Redox Titrations!

Reactions involving transfer of electrons between titrant and titrant system.

* For a redox reaction to be used for titration:-

① Reaction should be rapid and should go to completion.
② Reaction should be stoichiometric
③ A means of end-point detection should be available.
④ Equilibrium should be attained after each addition of titrant.

- Because of large number of oxidation-reduction reaction possible, there are large no. of redox titration than acid-base titration, precipitation titration, complexometric titr^n.

$$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2$$

The reducing and oxidizing tendency of a substance will depend on its reduction potential.

$M^{x+} + ne^- \longrightarrow M^{(x-n)}$; accept e^- → Red^n → Oxidizing agent → Greater Red^n Potential.

$M^{(x-n)} \longrightarrow M^{x+} + ne^-$; loss e^- → Oxd^n → Reducing agent → lower Red^n Potential.

eg. $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$.

→ After every addition, equilibrium is attained.
→ There will be four species which will be present in amounts depending upon their reaction equilibrium constant.

$$E_{system} = E_{Fe^{2+}/Fe^{3+}} = E_{Ce^{3+};Ce^{4+}}$$

The Electrode potential changes during the course of the titration.
The magnitude of change in electrode potential is maximum in the vicinity of equivalence point.

* Construction of Titration curve:-

→ Titration curve is obtained by plotting the electrode potential of the system as ordinate v/s volume of titrant as abscissa.

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→ Such a curve is obtained either by measuring electrode potential experimentally using reference electrode and setting up proper cell.

OR

calculating theoretically the potential using Nernst's equation.
- either analyte system / titrand system
- titrant system.

In Practice :-

before equivalence point :- analyte system.
after equivalence point :- titrant system.

* Redox Reactions are classified into two groups :-

① Titration where H_3O^+ or ^-OH donot participate directly into redox reaction.
② Titration where H_3O^+ or ^-OH participate directly in the reaction.

* Redox reactions are also classified into different types (based on the reagent):-

① Permanganate titration :-

→ Titrations which involve the use of $KMnO_4$ are called as Permanganate titration.
→ $KMnO_4$ needs to be standardized first.
→ $KMnO_4$ acts as oxidizing agent in acidic medium.

→ medium is maintained by dil. H_2SO_4.

→ acts as self indicator.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\underset{\text{(colourless)}}{2MnO_4^-} + 8H^+ + 5e^- \longrightarrow \underset{\text{(Pink)}}{2Mn^{2+}} + 4H_2O.$$ (ACID driven reaction)

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eg. Fe^{2+} salts, oxalic acid, oxalates, peroxide, etc.

2. Dichromate titration :-

- → $K_2Cr_2O_7$ acts as oxidizing agent in acidic medium.
- → acidic medium is maintained by dilute H_2SO_4.
- → $K_2Cr_2O_7$ can be used directly.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O].$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O.$$ (ACID driven Reaction)

→ estimation of ferrous salts, iodides.

a) $K_2Cr_2O_7$ v/s Ferrous salt.

indicator
- → diphenylamine indicator (internal indicator).
- → potassium ferricyanide (external indicator)

b) Iodide estimation.

$I_2 + 2e^- \longrightarrow 2I^-$ (redn)

$2I^- \longrightarrow I_2 + 2e^-$ (oxdn)

i. Iodimetric titrations :-

- → free iodine is used
- → difficult to prepare free iodine soln (highly volatile & low solubility)
  Hence, KI is used.

$$KI + I_2 \longrightarrow \underline{\underline{KI_3}}$$

- → soln needs to be standardized before use.
- → sulphite, thiosulphate, arsenate can be estimated.

ii. Iodometric titration :-

→ oxidizing agent is allowed to react in neutral medium / acidic medium

II. Iodometric titration :

→ oxidizing agent is allowed to react in neutral medium / acidic medium with excess of KI to liberate I_2.

$$KI + \text{oxidizing agent} \longrightarrow I_2.$$

→ I_2 is titrated against a reducing agent like sodium thiosulphate.

