

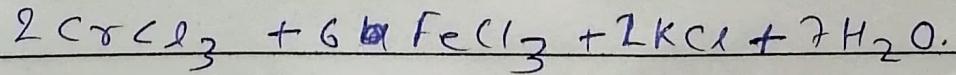
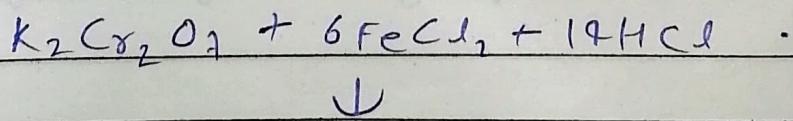
(3) Oxidation / Reduction Titration

- 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.

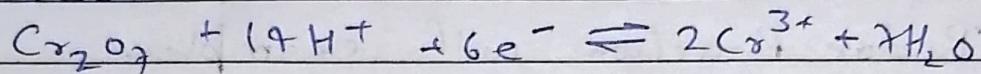
For example
 e.g. An oxidation reduction titration using potassium permanganate (Pink/purple) as the titrant does not require any indicator.

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

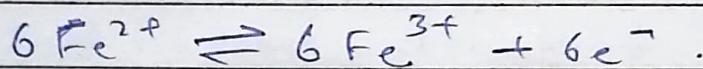


In acidic sol' the reduction of $K_2Cr_2O_7$ may be represented as

Reduction



Oxidation.



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

In redox titration a sharp colour change in indicator occurs only if its E° (Standard electrode potential) lies between standard potential of oxidation reduction when titrated against each other.

$0.76 \rightarrow E^\circ$ (v) of diphenyl amine indicator

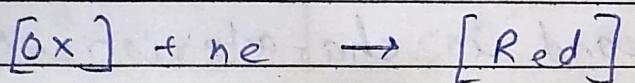
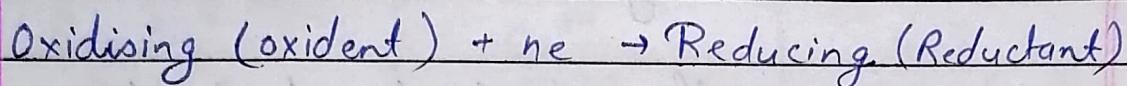
$0.77 \rightarrow E^\circ$ (v) of ferric ferrous system

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 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 -

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

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 , \oplus

T is the absolute temp,

F is Faraday constant ie. 96500

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

→ At 25°C

$$\left[\frac{2.303 RT}{F} = 0.05915 \right]$$

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 concⁿ 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 next 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 permanganate titration potassium (KMnO_4) changes 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 ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) 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% diphenylamine is added in the reaction mixture such indicator are called internal indicator.

Types of redox indicators :-

1) 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 often plotted in terms of pH or pOH vs the concentration of standard by 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:

① The start zero percent tit.

(i)

it is the point at which titration starts

② Buffering reason:-

Greater than 0.1 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

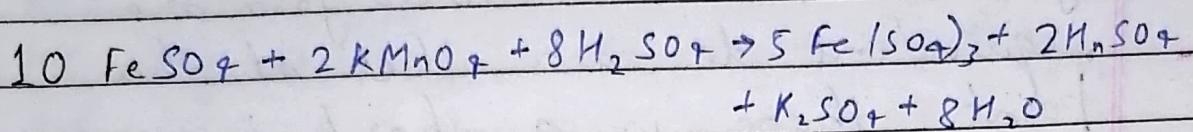
A point on a curve at which tangent crosses the curve itself

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

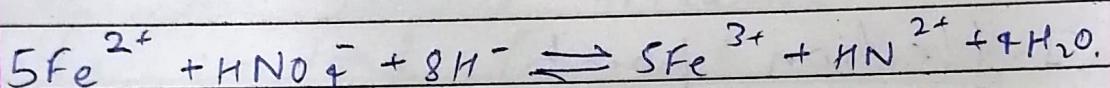
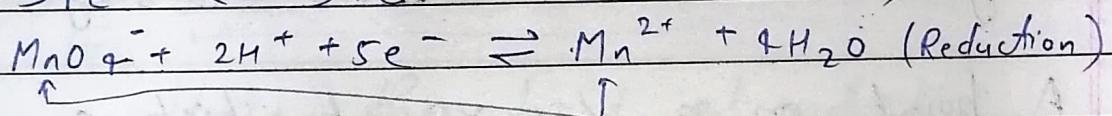
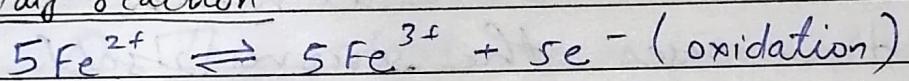
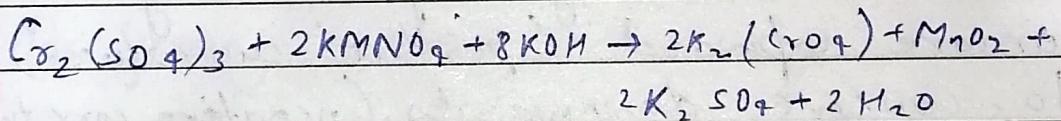
The curve changes from being concave upward (positive curvature) to concave downwards (negative curvature)

