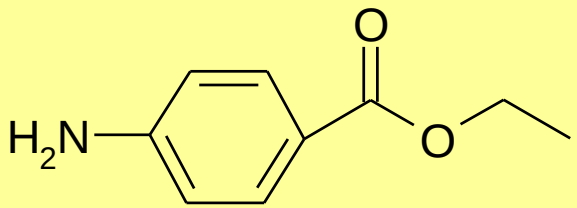
$NO_2^- + H_3O^+ \longrightarrow HNO_2$

$HNO_2 + Br^- + H_3O^+ \longrightarrow NOBr + 2\ H_2O$

nitrosyl bromide



Diazonium salt



Benzocain

Cerimetry

Titrant: Ce (IV) solution
like cerium ammonium sulfate dihydrate $(NH_4)_2$ [Ce $(SO_4)_3$].2 H_2O,
Cerium hydrogen sulfate, cerium hydroxide (pure primary standard)

Media: acidic (see chapter 17)

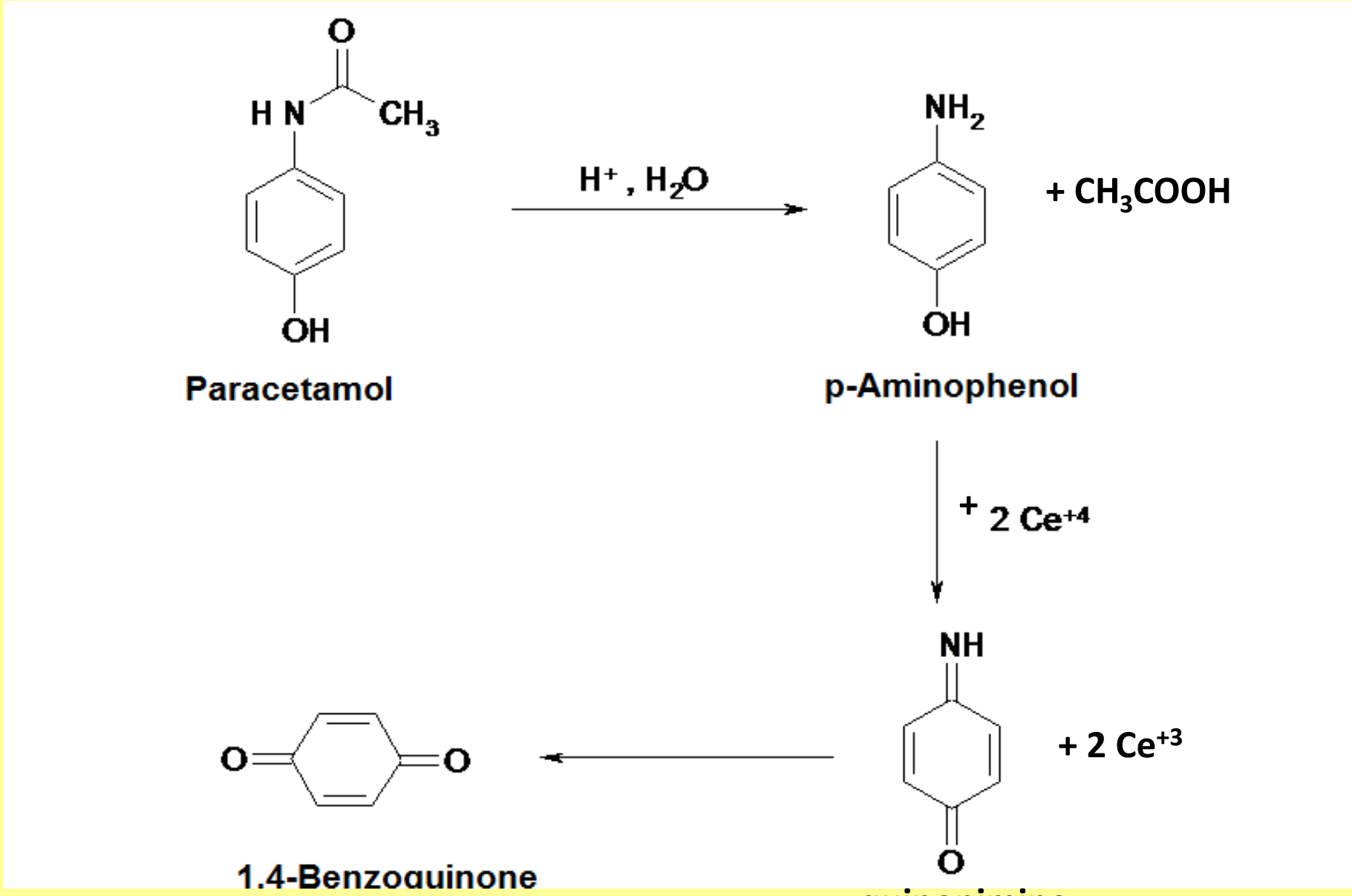
analyte: Fe (II), Sn (II), paracetamol

End point: indicator like ferroin

Standardization: **$Na_2C_2O_4$ (balance equation)**

