Practical Pharmaceutical Analytical Chemistry - II

Second Level
First Semester 2018-2019

Section 3

Oxidation - Reduction Titration
(Redox Titration)

Redox Indicators

- ✓ They are highly colored organic compounds that change their color when being oxidized or reduced.

- ✓ The color change depends on the change in the redox potential (E) of the system during titration.

- ✓ The half-reaction responsible for the color change of the indicator can be written as follows:

$$In_{Ox} + ne^- \rightleftharpoons In_{Red}$$

Oxidized form **Reduced form**

➢ **Requirements (specifications) of general redox indicators**:

1. Has a standard redox potential **intermediate** between that of the sample and that of the titrant.

$E^o_{sample} < E^o_{indicator} < E^o_{titrant}$ OR $E^o_{sample} > E^o_{indicator} > E^o_{titrant}$

So that the titrant reacts first with the sample and then with the indicator at the end point.

2. Exhibits a **sharp, readily detectable** color change.

3. The **transition potential** of the indicator (i.e. the potential range at which the indicator changes its color) should be close to the potential at the equivalence point.

➢ **Examples:**

- **1,10-Phenanthroline indicator:** { USP }

Used for the titration of ferrous $\{Fe^{2+}\}$ # cerric sulfate titrant $\{Ce(SO_4)_2\}$.

- **Diphenylamine indicator:**

Used for the titration of ferrous $\{Fe^{2+}\}$ # pot. dichromate titrant $\{K_2Cr_2O_7\}$.

Determination of Ferrous Salts
($FeSO_4.7H_2O$)

Experiment 1

Determination of Ferrous with 0.1 N Ceric Sulphate using 1,10-Phenanthroline Indicator

Principle

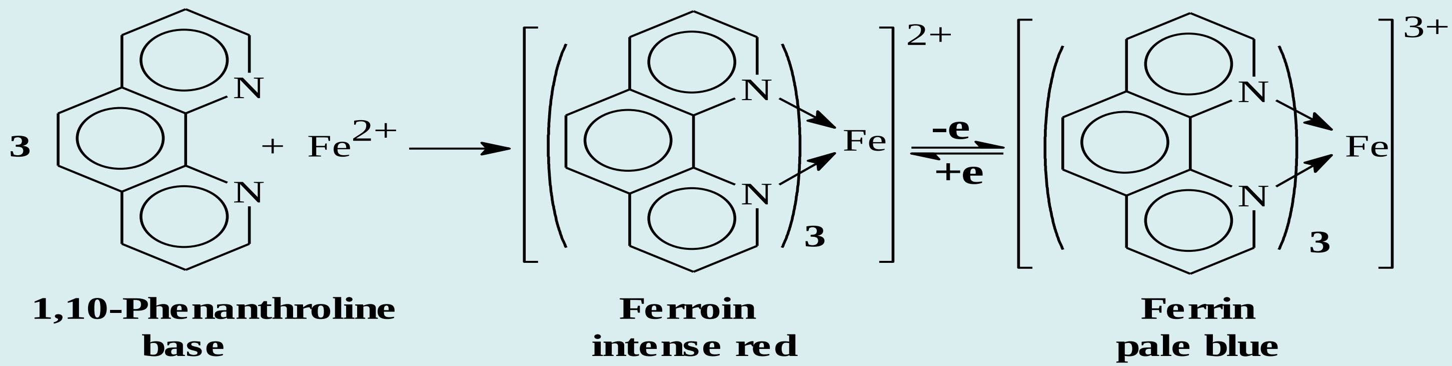
- ✓ Ferrous salts can be determined by titration with 0.1 N Ceric Sulphate using 1,10-Phenanthroline as a redox indicator.

- ✓ 1,10-Phenanthroline-ferrous complex (ferroin) is an intense red colored complex, which is reversibly oxidized (with strong oxidizing agents) to phenanthroline-ferric complex ion (ferrin), which has a pale blue color. The complex is used as an indicator in the titration of ferrous by ceric sulphate.

