



Amar Shaheed Baba Ajit Singh Jujhar Singh Memorial
COLLEGE OF PHARMACY
(An Autonomous College)
BELA (Ropar) Punjab



Program	:	B. Pharmacy
Semester	:	1 st
Subject /Course	:	Pharmaceutical Analysis-I/ B. Pharmacy
Subject/Course ID	:	Pharmaceutical Analysis- I/ BP102T
Module No.	:	04
Module Title	:	Redox Titration
Course coordinator	:	Mrs. Manpreet Kaur
Mobile No.	:	9592378971
Email id	:	manipreet663@gmail.com

Learning Outcome of Module-4

LO	Learning Outcome (LO)	CourseOutcome Code
1.	To gain knowledge about concept of oxidation and reduction.	BP102.4
2.	To understand techniques of oxidation and reduction titrations.	BP102.4

Module Content Table

No.	Topic
1.	Concepts of oxidation and reduction.
2.	Types of redox titrations (Principles and applications). Cerimetry, Iodimetry, Iodometry, Bromatometry, Dichrometry, Titration with potassium Iodate.

REDOX TITRATION

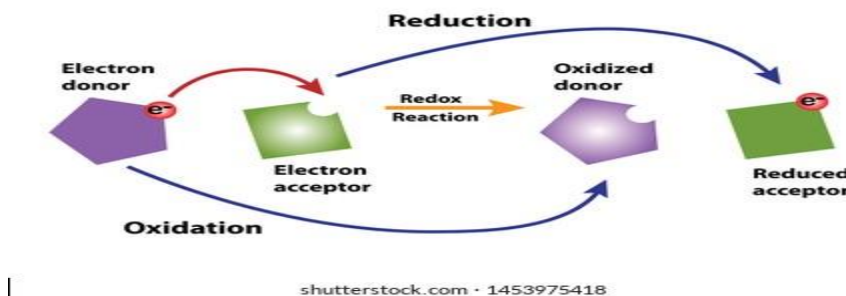
An oxidation-reduction titration or redox titration is one in which the substance to be determined is either oxidised or reduced by means of the solution with which the titration is made. In spite of this, titrimetric determinations based on oxidation-reduction reactions are most widely used methods in the quantitative analysis of inorganic as well as organic compounds. In order to understand the theory of redox titrimetry, we must know such terms as oxidation, reduction, oxidising agent or oxidant and reducing agent or reductant.

Redox (short for reduction–oxidation reaction) is a chemical reaction in which the oxidation states of atoms are changed. Any such reaction involves both a reduction process and a complementary oxidation process, two key concepts involved with electron transfer processes. Redox reactions include all chemical reactions in which atoms have their oxidation state changed; in general, redox reactions involve the transfer of electrons between chemical species. The chemical species from which the electron is stripped is said to have been oxidized, while the chemical species to which the electron is added is said to have been reduced.

- **Oxidation** is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.
- **Reduction** is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.

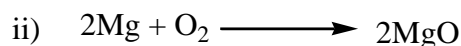
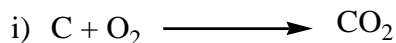
As an example, during the combustion of wood, oxygen from the air is reduced, gaining electrons from the carbon. Although oxidation reactions are commonly associated with the formation of oxides from oxygen molecules, oxygen is not necessarily included in such reactions, as other chemical species can serve the same function.

The reaction can occur relatively slowly, as in the case of rust, or more quickly, as in the case of fire. There are simple redox processes, such as the oxidation of carbon to yield carbon dioxide (CO_2) or the reduction of carbon by hydrogen to yield methane (CH_4), and more complex processes such as the oxidation of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in the human body.

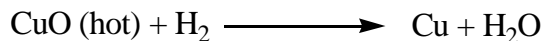


CONCEPT OF OXIDATION AND REDUCTION

Originally oxidation is defined as the addition of oxygen or any other electronegative element or removal of hydrogen or any other electropositive element. For example, the oxidation reactions are:



Reduction which was just the opposite of oxidation, meant removal of oxygen usually through the use of hydrogen such as:



Such a definition has a very limited scope, hence a wider definition was then proposed. According to this definition, oxidation involved an increase in valency. For example, when FeSO_4 is converted into $\text{Fe}_2(\text{SO}_4)_3$, it is a case of oxidation because during this conversion the valency of iron increases from 2 to 3. Change of $\text{Fe}_2(\text{SO}_4)_3$ to FeSO_4 will be called reduction because now the valency decreases from 3 to 2.

The processes of oxidation and reduction occur simultaneously and cannot happen independently of one another, similar to the acid-base reaction. The oxidation alone and the reduction alone are each called a half-reaction, because two half-reactions always occur together to form a whole reaction. When writing half-reactions, the gained or lost electrons are typically included explicitly in order that the half-reaction be balanced with respect to electric charge.

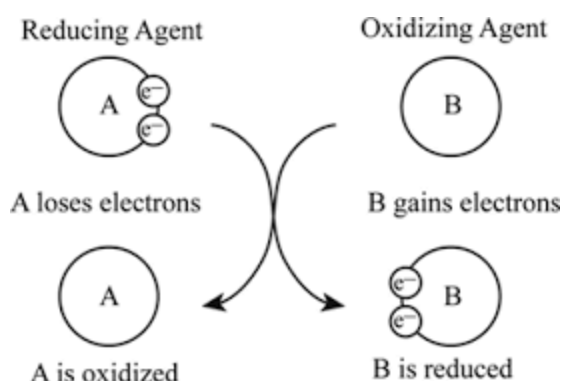
Though sufficient for many purposes, these general descriptions are not precisely correct. Although oxidation and reduction properly refer to a change in oxidation state — the actual transfer of electrons may never occur. The oxidation state of an atom is the fictitious charge that an atom would have if all bonds between atoms of different elements were 100% ionic. Thus, oxidation is best defined as an increase in oxidation state, and reduction as a decrease in

oxidation state. In practice, the transfer of electrons will always cause a change in oxidation state, but there are many reactions that are classed as "redox" even though no electron transfer occurs (such as those involving covalent bonds).

Oxidizing and Reducing Agents

An **oxidizing agent**, or **oxidant**, gains electrons and is reduced in a chemical reaction. Also known as the electron acceptor, the oxidizing agent is normally in one of its higher possible oxidation states because it will gain electrons and be reduced. Examples of oxidizing agents include halogens, potassium nitrate, and nitric acid.

A **reducing agent**, or **reductant**, loses electrons and is oxidized in a chemical reaction. A reducing agent is typically in one of its lower possible oxidation states, and is known as the electron donor. A reducing agent is oxidized, because it loses electrons in the redox reaction. Examples of reducing agents include the earth metals, formic acid, and sulfite compounds.