$$Ce^{+4} + C_2O_4^{-2} + H^+ \longrightarrow CO_2 + Ce^{+3}$$

Cerimetry


O
H N
CH3
OH
Paracetamol
H+ , H2O
NH2
OH
p-Aminophenol
+ CH3COOH
+ 2 Ce+4
NH
O
quinonimine
+ 2 Ce+3
O
O
1,4-Benzoquinone

Redox Titration

Part 5

Dr. Mai Ramadan

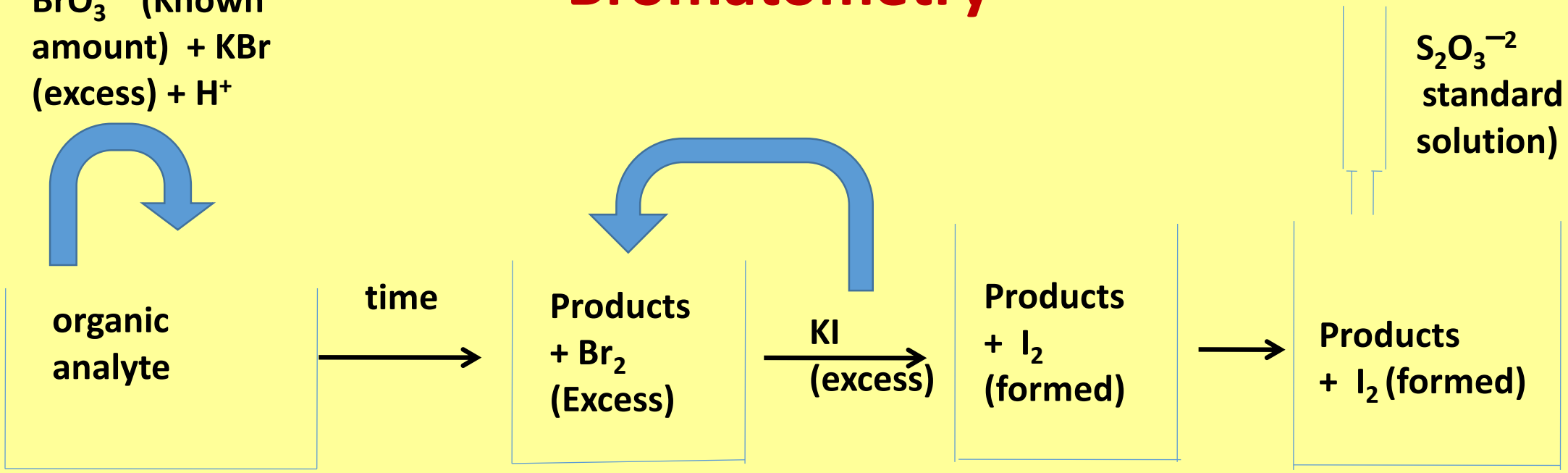
Bromatometry

$$BrO_3^- + 6\,e^- + 6\,H^+ \longrightarrow Br^- + 3\,H_2O$$

Bromate is a strong oxidizing agent. It can be used directly for determination of As (III), Sb (III), Sn (II)

The widely used procedure of bromatometry is an indirect method applied for organic analytes..