→ Halogen, Oxyhalogen, dichromates, cupric ions, peroxide can be estimated.

$$2\,CuSO_4 + 4\,KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2\uparrow$$
$$K_2Cr_2O_7 + 6\,KI + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4\,K_2SO_4 + 7H_2O + 3\,I_2\uparrow.$$

In both cases, starch indicator is used.

free iodine ⟶ starch indicator shows blue/violet colouration.
iodide ion ⟶ starch indicator shows colourless colour.

eg 1. Titration of Fe(II) ions with Ce(IV) ions :-

→ The reaction is performed in presence of acid to prevent hydrolysis of both reactant and products.

→ Hence, $[H_3O^+]$ affects the value of formal redox potential / reduction potential of both the system but doesnot directly participate in the reaction.

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

* 10 cm³ of 0.1 M Fe^{2+} v/s 0.1 M Ce^{4+} solⁿ :-

a) At the beginning :-

→ Initially only Fe^{2+} ions are present.
So reduction potential is determined by the $Fe^{2+}; Fe^{3+}$ system.

→ small quantity of Fe^{3+} can be present as a result of air oxidation. However, conc. of Fe^{3+} can't be determined and is likely to be very small. And thus, it is usually neglected.

b) 5.0 cm^3 of Ce(IV) is added :- $\underset{5\ cm^3}{\underline{Fe^{2+}}} + \underset{5\ cm^3}{\underline{Ce^{4+}}} = Fe^{3+} + Ce^{3+}$

$$\left.\begin{aligned} [Fe^{2+}] &= \frac{5 \times 0.1}{15} \\ [Fe^{3+}] &= \frac{5 \times 0.1}{15} \end{aligned}\right\} \quad \frac{[Fe^{2+}]}{[Fe^{3+}]} = 1.$$

$$E_{system} = E^\circ_{Fe^{2+}, Fe^{3+}} - \frac{0.05916}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= 0.771 - \frac{0.05916}{1} \log 1.$$

$$= 0.771$$

c) 9.9 mL of Ce(IV) is added :-

$$\left.\begin{aligned} [Fe^{2+}] &= \frac{0.1 \times 0.1}{19.9} \\ [Fe^{3+}] &= \frac{9.9 \times 0.1}{19.9} \end{aligned}\right\} \quad \frac{[Fe^{2+}]}{[Fe^{3+}]} = \frac{0.1}{9.9}$$

$$E_{system} = E^\circ_{Fe^{2+}, Fe^{3+}} - \frac{0.05916}{n} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= 0.771 - \frac{0.05916}{1} \log \frac{0.1}{9.9}$$

$$= 0.889$$

d) At equivalence point :-

→ neither the analyte nor the titrant is in excess.

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→ All Fe^{2+} is oxidized by Ce^{4+} ions.

Any Fe^{2+} present is because of the reduction of Fe^{3+} ions by Ce^{3+}

$$\left.\begin{aligned}[Fe^{3+}] &= [Ce^{3+}] \\ [Fe^{2+}] &= [Ce^{4+}]\end{aligned}\right\} 1.$$

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

$$\left.\begin{aligned}E_{eq\,pt} &= E^{\circ}_{Fe^{2+},Fe^{3+}} - \frac{0.05916}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} \\ E_{eq.\,pt} &= E^{\circ}_{Ce^{3+},Ce^{4+}} - \frac{0.05916}{1}\log\frac{[Ce^{3+}]}{[Ce^{4+}]}\end{aligned}\right\} ②$$

$$2E_{eq.\,pt} = E^{\circ}_{Fe^{2+},Fe^{3+}} - \frac{0.05916}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} + E^{\circ}_{Ce^{3+},Ce^{4+}} - \frac{0.05916}{1}\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$= E^{\circ}_{Fe^{2+},Fe^{3+}} + E^{\circ}_{Ce^{3+},Ce^{4+}} - \frac{0.05916}{1}\left(\log\frac{[Fe^{2+}]}{[Fe^{3+}]} + \log\frac{[Ce^{3+}]}{(Ce^{4+}]}\right)$$

$$= E^{\circ}_{Fe^{2+},Fe^{3+}} + E^{\circ}_{Ce^{3+},Ce^{4+}} - \frac{0.05916}{1}\log\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}$$

