

③ Oxidation / Reduction Titration

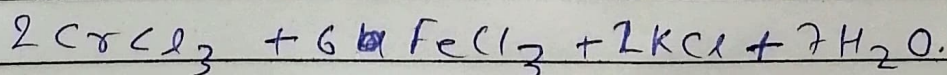
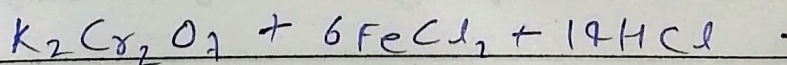
- ① Oxidation
- ② Reduction
- ③ Oxidation state
- ④ Oxidation number
- ⑤ Redox Reaction with examples.
- ⑥ Strength of oxidising and reducing agent.

⑦ Theory of redox indicators or redox titrations.

Every titration doesn't require an indicator. In some cases either the reactants or the products are strongly coloured and can serve as the indicator.

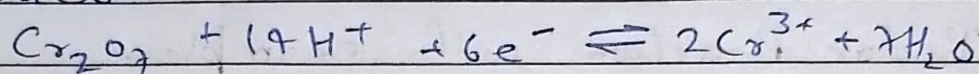
For example
~~eg~~ An oxidation reduction titration using potassium permanganate (Pink/purple) as the titrant does not require any indicator.

Diphenyl amine is used as redox indicator in dichromate titration for determining Fe^{++} from FeCl_2 .

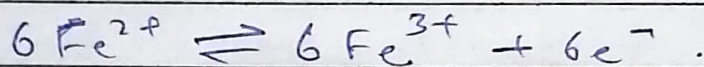


In acidic solⁿ the reduction of $K_2Cr_2O_7$ may be represented as

Reduction



Oxidation.



When all the Fe^{2+} ions are oxidised to Fe^{3+} ions excess of dichromate ions oxidized diphenyl amine to diphenyl benzidine

In redox titration a sharp colour change in indicators occurs only in its E_0 (Standard Electrode potential) lies between standard potential of oxidation reduction when titrated against each other.

$0.76 \rightarrow E^0 (v)$ of diphenylamine indicator

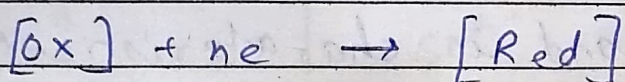
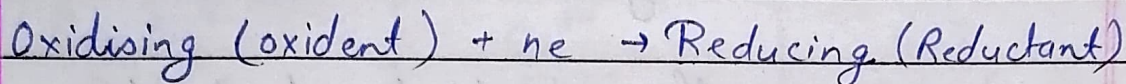
$0.77 \rightarrow E^0 (v)$ of ferrous ferric system

In

In order to overcome the variation of ± 0.01 phosphoric acid is added in the solⁿ in order to take sharp colour change at ^{the} end point.

Redox Potential :

Strength of an oxidising agent or reducing agent is ~~expressed~~ expressed in terms of normal or standard potential.



Redox titration :

It is based on the redox reaction (oxidation reduction) between analyte and titrate. In oxidation reduction titration method a reducing substance is titrated with a std solⁿ of an oxidising agent or an oxidising substance is titrated with a std. solⁿ of a reducing agent.

Such a system the nerst equation takes place that is -

$$E = E^{\circ} + \frac{2.303RT}{nF} \times \log_{10} \frac{[\text{Ox}]}{[\text{Red}]}$$

Where,

E is the formal potential at the specify concⁿ, n is no. of electron involved in the half reaction.,

R is gas constant that is
 8.314 J/mol/K , ϕ

T is the absolute temp,

F is Faraday constant i.e. 96500

and E° is the standard electrode potential and is characteristic of a particular system

$\rightarrow$ At 25°C

$$\boxed{\frac{2.303 RT}{F} = 0.05915}$$

Then eqⁿ (i) will be

$$E = E^\circ + \frac{0.05915}{n} \log_{10} \frac{[\text{ox}]}{[\text{Red}]}$$

The solution potential can be calculated if we know the conc.ⁿ of the two forms $[\text{ox}]$ (oxidising agent) and $[\text{Red}]$ (Reducing agent).

Also knowing the chemical reaction involved and the potential of the solution, we can use nerst equation to evaluate the relative conc. of oxidised and reduced forms. some of

the redox system with their std. reduction potential are below.

Oxidized form	Reduced form	E° volt.
MnO_4^-	Mn^{2+}	1.51
$Cr_2O_7^{2-}$	Cr^{3+}	1.33
Fe^{3+}	Fe^{2+}	0.76
Sn^{4+}	Sn^{2+}	0.15

★ Redox indicator:-

In the redox titration we need a chemical species that can change colour in potential range corresponding to the sharp change at the end point.

A chemical substance which changes colour when the potential of the solution reaches a definite value is termed oxidation-reduction or redox indicator. It is necessary while choosing a redox indicator for particular titration to ensure that its redox potential lies within that of the system.

A redox indicator may be defined as a substance whose oxidised form is of different colour from that of its reduced form. The oxidation and reduction of the indicator is readily reversible.