Bromatometry



A known amount of bromate is added along with KBr excess and acidified then keep for a time in a dark place. The organic analyte reacts with Br_2 in a reaction (substitution, addition, and oxidation.) A large excess of KI is then added and I_2 is formed which should be titrated with thiosulfate standard solution

Bromatometry

Equations:

$$BrO_3^- + 5\,Br^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$$

Organic analyte + $Br_{2\text{reacted}}$ ⟶ products

according to analyte is stoichiometry

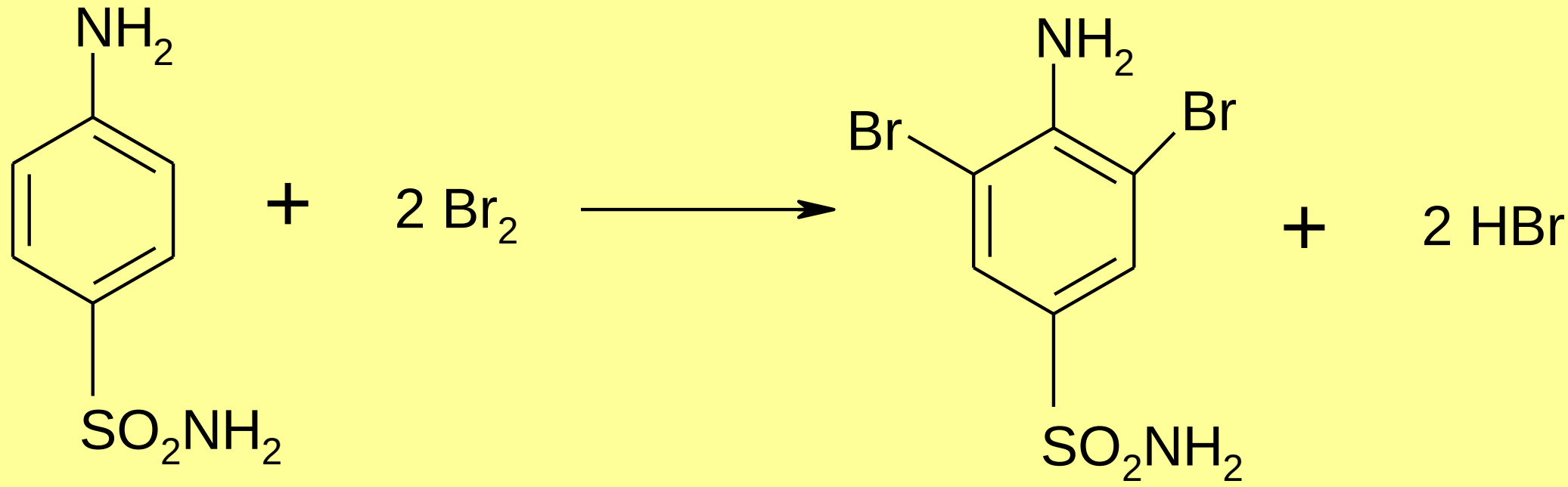
$$Br_{2\ \text{unreacted}} + 2\,I^- \longrightarrow I_2 + 2\,Br^-$$