In redox processes, the reductant transfers electrons to the oxidant. Thus, in the reaction, the reductant or reducing agent loses electrons and is oxidized, and the oxidant or oxidizing agent gains electrons and is reduced. The pair of an oxidizing and reducing agent that are involved in a particular reaction is called a **redox pair**. A **redox couple** is a reducing species and its corresponding oxidizing form, e.g., $\text{Fe}^{2+}/\text{Fe}^{3+}$.

Oxidizers

Substances that have the ability to **oxidize** other substances (cause them to lose electrons) are said to be **oxidative** or **oxidizing** and are known as oxidizing agents, oxidants, or oxidizers. That is, the oxidant (oxidizing agent) removes electrons from another substance, and is thus itself reduced. And, because it "accepts" electrons, the oxidizing agent is also called an electron acceptor. Oxygen is the quintessential oxidizer.

Oxidants are usually chemical substances with elements in high oxidation states (e.g. H_2O_2 , MnO_4^- , CrO_3 , OSO_4) or else highly electronegative elements (O_2 , F_2 , Cl_2 , Br_2) that can gain extra electrons by oxidizing another substance.

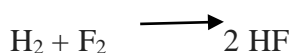
Reducers

Substances that have the ability to **reduce** other substances (cause them to gain electrons) are said to be **reductive** or **reducing** and are known as reducing agents, reductants, or reducers. The reductant (reducing agent) transfers electrons to another substance, and is thus itself oxidized. And, because it "donates" electrons, the reducing agent is also called an electron donor. Electron donors can also form charge transfer complexes with electron acceptors.

Reductants in chemistry are very diverse. Electropositive elemental metals, such as lithium, sodium, magnesium, iron, zinc, and aluminium, are good reducing agents. These metals donate or give away electrons readily. Hydride transfer reagents, such as NaBH_4 and LiAlH_4 , are widely used in organic chemistry,^{[5][6]} primarily in the reduction of carbonyl compounds to alcohols. Another method of reduction involves the use of hydrogen gas (H_2) with a palladium, platinum, or nickel catalyst. These catalytic reductions are used primarily in the reduction of carbon-carbon double or triple bond.

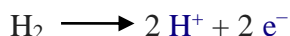
Example of redox reactions

A good example is the reaction between hydrogen and fluorine in which hydrogen is being oxidized and fluorine is being reduced:

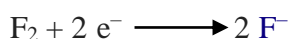


We can write this overall reaction as two half-reactions:

the oxidation reaction:



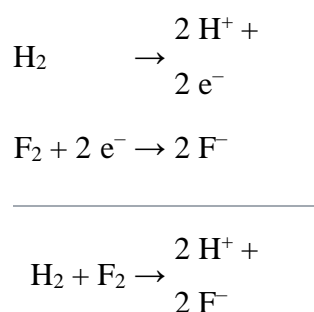
and the reduction reaction:



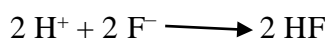
Analyzing each half-reaction in isolation can often make the overall chemical process clearer. Because there is no net change in charge during a redox reaction, the number of electrons in excess in the oxidation reaction must equal to the number consumed by the reduction reaction (as shown above).

Elements, even in molecular form, always have an oxidation state of zero. In the first half-reaction, hydrogen is oxidized from an oxidation state of zero to an oxidation state of +1. In the second half-reaction, fluorine is reduced from an oxidation state of zero to an oxidation state of -1.

When adding the reactions together the electrons are cancelled:



And the ions combine to form hydrogen fluoride:



The overall reaction is:



OXIDATION STATE

The **oxidation state**, often called the **oxidation number**, is an indicator of the degree of oxidation (loss of electrons) of an atom in a chemical compound. Conceptually, the oxidation state, which may be positive, negative or zero, is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic, with no covalent component. This is never exactly true for real bonds.

The term "oxidation" was first used by Antoine Lavoisier to signify reaction of a substance with oxygen. Much later, it was realized that the substance, upon being oxidized, loses electrons, and the use of the term "oxidation" was extended to include other reactions in which electrons are lost.

Oxidation states are typically represented by integers. In some cases, the average oxidation state of an element is a fraction, such as $\frac{8}{3}$ for iron in magnetite (Fe_3O_4). The highest known oxidation

state is reported to be +9 in the iridium tetroxide cation (IrO_4^+), while the lowest known oxidation state is -5 for boron, gallium, indium, and thallium in various Zintl phases, a type of intermetallic compound. It is predicted that even a +10 oxidation state may be achievable by platinum in the platinum tetroxide dication (PtO_4^{2+}).

The increase in oxidation state of an atom, through a chemical reaction, is known as an oxidation; a decrease in oxidation state is known as a reduction. Such reactions involve the formal transfer of electrons: a net gain in electrons being a reduction, and a net loss of electrons being an oxidation. For pure elements, the oxidation state is zero.

There are various methods for determining oxidation states.

In inorganic nomenclature, the oxidation state is determined and expressed as an oxidation number, and is represented by a Roman numeral placed after the element name.

In coordination chemistry, "oxidation number" is defined differently from "oxidation state".

IUPAC definitions of oxidation state and oxidation number

Oxidation state

"Oxidation state" is defined as the charge an atom might be imagined to have when electrons are counted according to an agreed-upon set of rules:

1. the oxidation state of a free element (uncombined element) is zero
2. for a simple (monatomic) ion, the oxidation state is equal to the net charge on the ion
3. hydrogen has an oxidation state of +1 and oxygen has an oxidation state of -2 when they are present in most compounds. Exceptions to this are that hydrogen has an oxidation state of -1 in hydrides of active metals, e.g. LiH , and oxygen has an oxidation state of -1 in peroxides e.g. H_2O_2 .
4. the algebraic sum of oxidation states of all atoms in a neutral molecule must be zero, while in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion.

Determining the oxidation state or number

There are two different methods for determining the oxidation state of elements in chemical compounds. First (and widely taught) a method based on the rules in the IUPAC definition.

Second, a method based on the relative electronegativity of the elements in the compound, where the more electronegative element is assumed to take the negative charge.

