Redox Titration

UNIT-IV

Redox titrations

(a) Concepts of oxidation and reduction

(b) Types of redox titrations (Principles and applications)

Cerimetry, Iodimetry, Iodometry, Bromatometry, Dichrometry, Titration with potassium iodate

Redox Titration

Oxidation :

1. Loss of electrons
2. Loss of hydrogen
3. Gain of oxygen
4. Increase the valancy

Reduction:

1. Gain of electrons
2. Gain of hydrogen
3. Loss of oxygen
4. Decrease the valancy

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Concept of oxidation and reduction

Oxidation :- It may be defined as a loss of electrons to an oxidizing agent (that undergoes reduction) to yield more positive or higher oxidation state. Examples:

1. Fe^{+2} (ferrous ion) into Fe^{+3} (ferric ion)
2. Cu (copper) into Cu^{+2} (cupric ion)
3. Cl^- (chloride) into Cl_2 (chlorine)

In all these 3 instances the valence of the atoms are enhanced (+2 to +3), (0 to +2) and (-1 to 0).

Reduction:- It may be defined as gain of electrons from reducing agent (that undergoes oxidation) to give more negative or lower oxidation state.

Example: **Ce^{+4} (cerric form) + e^- $\longrightarrow$ Ce^{+3} (cerrous form)**

Oxidising Agent

- Those molecule which reduce itself but oxidize other is called oxidizing agent. It is also called as oxidant.

Example :-

1. Potassium permanganate ($KMnO_4$)
2. Potassium dichromate ($K_2Cr_2O_7$)
3. Potassium bromate ($KBrO_3$)
4. Potassium iodate (KIO_3)
5. Hydrogen peroxide (H_2O_2)

Reducing Agent

- Those molecule which oxidize itself but reduce other is called reducing agent. It is also called as Reductant.

Example :-

1. Metals
2. Fe^{2+} salts
3. Iodide ion (I^-)
4. Hydrogen peroxide (H_2O_2)

Note :- Hydrogen peroxide acts as both a oxidizing agent and reducing agent.

The titration based on oxidation reduction reaction are called redox titration. In there titrations, an oxidising agent is titrated with a reducing agent.

E.g.:- $MnO^{4-} + 5Fe^{+2} + 8H^{+} \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$

(O.A) **(R.A)**

In this reaction MnO^{4-} is oxidising agent and Fe^{+2} is reducing agent. So titration of MnO^{4-} with Fe^{+2} is a redox titration.

 # Equivalent weight of oxidizing or reducing agent = $\dfrac{\text{Molecular weight}}{\text{Change in oxidizing number}}$

E.g. :- Equivalent weight of KMnO4 = 158/ 5 = 31.6

Equivalent weight of oxidising agent and reducing agent may be different for different reaction.

Titration

Titrations

- known → Standard
- unknown → test/sample

There are mainly 5 types of titrations. They are listed as following:-

1. Acid base titration
2. Redox titration
3. Precipitation titration
4. Complexometric titration
5. Gravimetric titration

Redox Titration

- The titration in which we determine the concentration of unknown reducing and oxidizing agent by using known oxidizing and reducing agent is called Redox Titration.
- Redox titration is also known as oxidation-reduction titration.

Types of Redox Titration

1. Cerimetry
2. Iodimetry
3. Iodometry
4. Bromatometry
5. Dichrometry
6. Titrations with potassium iodate (KIO_3)

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1. Cerimetry

- There are titrations involving cerric sulphate (Ce+4) as an oxidising agent.
- Cerric sulphate is a powerful oxidising agent and possess bright yellow colour, however during titration Cerric sulphate undergoes reduction to Cerrous sulphate (Ce+3) which is colourless in nature.

$$Ce^{+4} + 1e^{-} \longrightarrow Ce^{+3}$$

Principle

- Analysis involving the use of cerium solutions are known as cerimetry.
- The element cerium exists in two oxidation state, they are +3 (cerrous) and +4 (cerric).

In the +4 state it is a powerful oxidizing agent.

$$Ce^{+4} + 1e^{-} \longrightarrow Ce^{+3}$$

- The standard reduction potential (E^{o}) in 1M solutions of common acid of Ce^{4+} salts vary from 1.61-1.87 volts.
- It used in solutions of high acidity, since in alkaline solutions cerium hydroxide precipitation occurs solutions of Ce4+ are unstable as,

$$2Ce^{4+} + 2Cl^{-} \longrightarrow 2Ce^{3+} + Cl_2$$

- Ammonium cerric sulphate serves as a powerful oxidizing agent in acidic medium.
- On reduction, the resulting cerrous salt obtained is colourless in appearance and therefore strong solutions may be considered as self indicating.
- In general practice, 0.05N solutions are employed for estimations.

Applications:

1. Determination of % purity of FeSO4

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

2. Determination of total iron content (% iron)
3. Determination of the % purity of NaNO2 (sodium nitrite)

$$2Ce^{4+} + NO_2^- + H_2O \longrightarrow 2Ce^{3+} + NO_3^- + 2H^+$$

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Iodine Titrations

Iodimetry

Direct titration with I_2

Iodine acts as an mild oxidizing agent

Iodometry

Indirect titration with I_2

Iodide acts as reducing agent

Freshy prepared starch solution is used as indicator

Iodine Titration

Iodine is an oxidizing agent.

Titration, which involve iodine is known as iodine titration.

Iodine can be used in oxidation reduction in two ways-

Iodimetry :- In this method a standard solution of Iodine is directly used.

Iodometry :- In this method iodine solution is not directly used as an oxidizing agent but iodine is liberated during chemical reaction.