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

Bromatometry

Examples

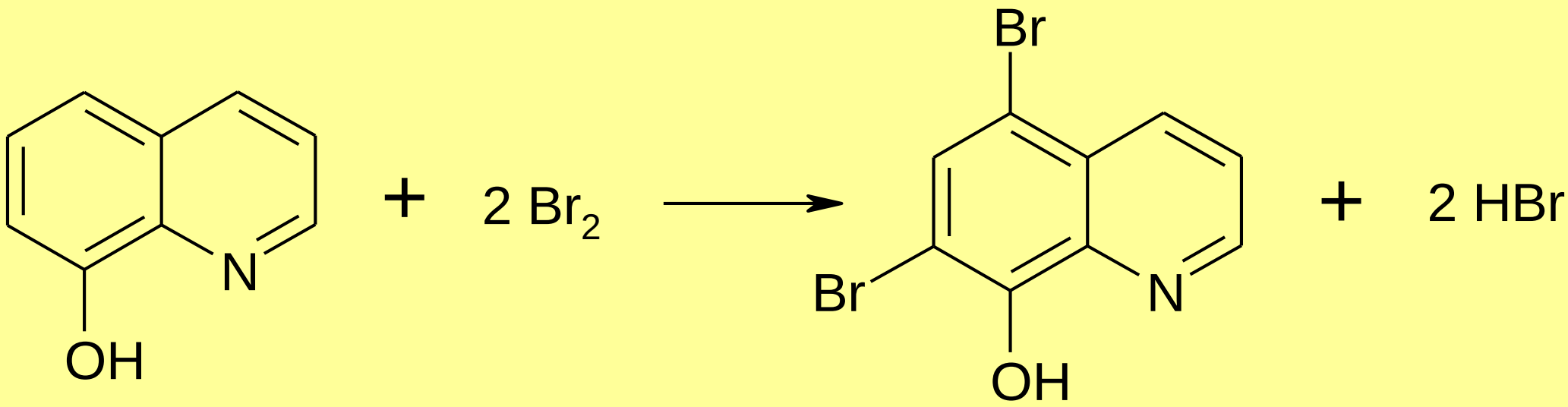
Sulfanilamide



Bromatometry

Examples

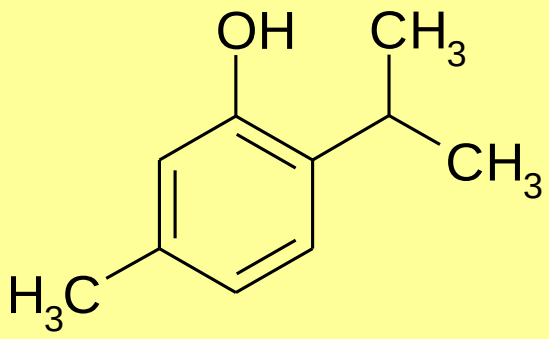
8-hydroxyquinoline



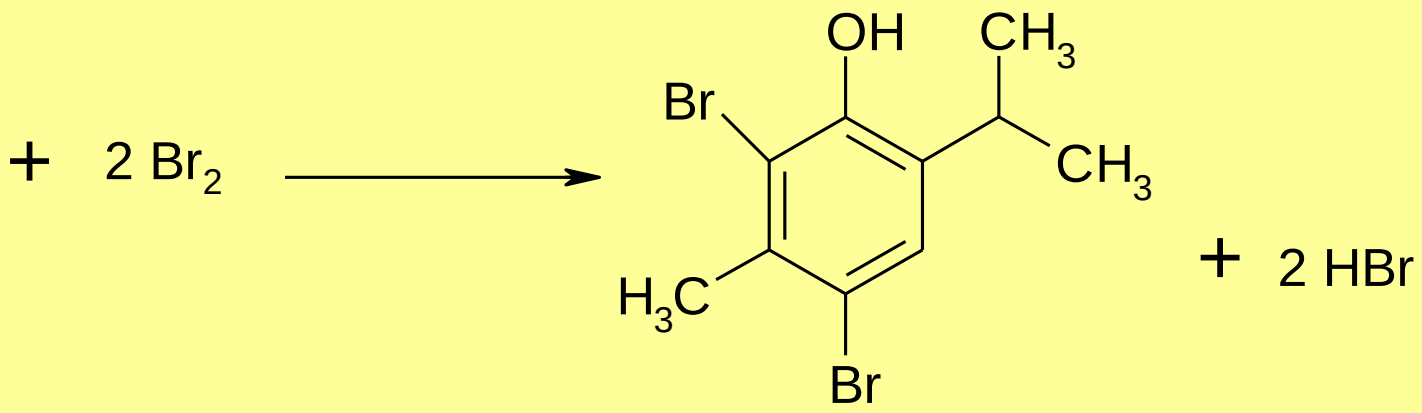
Bromatometry

Examples

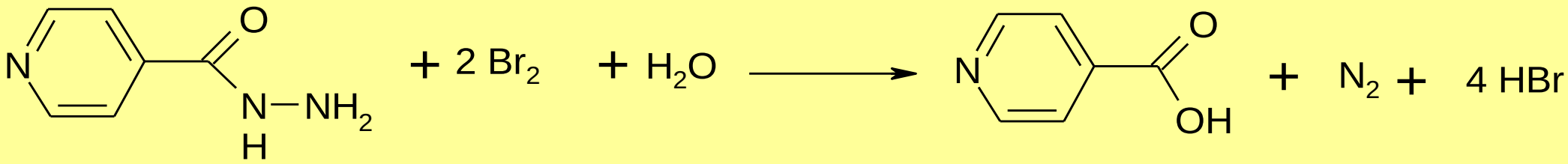
Thymol



Thymol



Isoniazide



Bromatometry

Example

a 0.2819 g sample of an antibiotic powder (sulfanilamide) was dissolved in HCl and the solution diluted to 100 ml. A 20.00 ml aliquot was transferred to a flask and followed by a 25.00 ml of a 0.01767 M $KBrO_3$. an excess of KBr was added to form bromine. The flask was stoppered, after 10 min. During which time the Br_2 brominated the sulfanilamide, an excess of KI was added. The liberated iodine was then titrated with 12.92 ml of 0.1215 M $Na_2S_2O_3$. The equation are given above.