Simple examples using IUPAC definition

- Any pure element even if it forms diatomic molecules like chlorine (Cl_2) has an oxidation state of zero. Examples of this are Cu or O_2 .
 - For monatomic ions, the oxidation state is the same as the charge of the ion. For example, the sulfide anion (S^{2-}) has an oxidation state of -2 , whereas the lithium cation (Li^+) has an oxidation state of $+1$.
 - The sum of oxidation states for all atoms in a molecule or polyatomic ion is equal to the charge of the molecule or ion. Thus, the oxidation state of one element can be calculated from the oxidation states of the other elements.
- An application of this rule is that the sum of the oxidation states of all atoms in a neutral molecule must be zero. Consider a neutral molecule of carbon dioxide, CO_2 . Oxygen is assumed to have its usual oxidation state of -2 , and so the sum of the oxidation states of all the atoms can be expressed as $x + 2(-2) = 0$, or $x - 4 = 0$, where x is the unknown oxidation state of carbon. Thus, it can be seen that the oxidation state of carbon in the molecule is $+4$.
 - In polyatomic ions, the sum of the oxidation states of the constituent atoms must be equal to the charge on the ion. As an example, consider the sulfate anion, which has the formula SO_4^{2-} . As indicated by the formula, the total charge of this ion is -2 . Because all four oxygen atoms are assumed to have their usual oxidation state of -2 , and the sum of the oxidation states of all the atoms is equal to the charge of the ion, the sum of the oxidation states can be represented as $y + 4(-2) = -2$, or $y - 8 = -2$, where y is the unknown oxidation state of sulfur. Thus, it can be computed that $y = +6$.

These facts, combined with some elements almost always having certain oxidation states (due to their very high electropositivity or electronegativity), allows one to compute the oxidation states for the remaining atoms (such as transition metals) in simple compounds.

Example for a complex salt: In $\text{Cr}(\text{OH})_3$, oxygen has an oxidation state of -2 (no fluorine or O-O bonds present), and hydrogen has a state of $+1$ (bonded to oxygen). So, each of the

three hydroxide groups has an overall oxidation state of $-2 + 1 = -1$. As the compound is neutral, chromium has an oxidation state of +3.

Using electronegativity

The use of electronegativity in this way was introduced by Linus Pauling in 1947. This method of determining oxidation state is found in some recent text books. This method allows the oxidation state of all atoms in a molecule to be determined whereas the IUPAC 1990/2005 definition does not. In the 1970 rules, IUPAC recommended that oxidation state be used in nomenclature and elsewhere in inorganic chemistry as the "charge that would be present on an atom if the electrons were assigned to the more electronegative atom", but with a convention that hydrogen is considered to be positive in combination with nonmetals and a bond between like atoms makes no contribution to the oxidation number.

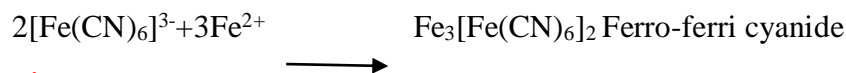
In practice the IUPAC 1990/2005 definition is usually extended by adding additional rules based on electronegativity.

- Fluorine has an oxidation state of -1 when bonded to any other element, since it has the highest electronegativity of all reactive elements.
- Halogens other than fluorine have an oxidation state of -1 except when they are bonded to oxygen, to nitrogen, or to another halogen that is more electronegative. For example, the oxidation state of chlorine in chlorine monofluoride (ClF) is $+1$. However, in bromine monochloride (BrCl), the oxidation state of Cl is -1 .
- Hydrogen has an oxidation state of $+1$ except when bonded to more electropositive elements such as sodium, aluminium, and boron, as in NaH, NaBH₄, LiAlH₄, where each H has an oxidation state of -1 .
- In compounds, oxygen typically has an oxidation state of -2 , though there are exceptions that are listed below, such as peroxides (e.g. hydrogen peroxide H₂O₂), where oxygen has an oxidation state of -1 .
- Alkali metals have an oxidation state of $+1$ in virtually all of their compounds (exception, see alkalide).
- Alkaline earth metals have an oxidation state of $+2$ in virtually all of their compounds.

Redox Indicator

Types of redox indicators: Several types of indicators used in redox titrations are:

- i. Self indicators: The KMnO_4 solutions are quite deeply coloured and a slight excess of this reagent in a titration is easily detected. Thus in the titration of oxalic acid, ferrous ammonium sulphate, hydrogen peroxide etc., with KMnO_4 , as soon as the reaction is complete, and a drop of the latter is in excess, a light pink colour is itself developed, indicating that the reaction is complete and the end point has reached.
- ii. Specific indicator: This is a substance which reacts in a specific manner with one of the reagents in a titration to exhibit a colour. Thus starch produces a deep blue colour with iodine; thiocyanate ion produces a red colour with Fe (III) ion.
- iii. External (or spot test) indicator: These were usually employed when no internal indicators were known. For example, Fe(CN)_6^{3-} , ferri cyanide ion is still used to detect Fe (II) ion by the formation of a deep blue-green complex (Turnbull's blue) on a spot plate outside the titration mixture. Thus, $\text{K}_3\text{Fe(CN)}_6$ is used in the titration of Fe (II) with $\text{K}_2\text{Cr}_2\text{O}_7$ solution in acid medium:



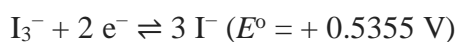
Types of redox titrations

Iodometry, also known as **iodometric titration**, is a method of volumetric chemical analysis, a redox titration where the appearance or disappearance of elementary iodine indicates the end point. Iodometry involves indirect titration of iodine liberated by reaction with the analyte, whereas iodimetry involves direct titration using iodine as the titrant.

Basic principles

Iodometry is commonly used to analyse the concentration of oxidizing agents in water samples, such as oxygen saturation in ecological studies or active chlorine in swimming pool water analysis. To a known volume of sample, an excess but known amount of iodide is added, which the oxidizing agents oxidizes iodide to iodine. Iodine dissolves in the iodide-containing solution to give triiodide ions, which have a dark brown color.

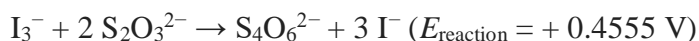
The triiodide ion solution is then titrated against standard thiosulfate solution to give iodide again using starch indicator:



Together with reduction potential of thiosulfate:



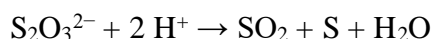
The overall reaction is thus:



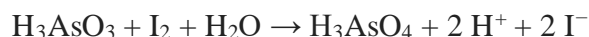
For simplicity, the equations will usually be written in terms of aqueous molecular iodine rather than the triiodide ion, as the iodide ion did not participate in the reaction in terms of mole ratio analysis.

The disappearance of deep blue color due to the decomposition of the iodine-starch clathrate marks the end point

The reducing agent used does not necessarily need to be thiosulfate; stannous chloride, sulfites, sulfides, arsenic(III), and antimony(III) are commonly used alternatives. At higher pH (> 8) At low pH would also react with the thiosulfate:



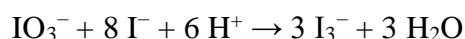
Some reactions involving certain reductants are reversible at certain pH, thus the pH of the sample solution should be carefully adjusted before the performing the analysis. For example, the reaction:



is reversible at $\text{pH} < 4$.