Principle :

Iodine is a weak oxidant and it is used for the redox titrations of easily oxidized substances.

Iodine is reduce by the reductants like stannous chloride, sodium thiosulphate and arsenious oxide.

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- In iodimetry know volume of standard iodine solution is titrated directly with the reductant which is to be determined using starch as an indicator. End point is detected by change of blue to colourless.

- In all iodimetric titration iodine is reduced to form iodine ion

$$I_2 + 2C \longrightarrow 2I^-$$

$$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$$

$$S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I$$

$$H_3ASO_3 + I_2 + H_2O \longrightarrow H_3ASO_4 + 2H^+$$

Applications

2. Iodimetry

Determination of sulphur dioxide (SO2) in wine.

$$SO_2 + I_2 + H_2O \longrightarrow 2I^- + SO_3 + 2H^+$$

3. Iodometry

Determination of concentration of hydroperoxide in any given lipid matrix (e.g. oils, facts for human consumption)

$$RCOOH + 2H^+ + 2I^- \longrightarrow ROH + I_2 + H_2O$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Nerns't Equation

Equation showing relation between potential of a non standard electrochemical cell and concentration of solution is known as Nerns't equation.

The *Nernst Equation* is derived from the Gibbs free energy **under standard conditions**.

$$E = E^o - 2.303\,\frac{RT}{nF}\,\log_{10}Q \text{------------------------- (1)}$$

At standard temperature $T = 298\ K$, the $2.303\,\frac{RT}{F}$ term equals $0.0592\ V$ and Equation (1) can be rewritten:

$$E = E^o - \frac{0.0592}{n}\,\log_{10}Q \text{ ----------------------- (1.8)}$$

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Substituting Q (reaction quotient) = $\frac{[Ox]}{[Red]}$ in eqution 1.8 we get **Nerns't equation**

$$E = E^o - \frac{0.0592}{n} \log_{10} \frac{[Ox]}{[Red]}$$

Where,

E^o – Standard electrode (or reduction) potential

E – Potential observed at absolute temperature (T)

R – Gas constant = 8.314 joules/deg/mol-1

F – Faraday's constant = 96500 coulumbs

T – Absolute temperature (T) = 298°K (25°C)

n – Number of electrons gained by an oxidant in being converted to reducing agent

4. Bromatometry

- The specific titrations with potassium bromate is referred to as Bromatometry.
- It may be exploited as an effective and useful oxidizing agent in the qualitative determination (assay) of pharmaceutical substances like mephenesin, phenol sodium and salicylate.
- It can also be used for the analysis of organoarsenicals like carbasone ($C_7H_9AsN_2O_4$).

Principle:

The fundamental underlying principle of 'Bromatometry' exclusively and predominanty depends upon the formation of iodine monobromide [IBr] in relatively higher actual strength of HCl solution.

5. Dichrometry

- These are titrations in which, potassium dichromate is used as in oxidising agent in acidic medium.

Potassium Dichromate :- used a titrant

- It is primary standard
- Purity & stability best
- Less oxidising agent as compared to $KMnO_4$

The half reaction for the dichromate system is:

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

The most important application of dichromate is in its reaction with iron (II) in which it is often preferred to permanganate.

The relevant half reaction is:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

and the total reaction is:

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

Application

1. Determination of Fe
2. Used for determination of ferrous salt
3. Determination of Cr in Cr-3 salt
4. Chemical oxygen demand can be determined by Dichrometry

6. Permanganometry

- Potassium permanganate, $KMnO_4$, is probably the most widely used of all volumetric oxidizing agents.
- It is a powerful oxidant and readily available at modest cost.
- The intense color of the permanganate ion, MnO_4^-, is sufficient to detect the end point in most titrations.

$$MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$$

$$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2(s) + 2H_2O$$

$$MnO_4^- + e^- \leftrightarrow MnO_4^{2-}$$

Preparation of Potassium Permanganate (0.02M)

Molecular formula: $KMnO_4$

Molecular weight: 158.03

Preparation:

Dissolve 3.2g of potassium permanganate in 1000ml of water, heat on a water bath for 1hour, allow to stand for 2 days and filter through glass wool. Store the solution in dark place, protected from light.

Standardization:

1. Pipette out 25ml prepared 0.1N oxalic acid solution, add 5ml of concentrated sulphuric acid along the side of the flask, swirl the contents carefully and warm upto 70°C.
2. Titrate the warmed solution against the potassium permanganate solution from the burette, till the pink colour persists for about 30 seconds.
3. Repeat the experiment three or more times until two consecutive results are same or precise and tabulate the results.
4. Take the precise readings for calculation of normality.

Reaction involved:

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \rightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

Titration with Potassium Iodide

Theory:

Potassium bromate ($KBrO_3$) may be assayed by the addition of potassium iodide (KI) and dilute HCl and the chemical reaction involved may be expressed as given below:

$$KBrO_3 + HI \rightarrow HIO_3 + KBr$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Preparation:

Weigh accurately about 3.34g previously dried for 1-2 hours at 120°C and cooled pure potassium bromate and dissolved sufficient amount of water and finally make the solution to 1000ml with water.

Titration with Potassium Iodide

Standardization:

1. Standardization of $KBrO_3$ solution (say 0.1N $KBrO_3$) may be accomplished by taking an aliquot of the $KBrO_3$ solution, adding 3g of KI and 3ml of conc. HCl.
2. The contents are taken in iodine flask and shaken well and allowed to stand for 5-10 minutes so as to complete the liberation of I_2 from the reaction mixture.
3. The liberated I_2 is duly titrated with previously standardized 0.1N $Na_2S_2O_3$ solution using freshly prepared starch solution as an indicator towards the end point.