Calculate the percent $NH_2C_6H_4SO_2NH_2$ (FW = 172.21) in the powder.

Bromatometry

Solution

No mmol Br_2 (total) = $\frac{3 \text{ mol } Br_2}{1 \text{ mol } KBrO_3}$ * no mmol $KBrO_3$ =

= $\frac{3}{1}$ * 25 (mL) * 0.01767 (M) = **1.3253 (mmol)**

No mmol Br_2 (unreacted) = no mmol I_2 (formed) =

no mmol I_2 (formed) = $\frac{1 \text{ mol } I_2}{2 \text{ mol } Na_2S_2O_3}$ * no mmol $Na_2S_2O_3$ = **0.7849 (mmol)**

No mmol Br_2 (reacted) = Total - unreacted = 0.5404 (mmol)

No mmol Sulfanilamide = $\frac{1 \text{ mol sulfanilamide}}{2 \text{ mol } Br_2}$ * no mmol Br_2 (reacted) =

Bromatometry

Solution

No mmol Sulfanilamide = **0.27 (mmol)** ---------- 20 mL

? ---------- 100 mL

No mmol sulfanilamide (100 ml) = 1.35 (mmol)

Weight sulfanilamide in powder (g) = $1.35 * 10^{-3}$ (mol) * 172.21 (g/mol)

= 0.2325 (g)

$$\% \text{ sulfanilamide} = \frac{\text{Wt of drug (g)}}{\text{Wt of sample (g)}} * 100 = 82.48\%$$

Bromatometry

P-hydroxyacetanilide (FW = 151.6) is the active ingredient of headache remedy. A five tablets sample was dissolved and diluted to 500 mL in a volumetric flask. Treatment of 50 mL aliquots of this solution with an **identical** volume of 0.0175 (M) $KBrO_3$, excess of KBr, and acidification caused replacement of two hydrogens with bromine

$$C_8H_9NO_2 + 2\,Br_2 \longrightarrow C_8H_7Br_2NO_2 + 2\,HBr$$

Potassium iodide was adde, following which the liberated iodine required an average titration of 14.77 mL of 0.06521 (M) sodium thiosulfate. Calculate average weight p-hydroxyacetanilide **mg** in each of these tablets.

Bromatometry

$$BrO_3^- + 5\,Br^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$$

P-hydroxyacetanilide + $2\,Br_{2\text{reacted}}$ ⟶ products

$$Br_{2\ \text{unreacted}} + 2\,I^- \longrightarrow I_2 + 2\,Br^-$$

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

Bromatometry

No mmol Br_2 (total) = $\frac{3 \text{ mol } Br_2}{1 \text{ mol } KBrO_3}$ * no mmol $KBrO_3$ =

= $\frac{3}{1}$ * 50 (mL) * 0.0175 (M) = **2.625 (mmol)**

No mmol Br_2 (unreacted) = no mmol I_2 (formed) =

no mmol I_2 (formed) = $\frac{1 \text{ mol } I_2}{2 \text{ mol } Na_2S_2O_3}$ * no mmol $Na_2S_2O_3$ =

= $\frac{1}{2}$ * 14.77 mL * 0.06521 (M) = **0.4816 (mmol)**

No mmol Br_2 (reacted) = Total - unreacted **= 2.1434 (mmol)**

Bromatometry

Solution

No mmol drug = $\frac{1 \text{ mol drug}}{2 \text{ mol } Br_2}$ * no mmol Br_2 (reacted) =

= $\frac{1}{2}$ * 2.1434 = 1.0717 (mmol)

1.0717 (mmol) ---------- 50 mL
10.717 (mmol) ---------- 500 mL

Weight of drug in 5 tablets = $10.717*10^{-3}$ (mol) * 151.6 (g/mol)= 1.6183 (g)

Weight per tablet (mg) = $\frac{1.6183 * 10^3}{5}$ = 324 (mg)