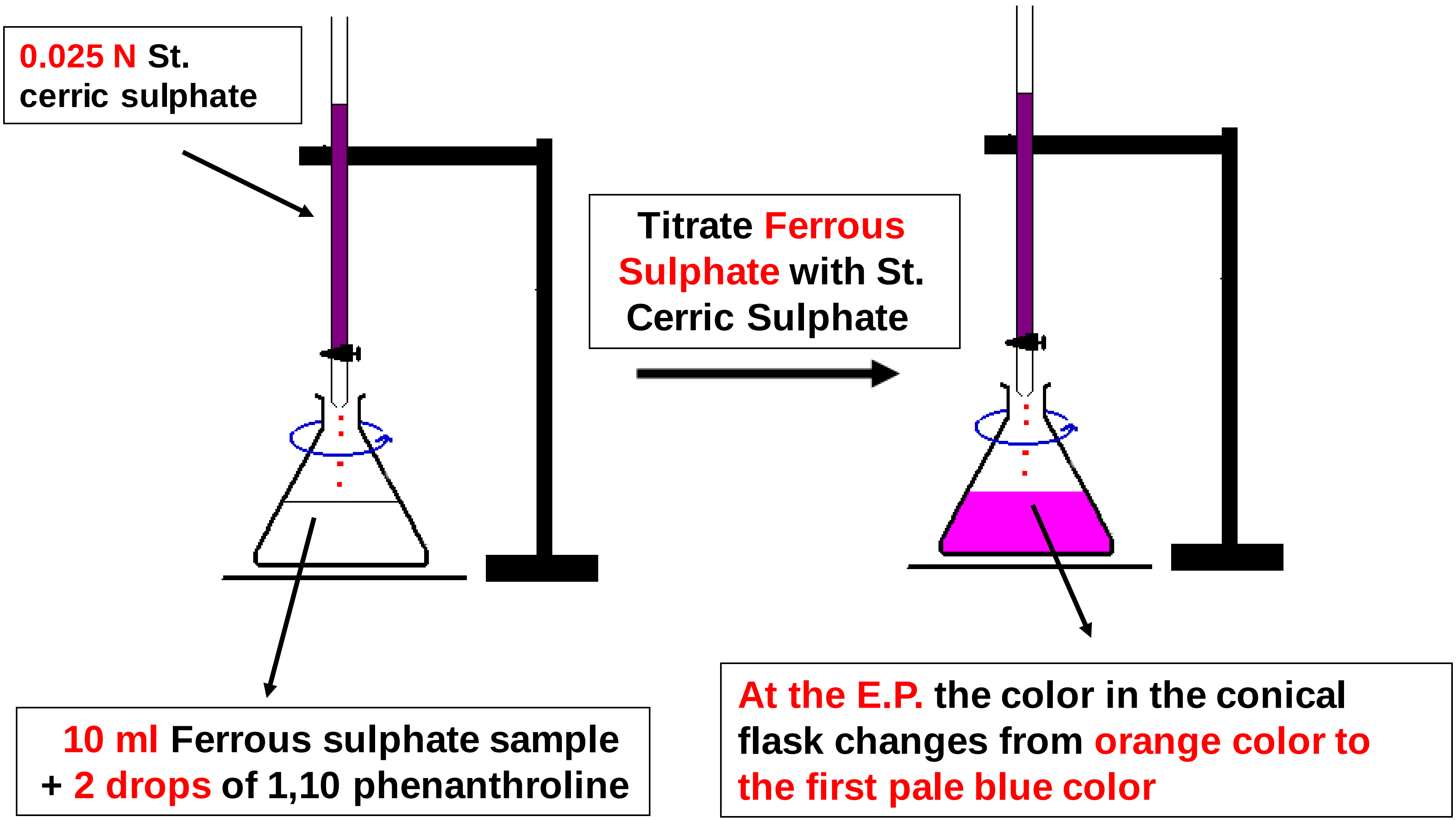
✓ During Titration:

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

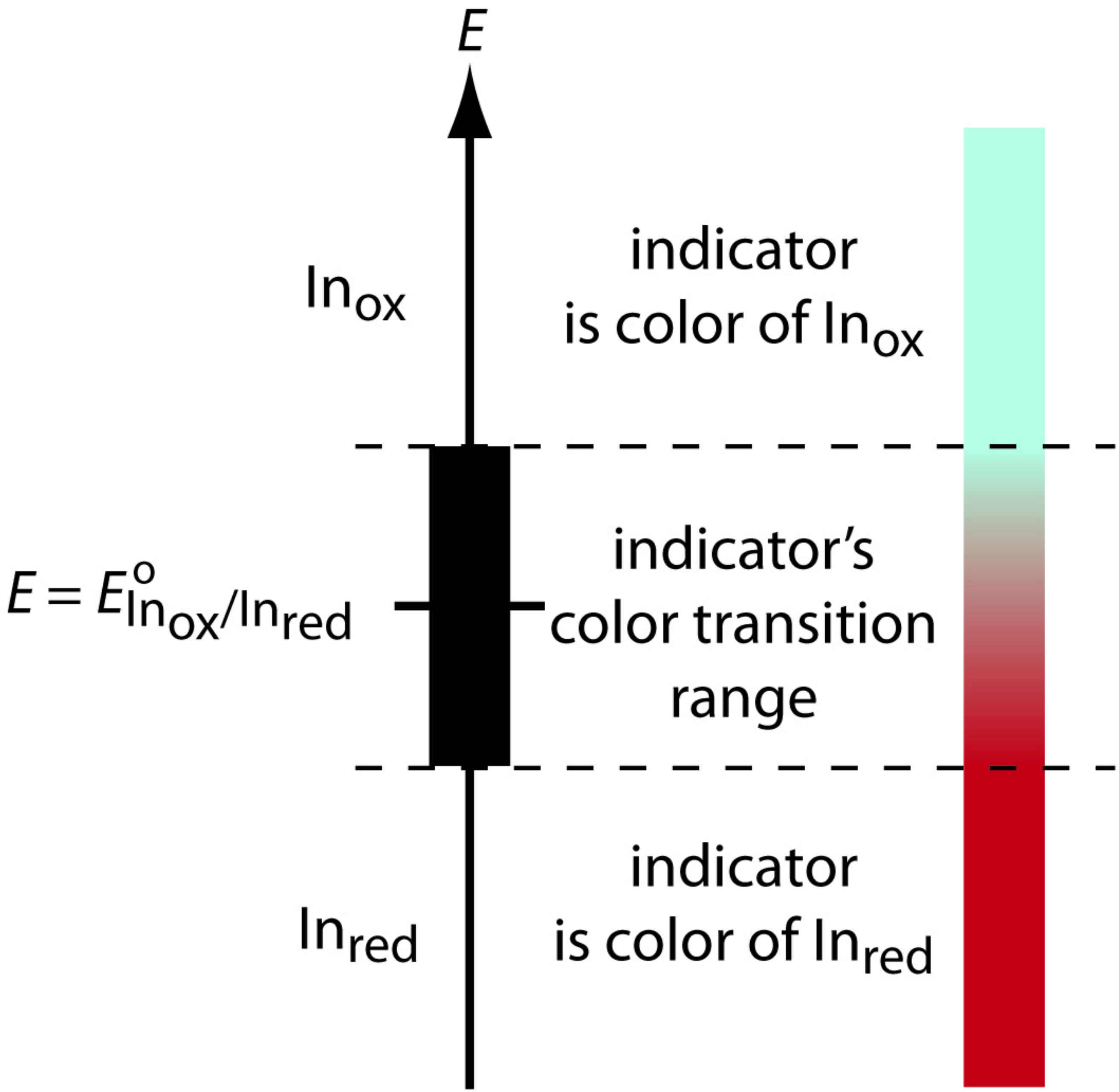
✓ At End point:



Procedure



0.025 N St. cerric sulphate
Titrate Ferrous Sulphate with St. Cerric Sulphate
10 ml Ferrous sulphate sample + 2 drops of 1,10 phenanthroline
At the E.P. the color in the conical flask changes from orange color to the first pale blue color



E
In_{ox}
indicator
is color of In_{ox}
$E = E^{o}_{In_{ox}/In_{red}}$
indicator's
color transition
range
In_{red}
indicator
is color of In_{red}

Calculations

Calculation of equivalent:

Each 1 ml 0.025 N $Ce(SO_4)_2$ = $\frac{278 \times 0.025}{1000}$ = 0.00695 g $FeSO_4.7H_2O$.