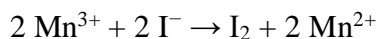
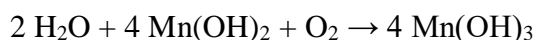
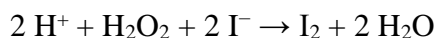
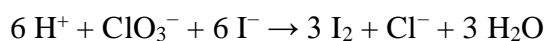
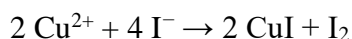
The volatility of iodine is also a source of error for the titration, this can be effectively prevented by ensuring an excess iodide is present and cooling the titration mixture. Strong light, nitrite and copper ions catalyzes the conversion of iodide to iodine, so these should be removed prior to the addition of iodide to the sample.

For prolonged titrations, it is advised to add dry ice to the titration mixture to displace air from the erlenmeyer flask so as to prevent the aerial oxidation of iodide to iodine. Standard iodine solution is prepared from potassium iodate and potassium iodide, which are both primary standards:



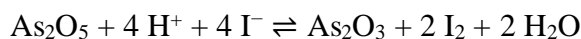
Applications

Iodometry in its many variations is extremely useful in volumetric analysis. Examples include the determination of copper (II), chlorate, Hydrogen peroxide, and dissolved oxygen:



Available chlorine refers to chlorine liberated by the action of dilute acids on hypochlorite. Iodometry is commonly employed to determine the active amount of hypochlorite in bleach responsible for the bleaching action. In this method, excess but known amount of iodide is added to known volume of sample, in which only the active (electrophilic) can oxidize iodide to iodine. The iodine content and thus the active chlorine content can be determined with iodometry.

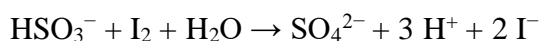
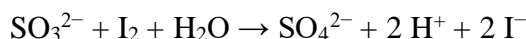
The determination of arsenic (V) is the reverse of the standardization of iodine solution with sodium arsenite, where a known and excess amount of iodide is added to the sample:



For analysis of antimony (V), some tartaric acid is added to solubilize the antimony(III) product.

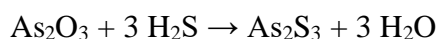
Determination of hydrogensulfites and sulfites

Sulfites and hydrogensulfites reduce iodine readily in acidic medium to iodide. Thus when a diluted but excess amount of standard iodine solution is added to known volume of sample, the sulfurous acid and sulfites present reduces iodine quantitatively:



Determination of sulfides and hydrogensulfides

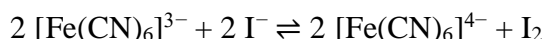
Although the sulfide content in sample can be determined straightforwardly as described for sulfites, the results are often poor and inaccurate. A better, alternative method with higher accuracy is available, which involves the addition of excess but known volume of standard sodium arsenite solution to the sample, during which arsenic trisulfide is precipitated:



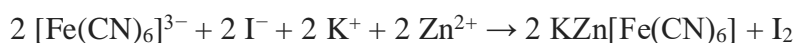
The excess arsenic trioxide is then determined by titrating against standard iodine solution using starch indicator. Note that for the best results, the sulfide solution must be dilute with the sulfide concentration not greater than 0.01 M.

Determination of hexacyanoferrate(III)

When iodide is added to a solution of hexacyanoferrate(III), the following equilibrium exists:



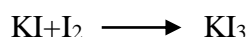
Under strongly acidic solution, the above equilibrium lies far to the right hand side, but is reversed in almost neutral solution. This makes analysis of hexacyanoferrate (III) troublesome as the iodide and thiosulfate decomposes in strongly acidic medium. To drive the reaction to completion, an excess amount of zinc salt can be added to the reaction mixture containing potassium ions, which precipitates the hexacyanoferrate(II) ion quantitatively:



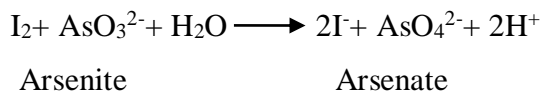
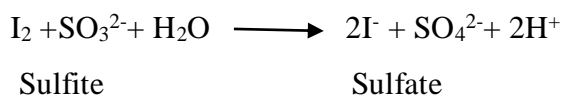
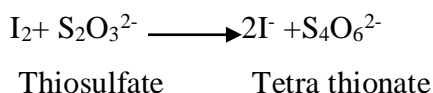
The precipitation occurs in slightly acidic medium, thus avoids the problem of decomposition of iodide and thiosulfate in strongly acidic medium, and the hexacyanoferrate(III) can be determined by iodometry as usual.

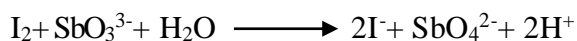
Iodimetry

When an analyte that is a reducing agent (like hypo) is titrated directly with a standard iodine solution, the method is called "iodimetry". In iodimetric titrations, free iodine is used. Since it is difficult to prepare the solution of iodine (iodine sublimates and is less soluble in water) it is dissolved in KI solution.



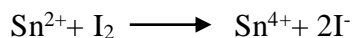
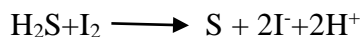
In an Iodimetric titrations (reduction of iodine) the direct use of iodine as an oxidizing agent in neutral or slightly acidic medium using starch as an indicator is made. The various reducing agents used in these titrations are thiosulfates, sulfites, arsenites or antimonites.





Antimonite

Antimonite

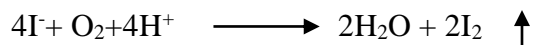


Iodine Solution: It is a primary standard (equivalent weight, 126.91) but cannot be weighed out directly as it is highly volatile at room temperature. Iodine is only slightly soluble in water ($0.00134 \text{ mol dm}^{-3}$ at 25°C) but is quite soluble in solutions containing iodide (I^-) ions. An excess of KI is added to increase the solubility and decrease the volatility of iodine. The weighing of iodine is carried out in some form of well stoppered weighing bottle containing an excess than calculated amount of solid KI. Generally for every 12g of iodine, 20 g of KI are required for preparing its solution. If the solution is to be kept for any time, it should be placed in a glass (amber coloured) stoppered bottle in a cool and dark place. Commercial iodine may contain a little moisture and iodine chloride. It is mixed with solid AR grade KI and subjected to sublimation for purification. The pure I_2 after sublimation is used for preparing a solution.

The reasons for its wider applicability is that it is readily detected with a great accuracy either by its own colour or by the blue colour produced with the starch as indicator or by the red-purple colour when extracted into organic solvents such as CCl_4 / CHCl_3 / CS_2 etc.

Drawbacks: i) The titrations using I_2 solution must be carried out in cold and out of direct sunlight in a long necked conical flask. The titrations cannot be performed in open beakers.

ii) I^- ion is oxidized by oxygen of the air or in water:



Such an oxidation is fast in acid solutions and is catalysed by strong light, heat and if the water contains substances like NO_2^- , Cu and oxides of nitrogen. Hence the water should be boiled and cooled before use. The titration is usually carried out in neutral or dilute acetic acid medium.

