REDOX TITRATIONS

CONCEPT OF OXIDATION AND REDUCTION

In titrimetric analysis we can find out the quantity of pure component based on measurement of volume of standard solution that reacts completely with the analyte. This measurement of standard solution can be possible in different reactions, and if the reaction involved in this measurement is oxidation-reduction reaction, that method is called ns "oxidation reduction titration" or "Redox titration.

In Redox titration, oxidation & Reduction reaction occurs simultaneously.

OXIDATION

Oxidation of a cpmpound can be demonstrated in 3 main ways,

1. Combination of the substance with oxygen is termed as oxidation.

Eg. $C (s) + O_2 (g) \longrightarrow CO_2 (g)$

2. Removal of Hydrogen

Eg. $H_2S + O \longrightarrow S + H2O$

3. Loss of electron(s) is also known as oxidation.

By loosing electron ,positive valency of element increases and negative valency of element decreases.

Eg. $Fe^{2+} \longrightarrow Fe^{3+} + e-$ (Increase in oxidation number)

REDUCTION

1. Removal of Oxygen from substance

CuO + 2H Cu + H2O

2. Additon of Hydrogen

C2H2 + 2H C2H4

3. Gain of electron,

By taking on electron positive valency is decreased and negative valency is increased.

$Fe^{3+} + e^{-} \longrightarrow$ Fe2+ (Decrease in Oxidation number.)

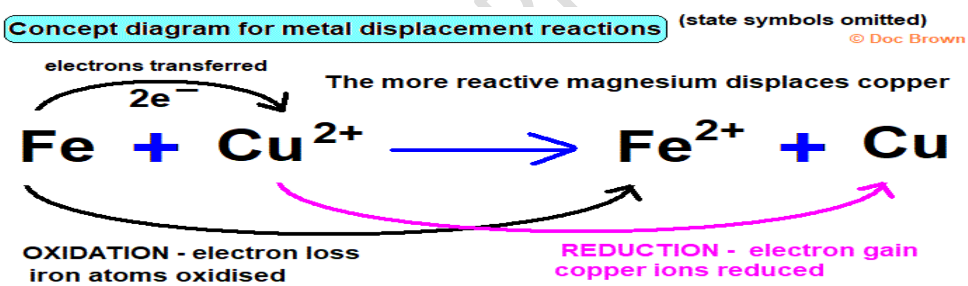
OXIDATION-REDUCTION REACTION

Oxidation-reduction reactions are the chemical processes in which a change in the valency of reacting elements or ions takes place. The valency of an element represents the number of electrons which the atoms take on or give up on reacting with other elements to form the compound.

Depending on the compound in which element is available, the valency of some elements varies

e.g. Iron can be bivalent or trivalent (in $FeCl_2$, $FeCl_3$, respectively), the manganese can have valencies from 2 to 7 (MnO, MnO_2, Mn_2O_3, Mn_2O_7).

Oxidation-reduction reaction is thus a process involving the transfer of electrons from one element or ion to another resulting in the change of the valency of reacting atoms or ions. Oxidizing agents oxidizes reducing agent by accepting their electron and itself get reduced,whereas Reducing agent reduces oxidizing agent by giving up their electron and itself get oxidised .



Processes Leading to Oxidation and Reduction	
Oxidation	**Reduction**
Complete loss of electrons (ionic reactions)	Complete gain of electrons (ionic reactions)
Shift of electrons away from an atom in a covalent bond	Shift of electrons towards an atom in a covalent bond
Gain of oxygen	Loss of oxygen
Loss of hydrogen by a covalent compound	Gain of hydrogen by a covalent compound
An increase in oxidation number	A decrease in oxidation number