Conc. of ferrous = $\frac{E.p \times eq. \times 100}{10}$ = % w/v

Experiment 2

Determination of Ferrous with 0.1 N Potassium Dichromate using Diphenylamine Indicator

Principle

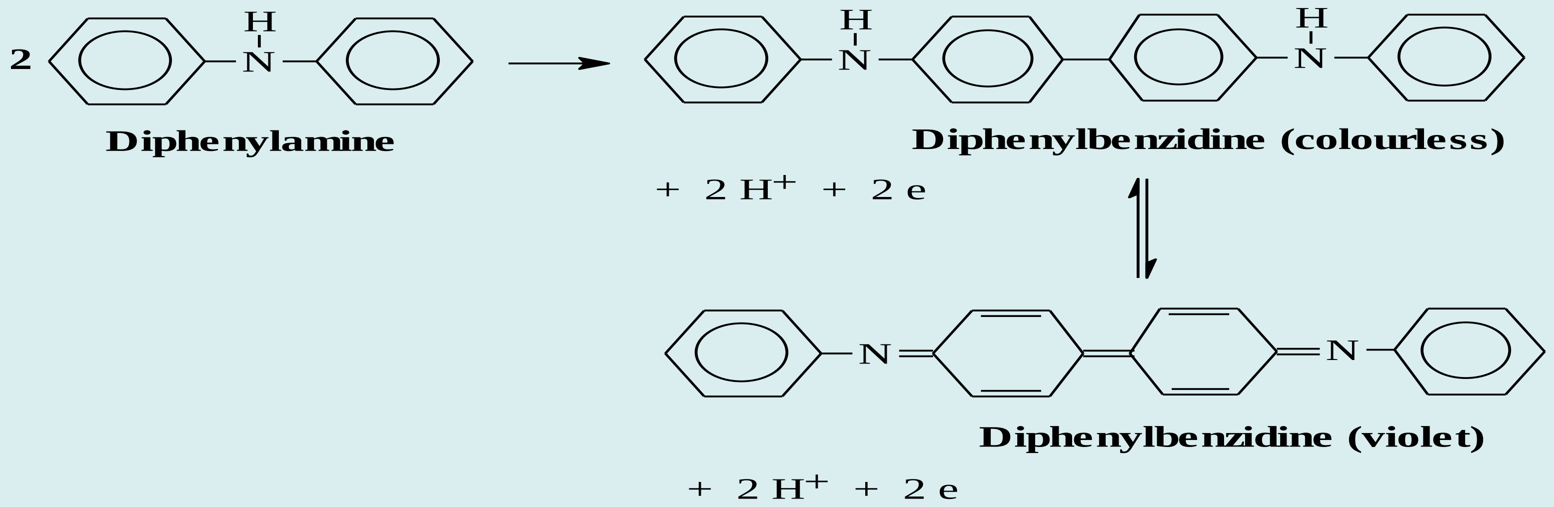
- Ferrous salts can be determined by titration with 0.1 N Potassium Dichromate using Diphenylamine as a redox indicator.

- During Titration:

$$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6\ Fe^{3+} + 7H_2O$$

- At End point:

The diphenylamine (I) undergoes oxidation first into a colourless diphenylbenzidine (II) which is the real indicator and is reversibly further oxidized to diphenylbenzidine violet (III).



- ✓ The oxidation potential of the system diphenylamine/diphenylbenzidine (colourless)/diphenylbenzidine (violet) = 0.76 volt
- ✓ The oxidation potential of Fe^{3+}/Fe^{2+} = 0.77 volt
- ✓ The oxidation potential of $Cr_2O_7^{2-}$/ 2 Cr^{3+} = 1.36 volt
- ➢ It is obvious that there is an overlapping between Eind & $E_{Fe^{3+}/Fe^{2+}}$
- ➢ For this, diphenylamine is only able to function as indicator in this reaction when **phosphoric acid** is present in the solution.
- ➢ **What is the role of Phosphoric acid?**
- ❑ **Formation of a colorless complex with the produced ferric ions leading to:**

1. Decreasing the molar concentration of Ferric and hence reduces the actual potential of (Fe^{3+}/Fe^{2+}) system so that Fe^{2+} ion will be oxidized before the indicator.
2. Removing the dark yellow color of Fe^{3+} ion giving a more clear color change.