$$= E^{\circ}_{Fe^{2+},Fe^{3+}} + E^{\circ}_{Ce^{3+},Ce^{4+}} - \frac{0.05916}{1}\log\frac{\cancel{[Ce^{4+}]}\cancel{[Ce^{3+}]}}{\cancel{[Ce^{3+}]}\cancel{[Ce^{4+}]}}$$

$$= E^{\circ}_{Fe^{2+},Fe^{3+}} + E^{\circ}_{Ce^{3+},Ce^{4+}}$$

$$= 0.771 + 1.44$$

$$E_{eq.\,pt} = 1.105$$

e) 10.1 cm^3 of 0.1 M Ce(IV).

$[Ce^{4+}] = \underline{0.1 \times 0.1}$)

$$[Ce^{4+}] = \frac{0.1 \times 0.1}{20.1}$$

$$[Ce^{3+}] = \frac{10 \times 0.1}{20.1}$$

$$\left.\right\} \frac{[Ce^{3+}]}{[Ce^{4+}]} = \frac{10}{0.1} = 100$$

$$E_{system} = E^{\circ}_{Ce^{3+},Ce^{4+}} - \frac{0.05916}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$= 1.44 - \frac{0.05916}{1} \log 100$$

$$= 1.322 \text{ V}$$

e) 11 cm^3 of 0.1M Ce (IV) is added:-

$$[Ce^{4+}] = \frac{1 \times 0.1}{21}$$

$$[Ce^{3+}] = \frac{10 \times 0.1}{21}$$

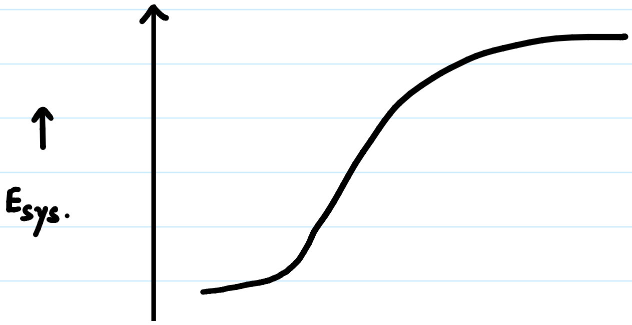
$$\left.\right\} \frac{[Ce^{3+}]}{[Ce^{4+}]} = \frac{10}{1} = 10$$

$$E_{system} = E^{\circ}_{Ce^{3+},Ce^{4+}} - \frac{0.05916}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$= 1.44 - \frac{0.05916}{1} \log \frac{10}{1}$$

$$= 1.44 - 0.05916$$

$$= 1.381 \text{ V}.$$



*** Titration of Fe (II) ions with $KMnO_4$:-**

→ The reaction is carried out in presence of acid.

$$5Fe^{2+} + MnO_4^- + 8H_3O^+ \rightleftharpoons 5Fe^{3+} + Mn^{2+} + 12H_2O.$$

H_3O^+ is required for the following reaction to go to completion.

$$MnO_4^- + 8H_3O^+ + 5e^- \rightleftharpoons Mn^{2+} + 12H_2O$$

* 10 cm³ of 0.1 M Fe (II) v/s 0.02 M $KMnO_4$ at pH = 1

$$Fe^{2+} + e^- \rightleftharpoons Fe^{3+}$$
$$MnO_4^- + 8H_3O^+ + \underline{5}e^- \rightleftharpoons Mn^{2+} + 12H_2O$$

← BEFORE EQUIVALENCE POINT, SYSTEM IS SAME AS Fe (II) v/s CE (IV) SYSTEM →

upto equivalence point, calculation is done same as for Fe(II) - Ce (IV) system.

$$E_{system} = E^\circ_{Fe^{2+},Fe^{3+}} - \frac{0.05916}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$ — (before equivalence point)

Multiply by 5

$$5E_{system} = 5E^\circ_{MnO_4^-,Mn^{2+}} - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H_3O^+]^8}$$ — (after equivalence point)

