Pharmaceutical Analysis.

(3) Oxidation / Reduction Titration

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1. Oxidation
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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 colored 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 $FeCl_2$.

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl \rightarrow 2CrCl_3 + 6FeCl_3 + 2KCl + 7H_2O.$$

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

Reduction

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

Oxidation.

$$6Fe^{2+} \rightleftharpoons 6Fe^{3+} + 6e^-.$$

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

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

0.76 → E° (v) of diphenyl amine indicator

0.77 → E° (v) of ferrous ferric system

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

Redox Potential :

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

Oxidising (oxident) + ne → Reducing (Reductant)

$$[Ox] + ne \longrightarrow [Red]$$

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 sol^n of an oxidising agent or an oxidising substance is titrated with a std. sol^n 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 conc^n., n is no. of electron involved in the half reaction.,

R is gas constant that is 8.314 J/mol/k, ✓

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

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

Then eqⁿ (i) will be

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

The solution potential can be calculated if we know the concⁿ of the two forms [ox] (oxidising agent) and [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+}	0.776
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 permagnetic 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 ferricyanide ($K_3Fe(CN)_6$) 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 chromatometoy the indicators such as 1% diphenyl amine 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.

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Oxidation Reduction Curve

In acid-base titration curves are ~~deno~~ plotted in terms of pH or poh vs the concentration of standard by ~~red~~ 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:

① The start redo percent titr

~~(ii)~~ :

it is the point at which titration starts.

② 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 electoons are gained by an oxidizing agent to reach the equivalance point.

(iii) The equivalance 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 showing the constant curve or potential and colour showing by there indicators at a significant region.

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Equivalence weight of $KMnO_4$:

① In acidic medium (H_2SO_4)

$$10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 \rightarrow 5\,Fe_2(SO_4)_3 + 2\,MnSO_4 + K_2SO_4 + 8\,H_2O$$

Ionic Form :

$$5Fe^{2+} + HNO_4^- + 8H^- \rightleftharpoons 5Fe^{3+} + HN^{2+} + 4H_2O.$$

Half reaction

$$5Fe^{2+} \rightleftharpoons 5Fe^{3+} + 5e^- \quad (\text{oxidation})$$

$$MnO_4^- + 2H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \quad (\text{Reduction})$$

② In alkanine ~~Form~~ medium [KOH]

$$Cr_2(SO_4)_3 + 2\,KMNO_4 + 8\,KOH \rightarrow 2K_2(CrO_4) + MnO_2 + 2K_2SO_4 + 2\,H_2O$$

Ionic Form:

$$MnO_4 + 2H_2O + 3e^- \rightarrow MnO_2 + 2H_2O$$

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

★ Preparation of 0.1 $KMnO_4$.

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Preparation of 0.1 $KMnO_4$

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

Weight accurately 31.61 g of $KMnO_4$ dissolve it in 1000 ml of distilled water. to give .1 N solution and 3.161 g of $KMnO_4$ in 1000 ml of distilled water to give 0.1 $KMnO_4$

Standardization of ~~oxalic acid by~~ 0.1 $KMnO_4$ by oxalic acid / ~~Sodium oxalate~~ sodium oxalate.

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(1) Iodometric and Iodimetric titration.

Iodine is a mild oxidizing agent. Iodine is reduced according to the half reaction as

$$I_2(s) + 2e^- \rightleftharpoons 2I^-$$

Iodine

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^n 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 intensly blue colored complex which is visible at very low conc of iodine.

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

Direct iodometric titr turned iodimetric refers. the first titr with a std sol^n of iodine.

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

① Iodimetry:

Std sol^n of I_2 may be prep^{od} from accurately ~~Mea~~ to weigh the pure reagent. It is simpler to make up the solution from a the 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 sol^n of iodide.

$$I_2 + I^- \rightarrow I_3^-$$

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.

(11) Iodometric:

The formation of iodine takes place as a result of hydrogen iodide with an oxidizing agent. The HI is ~~Dfo~~ obtained directly in the reaction flask by the action of dilute HCl or H_2SO_4 on the sol^{n} of potassium Iodide.

Free iodine is librated as a result of oxidation of KI in acidic sol^{n}. The liberated iodine is treated with std sol^{n} of sodium thiosulphate.

$$2KI + H_2SO_4 \rightarrow K_2SO_4 + 2HI$$

Potassium iodide — Hydrogen iodide.

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

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

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Titration of ~~ferric~~ 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. Ce^{+4} (IV) in HNO_3 and $HClO_4$.

The flourides and phosphates have tendency to interfare with concerned ions because they form precipitate with them as cerric flouride and ceric phosphate.

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

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Preparation of 0.1N ~~Ferric~~ Cerric sulfate

$$Ce^{+4} + e \rightleftharpoons Ce^{+3}$$

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

Weight accurately 333.25 gm of cerric sulfate and dissolve it in 1000 ml of dis. water to give 1N sol^n and 33.325 gm of Cerric sulfate in 1000 ml of distilled water to give 0.1 N cerric sulfate sol^n.

$FeSO_4$ the acidic constituent of Mohr's salt $FeSO_4(NH_4)SO_4.6H_2O$ reduced Ce(IV) to Ce(III) itself getting oxidised to $FeSO_4$.

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

Procedure:

Pippete out 25 ml ferrous ammonium sulphate sol^n into a conical flask.

Add 25 ml H_2SO_4 and two drops of ferroous indicator.

Titrate it against ~~ferric~~ cerric sulphate sol^n. till the orange change to blue.