The indicators which is used in redox titration are of three types.

i) Self indicator:-

In permanganetic titration potassium (KMnO_4) change colour at the end point is called self indicator.

ii) External Indicator:-

These indicator are not added internally to the reaction medium but are used externally in the form of small droplets on a white tile. i.e. Potassium ferriocyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) is used as an external indicator in the chromatometry. However, the method of using external indicator has become absolute as it introduces errors in quantitative volumetric analysis.

iii) Internal Indicator:-

These are the substances which are added in the flask. In case of chromatometry the indicators such as 1% diphenyl amine is added in the reaction mixture such indicator are called internal indicator.

Types of redox indicators:-

i) Permagnet titration:

A large no. of reducing agent may be determined directly by titration with standard potassium permagnet.

Imp.

Oxidation Reduction Curve

In acid-base titration curves are denoted plotted in terms of pH or pOH vs the concentration of standard by ~~and~~ in redox titration the titration curves are plotted in terms of cell potential vs the percent titration of the standard. For each redox titration there are 5 significant reasons:

(i) The start zero percent titⁿ

(ii)

it is the point at which titration starts.

(iii) Buffering reason:-

Greater than 0% and less than equivalence point. It is a region where the reducing agent takes small amount of time to lose all the electrons and substituting the electrons are gained by an oxidizing agent to reach the equivalence point.

(iii) The equivalence point

It is the region where the percentage of oxidized and reduced form are equivalent to each other at this point there is a sharp increase in curve till the end point is reached.

(iv) Inflection point

A point on a curve at which tangent crosses the curve itself

A point on a curve at which a curvature changes sign.

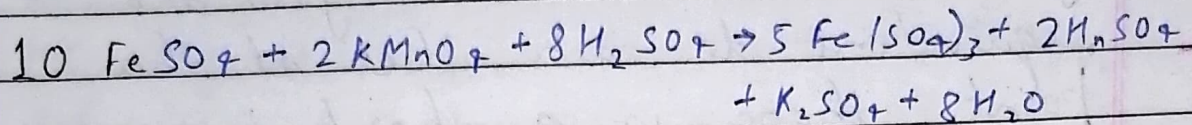
The curve changes from being concave upward (positive curvature) to concave downwards (negative curvature)

(v) Over titration

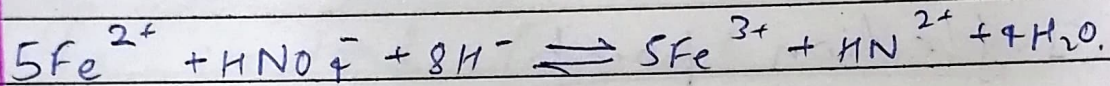
It is the region ~~at~~ showing the constant curve or potential and colour showing by these indicators at a significant region.

Equivalence weight of KMnO_4 .

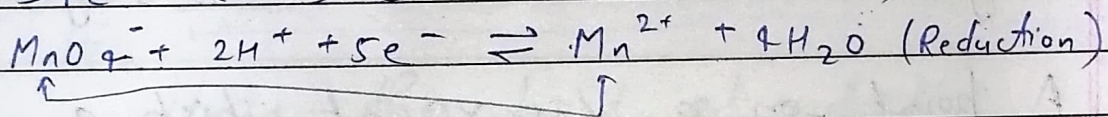
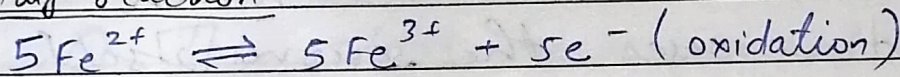
① In acidic medium (H_2SO_4)



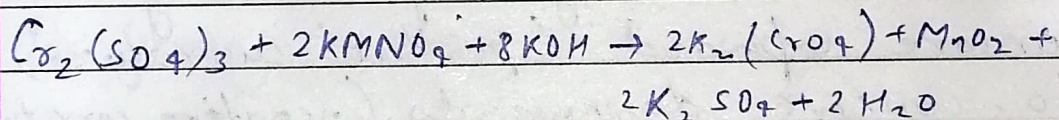
Ionic Form:



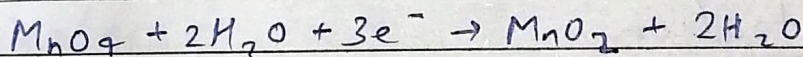
Half reaction



② In alkaline ~~form~~ medium (KOH)



Ionic Form:



$$\text{Equivalent weight} = \frac{158.03}{3} = 52.68$$

* Preparation of 0.1 KMnO_4 .

Preparation of 0.1 KMnO₄

$$Eqwt = \text{Mol. wt} / \text{gain of electrons} = \frac{158.03}{5} = 31.61g.$$

Weight accurately 31.61 g of KMnO₄ dissolve it in 1000 ml of distilled water to give 1 N solution and 3.161 g of KMnO₄ in 1000 ml of distilled water to give 0.1 KMnO₄.