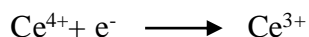
Starch indicator: Usually a solution of starch (colloidal dispersion) is used, since the deep blue colour of the starch-I₂ complex serves as a very sensitive test for even traces of iodine. Take about 2-3g of soluble starch powder in a small glass mortar, add 4-5 cm³ of boiling distilled water and make a paste with the help of a pestle, then add again 10-15 cm³ of the boiling distilled water and dilute the paste with the slow rotary motion of the pestle. Boil separately about 200-300 cm³ of distilled water in a beaker. Pour dropwise in a thin stream, the paste of starch into the boiling water, while stirring well during the addition with the help of a glass rod. Decant off the clear portion of the solution into clean glass container. Use 5-8 drops of this solution in each titration. Fresh solutions of starch should preferably be prepared on the working day. However, if it is to be kept for a longer period some preservatives are used, for example, boric acid, salicylic acid (1-1.5g) few drops of toluene, 5-10 mg of HgI₂, 2-3 cm³ of 5% HgCl₂ solution; any one of these may be added.

Cerimetry

Oxidation-reduction titrations involving ceric sulfate, symbolized here by Ce⁴⁺ as an oxidizing agent are sometimes grouped under the generic term “cerimetry”. Most of the time, ceric sulfate is used. Ceric sulfate is a powerful oxidant and can be used only in acidic solution. In neutral solution ceric hydroxide or basic salts precipitate [Ce(OH)₄]. Ceric sulfate have intense yellow colour and end point detection can be possible without any indicator in hot solutions.

The advantage of ceric salts (sulfate) over permanganate and dichromate as a standard oxidizing agent are:-

- Ceric sulfate solution is indefinitely stable, the concentration does not vary in sunlight or even on boiling.
- It may be employed in the titration of reducing agent in the presence of a high concentration of HCl.
- In acid solution with reducing agent, the simple valence change



Is assumed to take place. No intermediate products are formed.

- Cerous [Ce (III)] salt, which is the reduction product in ceric titrations, is practically colourless and hence allows a more effective use of indicators.

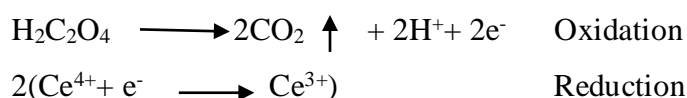
Example: - Cerimetry Titration of Oxalic acid (H₂C₂O₄)

Ceric sulfate solution reacts with hot solution of oxalic acid acidified with dilute sulfuric acid by the following reaction:-



In this reaction, an electron is transferred from $\text{H}_2\text{C}_2\text{O}_4$ to Ce^{4+} to form Ce^{3+} and $(\text{CO}_2 + \text{H}^+)$. A substance that has a strong affinity for electrons, such as Ce^{4+} , is called an oxidizing agent or an oxidant. A reducing agent or reductant is a species such as $\text{H}_2\text{C}_2\text{O}_4$ that easily donates electrons to another species.

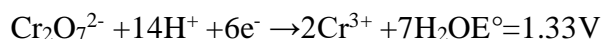
We can split any oxidation-reduction equation into two half-reactions that show which species gains electrons and which loses them.



The titration is carried out until the reaction mixture gets a pale yellow colour. The ceric sulfate solution acts as a self-indicator.

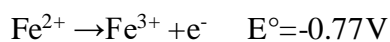
Dichrometry

As an oxidant, dichromate has some advantages over permanganate, but, as it is less powerful, its use is much more limited. It is obtainable in a state of high purity and can be used as a primary standard. Solutions of dichromate in water are stable indefinitely. The half reaction for the dichromate system is:

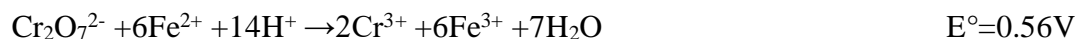


The most important application of dichromate is in its reaction with iron(II) in which it is often preferred to permanganate.

The relevant half reaction is:



and the total reaction is:

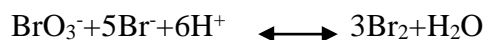


Unlike permanganate, dichromate titrations require an indicator. There are three indicators that may be used for the titration of Fe^{2+} with $\text{K}_2\text{Cr}_2\text{O}_7$. These are diphenylamine, diphenylbenzidine and diphenylamine sulfonate. The colour change for all three indicators is green to violet and the standard electrode potentials are all ca 0.78 V. According to Kolthoff and Sandell, this should lie between the electrode potentials of the two reduction reactions. This not being the case,

phosphoric acid is added to reduce the electrode potential for the $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ reaction by stabilising the ferric ion.

Bromometry

Potassium bromate is a powerful oxidizing agent in acid medium. Reducing agent first convert BrO_3^- to bromide and then with excess of BrO_3^- , free Br_2 is liberated



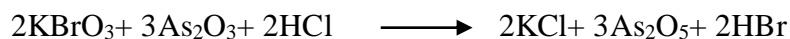
Usually bromide (KBr) is added to the test solution before the titration or, it is included in the standard BrO_3^- solution and thus the net reaction is the second one.

Preparation of 0.1N potassium bromate solution

Potassium bromate is dried at 120-130°C for 1-2 hours and allowed to cool in a closed vessel in a desiccator. The equivalent weight of KBrO_3 is one-sixth of its molecular weight. Weigh out accurately about 2.783g of pure AR KBrO_3 and dissolve it in water in a 1dm³ graduated flask. It is stable indefinitely. The only disadvantage with it is its small equivalent weight.

Determination of the strength of As(III) in a given solution of arsenic (III) oxide:

This determination is carried out in 1N HCl medium using methyl orange as an indicator. The reaction that takes place is:



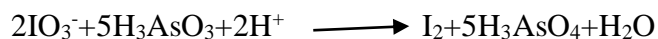
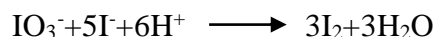
The reaction of Sb(III) oxide with KBrO_3 is exactly similar.