Redox Titration

Part 6

Dr. Mai Ramadan

Example

The Ca(II) in a 0.2437 g sample was precipitated as CaC_2O_4. the solid was filtered washed free of excess oxalate and then **redissolved** in H_2SO_4. The liberated $H_2C_2O_4$ required 31.44 mL titration with 0.02065 (M) $KMnO_4$**. Express the results of this analysis in terms of percent CaO.**

$$Ca^{+2} + C_2O_4^{-2} \longrightarrow CaC_2O_4$$

$$CaC_2O_4 + 2\,H^+ \longrightarrow H_2C_2O_4 + Ca^{+2}$$

$$2\,MnO_4^- + 5\,H_2C_2O_4 + 6\,H^+ \longrightarrow 10\,CO_2 + 2\,Mn^{+2} + 8\,H_2O$$

Problems

$$\text{No mmol } H_2C_2O_4 = \frac{5 \text{ mol } H2C_2O_4}{2 \text{ mol } MnO_4^-} * 31.44 \text{ (mL)} * 0.02065 \text{ (M)} =$$

$$= 1.6231 \text{(mmol)}$$

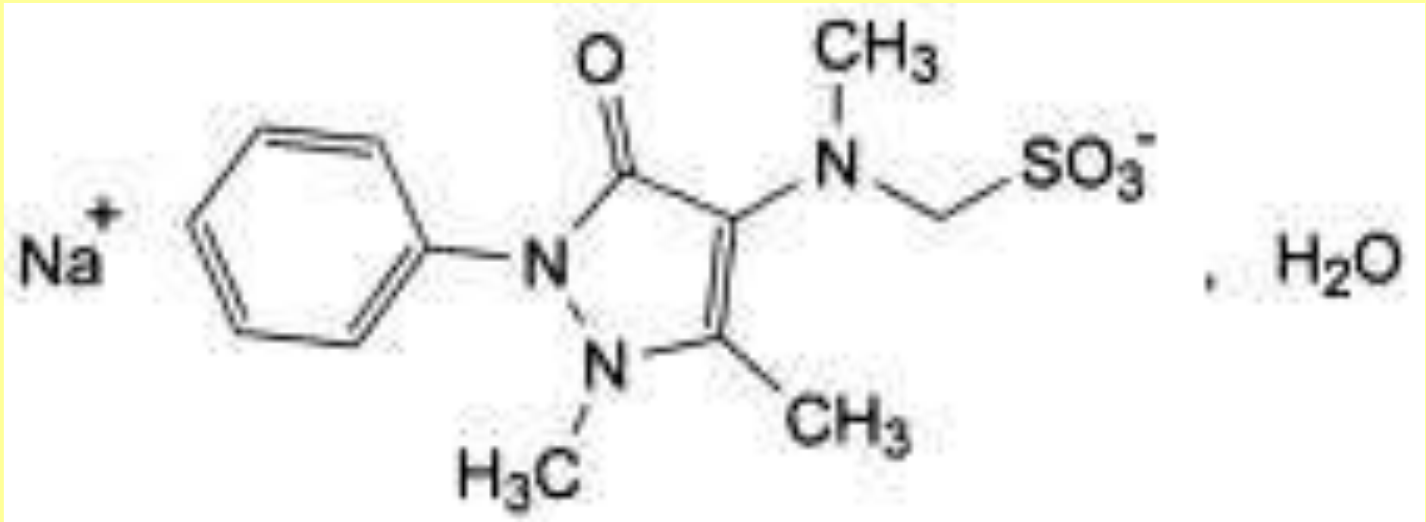
$$\text{No mmol } H_2C_2O_4 = \text{no mmol } CaC_2O_4 = 1.6231 \text{(mmol)}$$