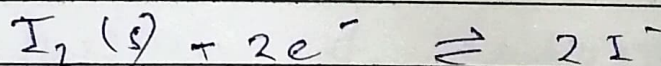
Standardization of ~~oxalic acid~~ ^{0.1} KMnO₄ by ~~oxalic acid / sodium oxalate~~ sodium oxalate.

V.V.T.
①

Iodometric and Iodimetric titration.

Iodine is a mild oxidizing agent.

Iodine is reduced according to ^{the} half reaction as



Iodine

~~The~~ A solution of iodine is aqueous iodide and has an intense yellow colour to brown colour. One drop of 0.05 M iodine solution imparts a perceptible yellow to 100 ml water.

In colourless solⁿ iodine can serve its own indicator. The taste is made much more sensitive by causing a solution of starch as indicator.

Starch reacts with iodine in the presence of iodide to form an intensely blue colored complex which is visible at very low conc of iodine.

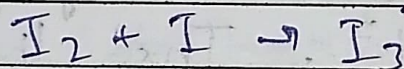
Starch should be added near the equivalence point in iodometric titⁿ because it gives water insoluble complex with iodine and indicates release of iodine from KI (Potassium iodide) (reducing agent).

Direct iodometric titⁿ turned iodimetric refers. the first titⁿ with a std solⁿ of iodine.

In direct iodometric titⁿ turned iodometry deals with the titⁿ of iodine liberated in conical flask even

① Iodimetry:

Std solⁿ of I_2 may be prep^d. from accurately ~~meas^o~~ weigh the pure reagent. It is simpler to make up the solution from a reagent grade product ~~to standardize~~ and then to standardize it. I_2 is slightly soluble in H_2O , but it forms a soluble triiodide ion in solⁿ of iodide.



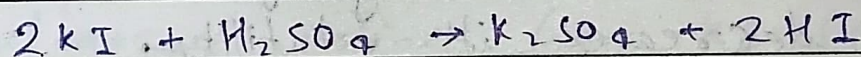
The Use of Iodide in solution both increase the solubility of the iodine and decreases its volatility. Thus controlling to the stability of the iodide solution. The arsenic trioxide is oxidized by iodine according.

The position of equilibrium depends upon the pH.

(ii) Iodometric:

The formation of iodine takes place as a result of hydrogen iodide with an oxidizing agent. The HI is ~~not~~ ^{liberated} directly in the reaction flask by the action of dilute HCl or H_2SO_4 on the solⁿ of potassium Iodide.

Free iodine is liberated as a result of oxidation of KI in acidic solⁿ. The liberated iodine is treated with std solⁿ of sodium thio sulphate.



Potassium
iodide

Hydrogen
iodide.

Starch mucilage acts as an indicator which gives blue color with free iodine.



Titration of ~~ferrous~~ ceric ammonium sulphate the titration involves the use ceric salt which is a powerful oxidizing agent. Ceric salt as intense yellow color. The oxidizing power of ceric salts depends upon the conc. and the type of acid used in the assay.

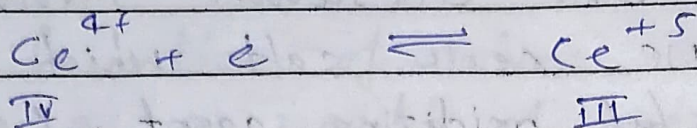
eg. $\text{Ce}^{+4}(\text{IV})$ in HNO_3 and HClO_4 .

The fluorides and phosphates have tendency to interfere with concerned ions because they form precipitate with them as ceric fluoride and ceric phosphate.

The end point of cerimetric titration is indicated by using redox indicator as ferroin, diphenyl sulphonate sulfonate and N-phenylanthroallic acid.

Sulphuric acid solution of ceric sulphate is stable even at boiling point but HCl acid solution is unstable due to its reduction resulting in the liberation of 3 chlorine.

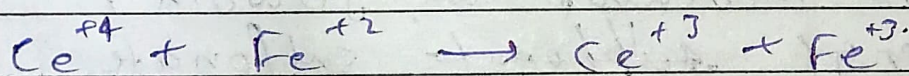
Preparation of 0.1N ^{Cerrie} ~~Ferrie~~ sulfate



$$\text{Eq. wt.} = \frac{333.25}{1} = 333.25$$

Weight accurately 333.25 gm of cerrie sulfate and dissolve it in 1000 ml of ^{dis.} water to give 1N solⁿ and 33.225 gm of cerrie sulfate in 1000 ml of distilled water to give 0.1 N cerrie sulfate solⁿ.

FeSO₄ the acidic constituent of Mohr's salt FeSO₄ (NH₄)₂SO₄ · 6H₂O reduced Ce(IV) to Ce(III) itself getting oxidised to FeSO₄.



Procedure :

Pipette out 25 ml ferrous ammonium sulphate solⁿ into a conical flask.

Add 25 ml H₂SO₄ and two drops of ferrous indicator.

Titrate it against ferrous ceric sulphate solⁿ. till the orange change to blue.