Procedure: Take a 25cm³ portion of 0.1 N As(III) oxide solution into a 250 cm³ conical flask, add 25 cm³ of water, 15 cm³ of a conc HCl, 0.5 g of pure and AR KBr and 2-3 drops of 0.1% methyl orange solution as indicator. Titrate it against 0.1 N KBrO_3 solution dropwise, with interval of 2-3 seconds between the consecutive drops, until the colour of the indicator changes sharply from orange red to colourless or pale yellow. In case the colour of the indicator fades, add a drop more of it. Using standard 0.1 N arsenic (III) oxide solution, KBrO_3 solution can be standardized and its value compared with the calculated value.

$$\begin{aligned} 1\text{cm}^3 \text{ of } 1\text{N } \text{KBrO}_3 &= 0.04946 \text{ g of } \text{As}_2\text{O}_3 \\ &= 0.03746 \text{ g of As} \end{aligned}$$

Titration with Potassium iodate

It is a powerful oxidizing agent. The reducing agents such as I^- ion or As_2O_3 in solution of moderate acidity an iodate is reduced only to iodine:



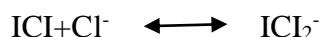
The liberated iodine may be titrated with a standard thiosulphate solution. With a more strong reductant such as TiCl_3 , the iodate is reduced to iodide:



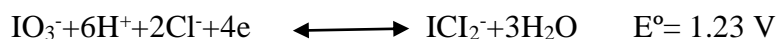
When the acid concentration is high, the reduction occurs to iodine monochloride:



In strong HCl solution, ICl reacts with Cl^- to form a stable complex ion:



Hence the net reaction is



And under such conditions KIO_3 acts as a very powerful oxidizing agent and the equivalent of KIO_3 is one-fourth of a mole i.e., $214.00/4 \times 10 = 5.3500 \text{ g dm}^{-3}$ is needed for a 0.1 N solution.

Reference for more learning

Reference Books

Sr. No	Name of Book	Author	Publisher
1.	Text Book of Quantitative Inorganic analysis.	A.L Vogel,	Pearson India
2.	Pharmaceutical Analysis	Dr. T.Sudha, L.Kaviarasan	S. Vikas and company
3.	Practical Pharmaceutical Chemistry	A.H. Beckett and J.B. Stenlake's	The Athlone Press

YOUTUBE LINK: <https://youtu.be/RYmdkld6FfA>

https://youtu.be/H3jU_LkGonE

IMPORTANT QUESTIONS

MCQ

1. Which indicator is example of self indicator?

- a. sudan red
- b. Methylene blue
- c. **Cerric Ions**
- d. Orange fe

2. Which instrument is used to detection of end point?

- a. Potentiometer
- b. Conductometer
- c. **a and b**
- d. None of the above

3. Which drug is not assay by redox titration?

- a.Acetomenaphthone tablets
- b.Ascorbic acid tablets
- c.Chlorpromazine tablets
- d.**Metformin**

4. Which drug is assay by redox titration ?

- a. Metformin
- b.Cinchonism
- c.Digioxin
- d.**Ferrous gluconate tablets**

5. Which of the following is a sensitive self indicator?

- (A) Cerium sulfate
- (B) 1, 10 panthrolin iron
- (C) **Iodine**
- (D) Diphenylamine

6. By convention, standard electrode potential is taken as

(A) Oxidation potential

(B) **Reduction Potential**

(C) Both

(D) None of the above

7. The oxidation state of Mn in KMnO_4 is

(A) 3

(B) 2

(C) 5

(D) **7**

8. High equilibrium constant of a redox cell indicates

(A) Spontaneous reaction

(B) Slow reaction

(C) Incomplete reaction

(D) **Complete reaction**

9. All of the following are oxidation, except

(A) Gain of oxygen

(B) **Loss of proton**

(C) Increase in oxidation state

(D) Loss of electrons

10. Which of the following is used as an indicator in the titration of iodine with hypo?

(a) Methyl red

(b) Methyl orange

(c) **Starch**

(d) Potassium ferricyanide

11. How many mmols of NaOH will be used in the titration with 33ml of 3 M HCl to form NaCl and water?

(a) 10 mmol

(b) **100 mmol**

(c) 3 mmol

(d) 33 mmol

12. The pH range of methyl orange as an indicator is

(a) **3-5**

(b) 8-9

(c) 2-4

(d) 6-8

13. The amount of NaOH used in the titration of 100 ml 0.1 N HCl is

(a) 4 g

(b) 0.04 g

(c) 2 g

(d) **0.4 g**

14. The equivalent weight of an acid can be calculated by

(a) Molecular weight \times basicity

(b) **Molecular weight/basicity**

(c) Molecular weight \times acidity

(d) Molecular weight/acidity

15. What will be the pH at the equivalence point in the titration of a weak acid and a strong base?

(a) 0

(b) **>7**

(c) 7

(d) <7

SHORT ANSWER QUESTIONS

1. Define pH

Ans. The term "pH" was first described by Danish biochemist Søren Peter Lauritz Sørensen in 1909. pH is an abbreviation for "power of hydrogen" where "p" is short for the German word for power, *potenz* and H is the element symbol for hydrogen. pH is a logarithmic measure of the hydrogen ion concentration of an aqueous solution:

$$\text{pH} = -\log[\text{H}^+]$$

2. What are hard acids?

Ans. Hard Lewis acids are characterized by small ionic radii, high positive charge, strongly solvated, empty orbitals in the valence shell and with high energy LUMOs.

3. What is standard electrode potential.

Ans. In electrochemistry, the standard electrode potential, abbreviated E° or E^\ominus is the measure of individual potential of a reversible electrode at standard state, which is with solutes at an effective concentration of 1 mol dm^{-3} , and gases at a pressure of 1 atm. The reduction potential is an intensive property. The values are most often tabulated at 25°C . The basis for an electrochemical cell such as the galvanic cell is always a redox reaction which can be broken down into two half-reactions: oxidation at anode (loss of electron) and reduction at cathode (gain of electron).

4. Define electrochemical cell.

Ans. An electrochemical cell is a device capable of either generating electrical energy from chemical reactions or facilitating chemical reactions through the introduction of electrical energy. A common example of an electrochemical cell is a standard 1.5 - volt cell meant for consumer use. This type of device is known as a single galvanic cell. A battery consists of one or more cells, connected in either parallel or series pattern.

5. Define pK_a .

Ans. pK_a is the negative base-10 logarithm of the acid dissociation constant of a solution.

$$\text{pK}_a = -\log_{10} K_a$$

The lower the pK_a value, the stronger the acid.

6. What is redox potential?

Ans. Reduction potential (also known as redox potential, oxidation / reduction potential) is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Reduction potential is measured in volts (V), or millivolts (mV). Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. ORP is a common measurement for water quality.

7. Define nerst equation.

Ans. In electrochemistry, the Nernst equation is an equation that relates the reduction potential of an electrochemical reaction to the standard electrode potential, temperature, and activities of the chemical species undergoing reduction and oxidation.

$$E_{\text{cell}} = E^0_{\text{cell}} - (RT/nF)\ln Q$$

Where:

E_{cell} = cell potential under nonstandard conditions (V)

E^0_{cell} = cell potential under standard conditions

R = gas constant, which is 8.31 (volt-coulomb)/(mol-K)

T = temperature (kelvin), which is generally 298°K (77°F/25°C)

n = number of moles of electrons exchanged in the electrochemical reaction (mol)

F = Faraday's constant, 96500 coulombs/mol

Q = reaction quotient, which is the equilibrium expression with initial concentrations rather than equilibrium concentrations

The equation can be rearranged to give $\ln K_c = nFE/RT$ where K_c is the equilibrium constant at the equilibrium state. The equilibrium potential is dependent on temperature and concentration of reaction partners.