$$\text{No mmol CaO} = \text{no mmol } CaC_2O_4 = 1.6231 \text{(mmol)}$$

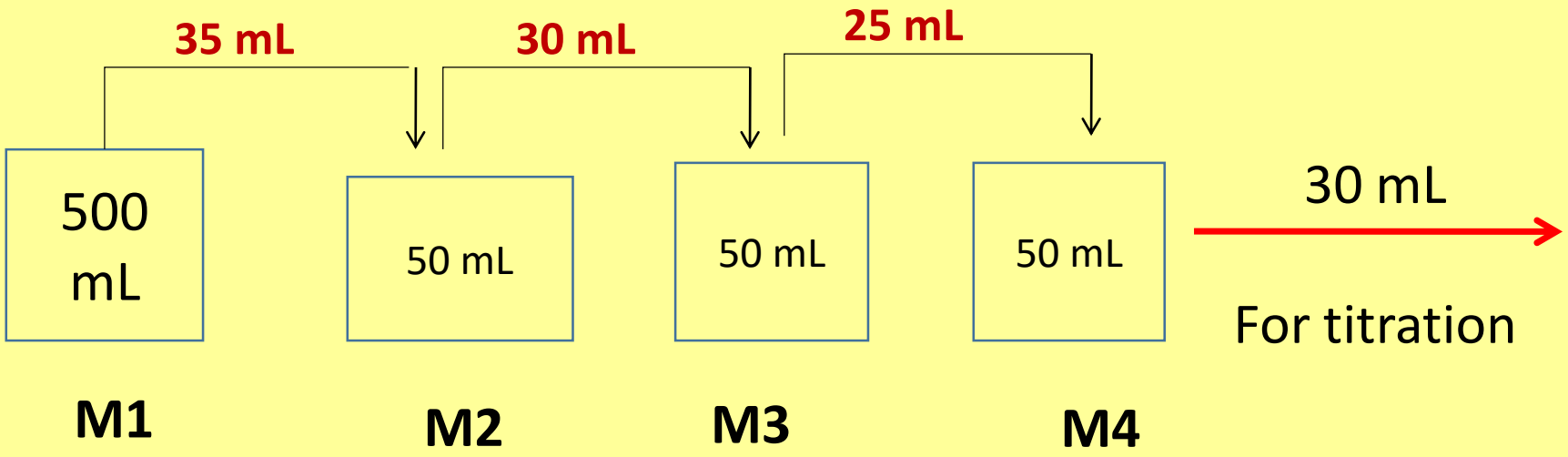
$$\% \text{ CaO} = \frac{1.6231 * 10^{-3} \text{ (mol)} * 56.08 \text{ (g/mol)}}{0.2437 \text{ (g)}} * 100 = \mathbf{37.35\%}$$

Example

Analgin® tablets contain Metamizol sodium monohydrate (MW = 351.4) which is used as analgesic. To be analysed iodimetry was applied. **20 tablets** were powdered and dissolved in 500 ml of 0.01 M HCl. 35 ml of the solution were diluted in 50 ml. 30 ml of the resulting solution were diluted to 50 ml. From the resulting solution 25 ml were further diluted in 50 ml. 30 ml of the end solution had required 7.49 ml of 0.1 N iodine standard solution until the starch indicator was blue coloured. **Calculate the average weight of metamizol sodium monohydrate per each tablet in mg?**



Example



$$\text{Metamizol Na} + H_2O \longrightarrow R\text{-}NH_2 + HCHO + HSO_3^- + Na^+$$

$$HSO_3^- + I_2 + H_2O \longrightarrow HSO_4^- + 2\,I^- + 2\,H^+$$

$$\text{Conc (M) of } I_2 = \frac{N}{a} = 0.05\ (M)$$

Example

$$\text{No mmol drug} = \frac{1 \text{ mol drug} \;*\; 1\text{mol } HSO_3^- \;*\; \text{no mmol } I_2}{1 \text{ mol } HSO_3^- * \; 1 \text{ mol } I_2}$$

$$= 7.49 \text{ (ml)} * 0.05 \text{ (M)} = 0.3745 \text{ (mmol)}$$

$$\text{Conc (M4)} = \frac{0.3745 \text{ (mmol)}}{30 \text{ (mL)}} = 0.0125 \text{ M}$$

Conc of the end solution (M4) = 0.0125 M

Example

Conc (M4) *50 (mL) = 25 (mL)* Conc (M3) ⟶ **M3 = 0.025 M**

Conc (M3)* 50 (mL) = 30 (mL) * Conc (M2) ⟶ **M2 = 0.0417 M**

Conc (M2) * 50 (mL) = 35 (mL) * Conc (M1) ⟶ **M1 = 0.0596 M**

No moles drug = Conc (M1) * Vol (L)= 0.0596 (M) * 0.5 (L)= 0.0298 mol

Wt of drug per tablet = $\dfrac{\textbf{0.0298 (mol) * 351.4 (g/mol)}}{\textbf{20}}$ **= 0.524 (g)**

Problems and application

Examples : Chapter 17 : 1 - 7

Problems: Chapter 17 : 7-19, 22, 26, 27, 28, 29, 30 – 36, 38, 39, 40, 41, 43, 45, 46, 51

Next subject is precipitation titration