$6\ E_{system} = \ldots\ldots\ldots$

At equivalence point,

$$6E_{eq} = E^\circ_{Fe^{2+},Fe^{3+}} - \frac{0.05916}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} + 5E^\circ_{MnO_4^-,Mn^{2+}} - \frac{0.05916}{1} \log \frac{[Mn^{2+}]}{[MnO_4^-][H_3O^+]^8}$$

$$= E^\circ_{Fe^{2+},Fe^{3+}} - \frac{0.05916}{1} \log \frac{[Fe^{2+}][Mn^{2+}]}{[Fe^{3+}][MnO_4^-][H_3O^+]^8} + 5E^\circ_{MnO_4^-,Mn^{2+}}$$

$$= E_{Fe^{2+},Fe^{3+}} - \frac{0.05916}{1} \log \frac{[Fe^{2+}][Mn^{2+}]}{[Fe^{3+}][MnO_4^-][H_3O^+]^8} + 5E_{MnO_4^-,Mn^{2+}}$$

$$= E^\circ_{Fe^{2+},Fe^{3+}} + 5E^\circ_{MnO_4^-,Mn^{2+}} - \frac{0.05916}{1} \log \frac{[Fe^{2+}][Mn^{2+}]}{[Fe^{3+}][MnO_4^-][H_3O^+]}$$

$[Fe^{2+}] = 5[MnO_4^-]$
$[Fe^{3+}] = 5[Mn^{2+}]$

$$6E_{eq.} = E^\circ_{Fe^{2+},Fe^{3+}} + 5E^\circ_{MnO_4^-,Mn^{2+}} - \frac{0.05916}{5} \times \log \frac{1}{[H_3O^+]^8}$$

$pH = 1$
$\therefore [H^+] = 10^{-1}$

$$E_{eq.} = \frac{0.770 + 5 \times 1.51}{6} - \frac{0.05916}{6} \log \frac{1}{(10^{-1})^8}$$

$= 1.377.$

b) 10.1 cm^3 of 0.02 M $KMnO_4$.

$$[MnO_4^-] = \frac{0.1 \times 0.02}{20.1}$$

$$[Mn^{2+}] = \frac{10 \times 0.02}{20.1}$$

$$\frac{[Mn^{2+}]}{[MnO_4^-]} = \frac{10}{0.1} = 100$$

$$E_{sy} = E^\circ_{MnO_4^-,Mn^{2+}} - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H_3O^+]^8}$$

$E_{sys.} = 1.39$ V

c) 11 cm^3 of 0.02 M $KMnO_4$ is added :-

$$[MnO_4^-] = \frac{1 \times 0.02}{21}$$

$[Mn^{2+}] = 10 = 10$

$$\left.\begin{aligned}[MnO_4^-] &= \frac{1 \times 0.02}{21} \\ \\ [Mn^{2+}] &= \frac{10 \times 0.02}{21}\end{aligned}\right\} \frac{[Mn^{2+}]}{[MnO_4^-]} = \frac{10}{1} = 10$$

$$E_{sys} = E^\circ_{MnO_4^-, Mn^{2+}} - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H_3O^+]^8}$$

$$= 1.40\ V.$$

* Theory of Redox Indicator :-

→ Certain organic cmpds are capable of oxdⁿ- redⁿ reaction and their oxidized and reduced form have different colour.

$$In_{(ox)} + ne^- \rightleftharpoons In_{(red)}.$$

- rapid
- go to completion
- reversible

} abrupt change in the point otherwise slow & gradual changes will occur.

$$\boxed{E_{In}} = \underline{E^\circ_{In}} - \frac{0.05916}{n} \log \frac{[In_{(red)}]}{[In_{(oxd)}]}$$

E°_{In} is constant, E_{In} depends upon the ratio $\frac{[In_{(red)}]}{[In_{(ox)}]}$

colour of Reduced form will dominate $\Rightarrow \frac{In_{(ox)}}{In_{(red)}} \leq 10$ OR $\frac{In_{(red)}}{In_{(ox)}} \geq 10$