LONG ANSWER QUESTIONS

1. Electrode potential describes.

Ans. Electrode potential (or *Electropotential*), E , in chemistry or electrochemistry, according to a IUPAC definition, is the electromotive force of a cell built of two electrodes:

- on the left-hand side is the standard hydrogen electrode, and
- on the right-hand side is the electrode the potential of which is being defined.

By convention:

$$E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

From the above, for the cell with the standard hydrogen electrode (potential of 0 by convention), one obtains:

$$E_{\text{Cell}} = E_{\text{Right}} - 0 = E_{\text{Electrode}}$$

The left-right convention is consistent with the international agreement that redox potentials be given for reactions written in the form of reduction half-reactions. Electrode potential is measured in volts (V).

2. What is significance of salt bridge?

Ans. (i) Salt bridge is U – shaped glass tube filled with a gelly like substance, agar – agar (plant gel) mixed with an electrolyte like KCl, KNO₃, NH₄NO₃ etc.

(ii) The electrolytes of the two half-cells should be inert and should not react chemically with each other.

(iii) The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number.

(iv) The following are the functions of the salt bridge,

(a) It connects the solutions of two half - cells and completes the cell circuit.

(b) It prevents transference or diffusion of the solutions from one half cells to the other.

(c) It keeps the solution of two half - cells electrically neutral.

(d) It prevents liquid – liquid junction potential i.e. the potential difference which arises between two solutions when they contact with each other.

3. What is cell constant and give its mathematical representation.

Ans. Conductivity sensors are characterized by a cell constant – a geometry dependent parameter that relates the conductance (or resistance) measured by the cell to the solution's conductivity (or bulk resistivity), as,

$$\sigma = K G$$

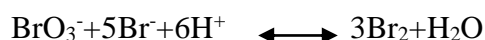
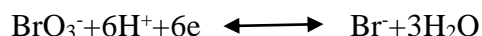
Where, G is the cell conductance, in Siemens (or mhos),
 K is the cell constant, in cm^{-1} , and,
 σ is the solution conductivity, as S/cm or $\mu\text{S}\cdot\text{cm}^{-1}$.

Conductivity sensors are fabricated using a variety of electrode geometries. In the past the use of parallel planar electrodes made determination of the sensor's cell constant an easy computation. In that case the cell constant is given by the ratio of electrode separation to electrode area:

$$K = S/A$$

4 Explain the in detail of Bromatometry Titration.

Ans. Potassium bromate is a powerful oxidizing agent in acid medium. Reducing agent first convert BrO_3^- to bromide and then with excess of BrO_3^- , free Br_2 is liberated



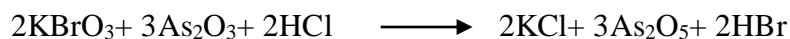
Usually bromide (KBr) is added to the test solution before the titration or, it is included in the standard BrO_3^- solution and thus the net reaction is the second one.

Preparation of 0.1N potassium bromide solution

Potassium bromide is dried at $120-130^\circ\text{C}$ for 1-2 hours and allowed to cool in a closed vessel in a desiccator. The equivalent weight of KBrO_3 is one-sixth of its molecular weight. Weigh out accurately about 2.783g of pure AR KBrO_3 and dissolve it in water in a 1 dm^3 graduated flask. It is stable indefinitely. The only disadvantage with it is its small equivalent weight.

Determination of the strength of As(III) in a given solution of arsenic (III) oxide:

This determination is carried out in 1N HCl medium using methyl orange as an indicator. The reaction that takes place is:



The reaction of Sb(III) oxide with KBrO_3 is exactly similar.

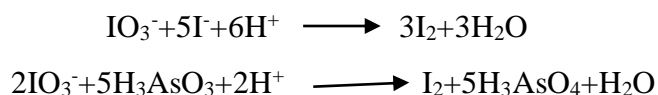
Procedure: Take a 25 cm^3 portion of 0.1 N As(III) oxide solution into a 250 cm^3 conical flask, add 25 cm^3 of water, 15 cm^3 of a conc HCl, 0.5 g of pure and AR KBr and 2-3 drops of 0.1% methyl orange solution as indicator. Titrate it against 0.1 N KBrO_3 solution dropwise, with interval of 2-3 seconds between the consecutive drops, until the colour of the indicator changes sharply from orange red to colourless or pale yellow. In case the colour of the indicator fades,

add a drop more of it. Using standard 0.1 N arsenic (III) oxide solution, KBrO_3 solution can be standardized and its value compared with the calculated value.

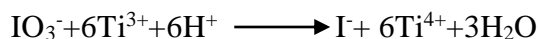
$$\begin{aligned} 1\text{cm}^3 \text{ of } 1\text{N } \text{KBrO}_3 &= 0.04946 \text{ g of } \text{As}_2\text{O}_3 \\ &= 0.03746 \text{ g of As} \end{aligned}$$

Titration with Potassium iodate

It is a powerful oxidizing agents. The reducing agents such as I^- ion or As_2O_3 in solution of moderate acidity an iodate is reduced only to iodine:



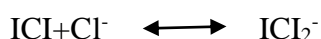
The liberated iodine may be titrated with a standard thiosulphate solution. With a more strong reductant such as TiCl_3 , the iodate is reduced to iodide:



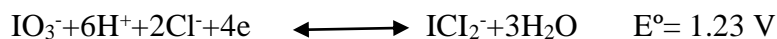
When the acid concentration is high, the reduction occurs to iodine monochloride:



In strong HCl solution, ICl reacts with Cl^- to form a stable complex ion:



Hence the net reaction is



And under such conditions KIO_3 acts as a very powerful oxidizing agent and the equivalent of KIO_3 is one-fourth of a mole i.e., $214.00/4 \times 10 = 5.3500 \text{ g dm}^{-3}$ is needed for a 0.1 N solution.

5. Note on indicators used in redox titration.

Redox Indicator- Types of redox indicators: Several types of indicators used in redox titrations are:

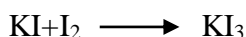
- i. **Self indicators:** The KMnO_4 solutions are quite deeply coloured and a slight excess of this reagent in a titration is easily detected. Thus in the titration of oxalic acid, ferrous ammonium sulphate, hydrogen peroxide etc., with KMnO_4 , as soon as the reaction is complete, and a drop of the latter is in excess, a light pink colour is itself developed, indicating that the reaction is complete and the end point has reached.