v) Overtitration

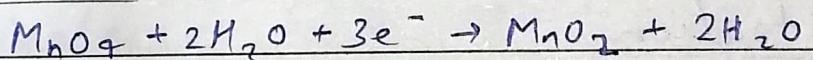
It is the region showing the constant curve or potential and colour showing by these indications at a significant region.

Equivalence weight of KMnO_4 :① In acidic medium (H_2SO_4)

Ionic Form:

Half reaction② In alkaline medium (KOH)

Ionic Form:



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

Preparation of 0.1 KMnO_4

Preparation of 0.1 KMnO₄

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

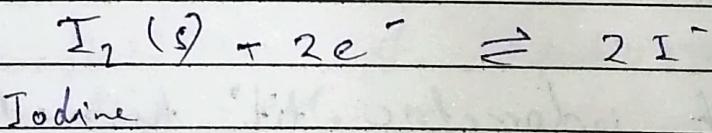
Weight accurately 31.61 g of KMnO₄
dissolve it in 1000 ml of distilled water.
to give 1 N solution and 3.161 g of
KMnO₄ in 1000 ml of distilled water
to give 0.1 KMnO₄.

Standardization of oxalic acid by 0.1 KMnO₄
by oxalic acid / sodium oxalate sodium oxalate.

① Iodometric and Iodimetric titration.

Iodine is a mild oxidizing agent.

Iodine is reduced according to half reaction as



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 sol' 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.

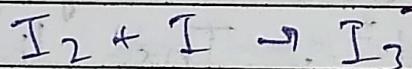
Starch should be added near the equivalence point in iodometric titⁿ because it gives water insoluble complex with iodine and indicates release of iodine from KI (potassium iodide) (reducing agent).

Direct iodometric titⁿ turned iodometric repress. the first titⁿ with a std sol' of iodine.

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

① Iodimetry:

Std solⁿ of I_2 may be prep^{ed} from accurately ~~meas~~^{weigh} the pure reagent. It is simpler to make up the solution from a reagent grade product to standardize and then do 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.

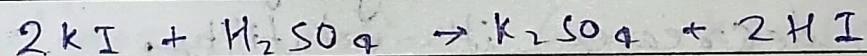
Thus controlling to the stability of the iodide solution. The arsenic trioxide is oxidized by iodine according.

The position of equilibrium depends upon the pH.

Iodometric:

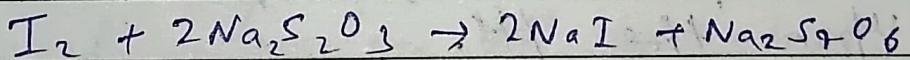
The formation of iodine takes place as a result of hydrogen iodide with an oxidizing agent. The HI is often obtained directly in the reaction flask by the action of dilute HCl or H_2SO_4 on the soln. of potassium Iodide.

Free iodine is liberated as a result of oxidation of KI in acidic sol⁻. The liberated iodine is treated with std sol^m of sodium thiosulphate.



Potassium iodide. At the bottom of the flask Hydrogen iodide.

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



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

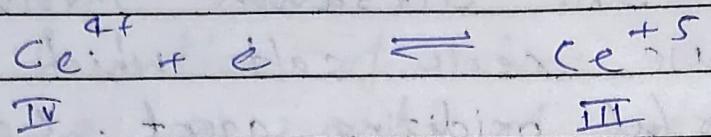
e.g. $\text{Ce}^{+4}(\text{m})$ in HNO_3 and HClO_4 .

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-phenylanthraffic 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 Ferric Ceric sulfate



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

Weight accurately 333.25 gm of cerriic sulfate and dissolve it in 1000 ml of ^{dis.} water to give 1 N solⁿ and 33.325 gm of cerriic sulfate in 100 ml of distilled water to give 0.1 N cerriic sulfate solⁿ.

FeSO_4 the acidic constituent of Mohr's salt $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ reduced $\text{Ce}(\text{IV})$ to $\text{Ce}(\text{III})$ itself getting oxidised to FeSO_4 .



Procedure

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

Add 25 ml H_2SO_4 and two drops of ferrous indicator.

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