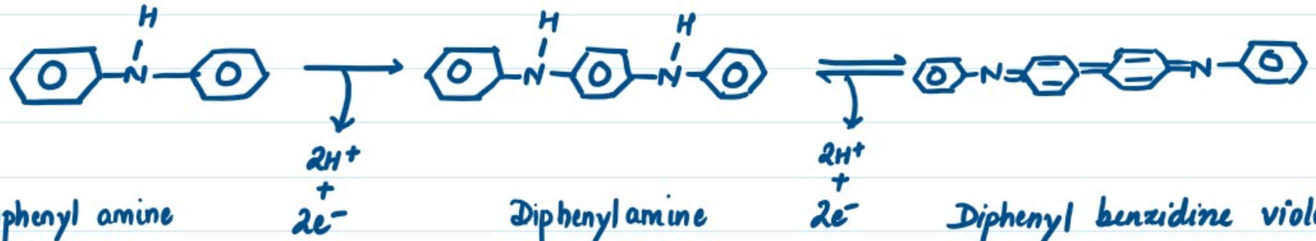
colour of reduced form will dominate → $\frac{In_{(ox)}}{In_{(red)}} \leq 10$ OR $\frac{In_{(red)}}{In_{(ox)}} \geq 10$

colour of oxidized form will dominate ⇒ $\frac{In_{(ox)}}{In_{(red)}} \geq 10$ OR $\frac{In_{(red)}}{In_{(ox)}} \leq 10$

OXIDⁿ - REDⁿ Indicators.

Indicator	Oxid. form	Red. form	Transition Potential.
① Nitro ferroin	Pale blue	Red	1.25 V
② Ferroin	Pale blue	Red	1.06 V
③ Diphenyl amine sulphonic acid	Purple	Colourless	0.84 V
④ Diphenyl amine	Violet	Colourless	0.76 V
⑤ Methylene blue	Colourless	Blue	0.53 V
⑥ Indigo Tetrasulfonate	Blue	Colourless	0.36 V

1) Diphenyl amine.
— solubility is low → Diphenyl amine sulphonic acid (0.85 V)



Diphenyl amine (Colourless)

Diphenyl amine benzidine (Colourless)

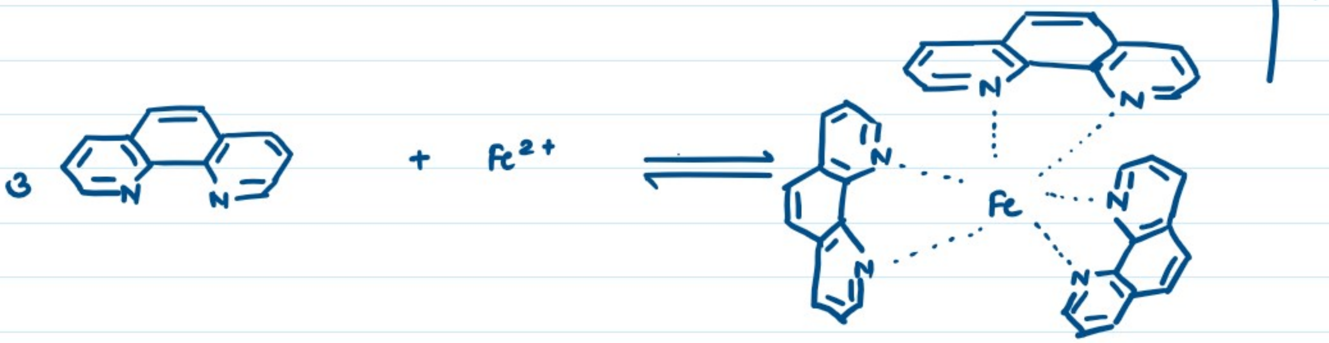
Diphenyl benzidine violet. (Violet)

eg. Fe(II) v/s $K_2Cr_2O_7$ Eq pt = 1.14 V.

→ indicator → phosphoric acid.

→ PO_4^{3-} ion of H_3PO_4 forms phosphate complex and thus decreases Fe^{2+}, Fe^{3+} potential.

2) Ferroin = Iron Orthophenanthroline



$E^{\circ}_{Red} = 1.06\ V$

Thank - You!