DIFFERENCE BETWEEN REDUCING AGENT AND OXIDIZING AGENT

BASIS OF COMPARISON	**REDUCING AGENT**	**OXIDIZING AGENT**
DESCRIPTION	A reducing agent is an element or compound that has ability to lose or 'donate' an electron in a redox chemical reaction.	An oxidizing agent is a reactant that removes electrons from other reactants during a redox reaction.
ALTERNATIVE NAME	Electron donor	Electron acceptor
NATURE	A reducing agent is usually a metal or a negative ion.	An oxidizing agent is generally a non-metal or positive ion.
DURING REACTION	During the reaction, a reducing agent is oxidized and loses one or more electrons.	During the reaction, an oxidizing agent is reduced and gains one or more electrons.
STRONGEST REDUCING/OXIDIZING AGENT	Lithium is the strongest reducing agent in solution state whereas cesium is the strongest reducing agent in dry state.	Fluorine is the strongest oxidizing agent.
OXIDATION STATE	The oxidation state of a reducing agent increases during a redox reaction.	The oxidation state of oxidizing agent decreases during a redox reaction.
EXAMPLE	Examples of reducing agents include the earth metals, formic acid, oxalic acid and sulfite compound.	Examples of oxidizing agents include halogens, potassium nitrate and nitric acid.
CHEMICAL REACTION	Reduction reaction stores energy.	Oxidation reaction releases energy.
GENERALIZATION	All metals, hydrides and polymeric hydrides are reducing agents.	Almost all non-metals are oxidizing agents.
ELECTRONEGATIVITY	All the good reducing agents have the atoms which have low electronegativity.	All the good oxidizing agents have the atoms which have high electronegativity.

REDOX POTENTIAL

ORP (Reduction- oxidation potential) is a measure of tendency of chemical species to acquire electrons and there by get reduced,its measured in Volts(V) or mV (milli volts).

Eg- $Li^{+} + e^{-} \longrightarrow Li$ (3.04)

$Mg^{2+} + 2e^{-} \longrightarrow Mg$ (-2.38)

It can be calculated by measuring the potential difference of a cell in which oxidation reduction half cell is coupled with standard reference cell, i.e. standard hydrogen electrode.

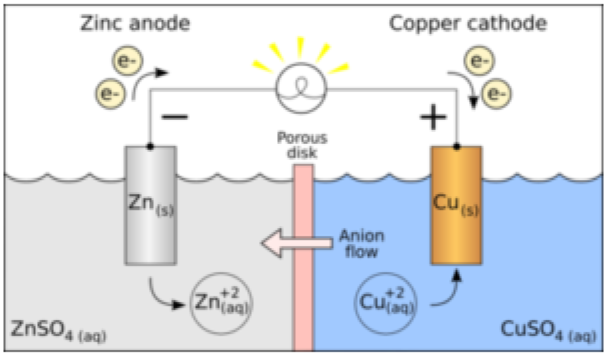
Oxidising agents gain electrons and get reduced while reducing agents lose electrons and get oxidised. This transfer of electrons leads to the changes in the valency of the atoms or ions. The positive valency of oxidised atom or ion is increased while that of reduced atom or ion is decreased. Oxidising and reducing agents may differ in strength i.e. chemical activity.

Strong oxidising agents have a pronounced tendency to accept/gain electrons and hence, they are having ability to take up the electrons from many reducing agents even relatively weak one. Weak oxidising agents have a much less pronounced tendency to gain electrons i.e. they can oxidise only strong reducing agents.

The direction of a redox reaction can be predicted provided some quantitative characteristic of the relative force involved is known. This characteristic is known as the 'Redox Potential.

It is possible to measure the potential difference between two systems by connecting them into a galvanic cell. Any galvanic element consists of two half elements. Each of which is oxidation-reduction couple i.e. a system consisting of the oxidised and the reduced form of the chemical element or ion.

The more powerful the oxidant of the pair, the weaker its reductant should be and vice versa; if Cl_2, is said to be a powerful oxidising agent, this means its atoms possess the pronounced ability to accept electrons, changing to Cl- . In other words, Cl should keep a strong hold on these electrons i. e. should be a weak reducing agent. One never comes across an absolutely pure oxidising or reducing agent. Their solutions always contain the products of their reduction or oxidation respectively.



Reaction:

At Zn anode, oxidation takes place (the metal loses electrons). This is represented in the following oxidation half-reaction.

$$Zn(s) \longrightarrow Zn2+ + 2e$$

At the Cu cathode, reaction takes place (electrons are accepted). This is represented in the following reduction half-reaction.

$$Cu2+ + 2e- \longrightarrow Cu(s)$$

Combined reaction:

$$Zn(s) + CuSO4(aq) \longrightarrow ZnSO4(aq) + Cu(s)$$