Electrochemical series (**Eº** values at 25°C)

TABLE 17.1 Standard Reduction Potentials at 25 °C

Stronger oxidizing agent | Weaker reducing agent

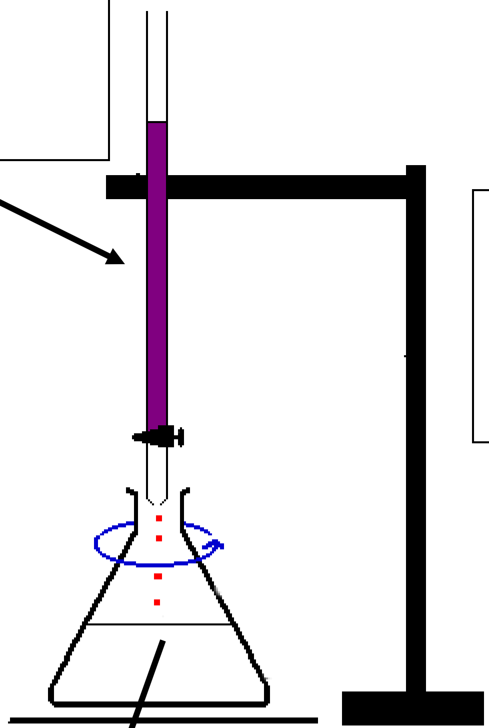
Reduction Half-Reaction		E° (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(aq) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	- 0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	- 0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	- 0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	- 0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	- 0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	- 0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	- 1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	- 2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	- 2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	- 3.04

Weaker oxidizing agent | Stronger reducing agent

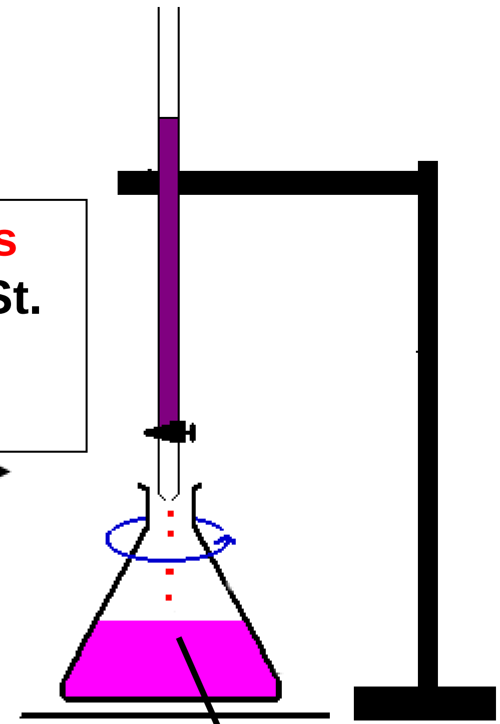
Table 17-1 Chemistry, 5/e

Procedure

0.1 N St. Potassium dichromate



Titrate Ferrous Sulphate with St. Potassium dichromate



10 ml Ferrous sulphate sample
+ 5 ml dil. H_2SO_4
+ 1 ml phosphoric acid

+ 7 drops of diphenylamine

The color in the conical flask changes from greenish blue color to greenish grey color then at the E.P. changes into intense violet blue color


200
150
100

Calculations

Calculation of equivalent:

$$\text{Each 1 ml 0.1 N } K_2Cr_2O_7 = \frac{278}{10 \times 1000} = 0.0278 \text{ g } FeSO_4.7H_2O.$$

$$\textbf{Conc. of ferrous} = \frac{E.P \times eq. \times 100}{10} = \quad \% \text{ w/v}$$


Thank You