- ii. Specific indicator: This is a substance which reacts in a specific manner with one of the reagents in a titration to exhibit a colour. Thus starch produces a deep blue colour with iodine; thiocyanate ion produces a red colour with Fe (III) ion.
- iii. External (or spot test) indicator: These were usually employed when no internal indicators were known. For example, $\text{Fe}(\text{CN})_6^{3-}$, ferri cyanide ion is still used to detect Fe (II) ion by the formation of a deep blue-green complex (Turnbull's blue) on a spot plate outside the titration mixture. Thus, $\text{K}_3\text{Fe}(\text{CN})_6$ is used in the titration of Fe (II) with $\text{K}_2\text{Cr}_2\text{O}_7$ solution in acid medium:

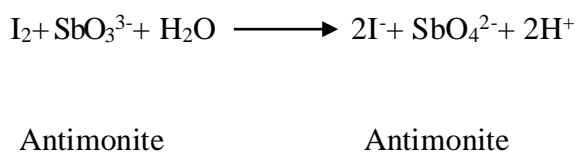
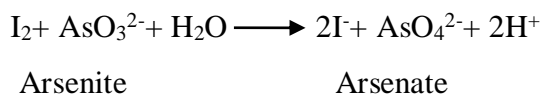
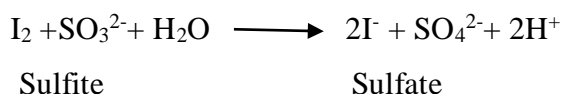
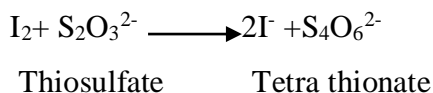


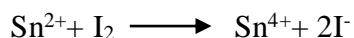
6. Write in detail of Iodimetry.

Ans. When an analyte that is a reducing agent (like hypo) is titrated directly with a standard iodine solution, the method is called "iodimetry". In iodimetric titrations, free iodine is used. Since it is difficult to prepare the solution of iodine (iodine sublimates and is less soluble in water) it is dissolved in KI solution.



In an Iodimetric titrations (reduction of iodine) the direct use of iodine as an oxidizing agent in neutral or slightly acidic medium using starch as an indicator is made. The various reducing agents used in these titrations are thiosulfates, sulfites, arsenites or antimonites.



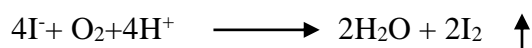


Iodine Solution: It is a primary standard (equivalent weight, 126.91) but cannot be weighed out directly as it is highly volatile at room temperature. Iodine is only slightly soluble in water ($0.00134 \text{ mol dm}^{-3}$ at 25°C) but is quite soluble in solutions containing iodide (I^-) ions. An excess of KI is added to increase the solubility and decrease the volatility of iodine. The weighing of iodine is carried out in some form of well stoppered weighing bottle containing an excess than calculated amount of solid KI. Generally for every 12g of iodine, 20 g of KI are required for preparing its solution. If the solution is to be kept for any time, it should be placed in a glass (amber coloured) stoppered bottle in a cool and dark place. Commercial iodine may contain a little moisture and iodine chloride. It is mixed with solid AR grade KI and subjected to sublimation for purification. The pure I_2 after sublimation is used for preparing a solution.

The reasons for its wider applicability is that it is readily detected with a great accuracy either by its own colour or by the blue colour produced with the starch as indicator or by the red-purple colour when extracted into organic solvents such as CCl_4 / CHCl_3 / CS_2 etc.

Drawbacks: i) The titrations using I_2 solution must be carried out in cold and out of direct sunlight in a long necked conical flask. The titrations cannot be performed in open beakers.

ii) I^- ion is oxidized by oxygen of the air or in water:



Such an oxidation is fast in acid solutions and is catalysed by strong light, heat and if the water contains substances like NO_2^- , Cu and oxides of nitrogen. Hence the water should be boiled and cooled before use. The titration is usually carried out in neutral or dilute acetic acid medium.

Starch indicator: Usually a solution of starch (colloidal dispersion) is used, since the deep blue colour of the starch- I_2 complex serves as a very sensitive test for even traces of iodine. Take about 2-3g of soluble starch powder in a small glass mortar, add 4-5 cm^3 of boiling distilled water and make a paste with the help of a pestle, then add again 10-15 cm^3 of the boiling distilled

water and dilute the paste with the slow rotary motion of the pestle. Boil separately about 200-300 cm³ of distilled water in a beaker. Pour dropwise in a thin stream, the paste of starch into the boiling water, while stirring well during the addition with the help of a glass rod. Decant off the clear portion of the solution into clean glass container. Use 5-8 drops of this solution in each titration. Fresh solutions of starch should preferably be prepared on the working day. However, if it is to be kept for a longer period some preservatives are used, for example, boric acid, salicylic acid (1-1.5g) few drops of toluene, 5-10 mg of HgI₂, 2-3 cm³ of 5% HgCl₂ solution; any one of these may be added

IMPORTANT TERMS

- **Redox** (short for reduction–oxidation reaction) is a chemical reaction in which the oxidation states of atoms are changed. Any such reaction involves both a reduction process and a complementary oxidation process, two key concepts involved with electron transfer processes. Redox reactions include all chemical reactions in which atoms have their oxidation state changed; in general, redox reactions involve the transfer of electrons between chemical species.
- **Oxidation** is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.
- **Reduction** is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.
- An **oxidizing agent**, or **oxidant**, gains electrons and is reduced in a chemical reaction. Also known as the electron acceptor, the oxidizing agent is normally in one of its higher possible oxidation states because it will gain electrons and be reduced. Examples of oxidizing agents include halogens, potassium nitrate, and nitric acid.
- A **reducing agent**, or **reductant**, loses electrons and is oxidized in a chemical reaction. A reducing agent is typically in one of its lower possible oxidation states, and is known as the electron donor. A reducing agent is oxidized, because it loses electrons in the redox reaction. Examples of reducing agents include the earth metals, formic acid, and sulfite compounds.

- **Self indicators:** The KMnO_4 solutions are quite deeply coloured and a slight excess of this reagent in a titration is easily detected. Thus in the titration of oxalic acid, ferrous ammonium sulphate, hydrogen peroxide etc., with KMnO_4 , as soon as the reaction is complete, and a drop of the latter is in excess, a light pink colour is itself developed, indicating that the reaction is complete and the end point has reached.
- **Specific indicator:** This is a substance which reacts in a specific manner with one of the reagents in a titration to exhibit a colour. Thus starch produces a deep blue colour with iodine; thiocyanate ion produces a red colour with Fe (III) ion.