



**SHREE H. N. SHUKLACOLLEGE OF SCIENCE**

(AFFILIATED TO SAURASHTRA UNIVERSITY)

Shree H.N. Shukla College Campus Nr. Lalpari lake, Behind old Marketing  
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Amargadh, Bhichari, Rajkot-360001, Ph. No-9727753360

**F.Y.B.SC.(SEM-1)(CBCS)**

**NEW PROPOSED SYLLABUS-JUNE 2019**

**BIOCHEMISTRY(101)**

**PHYSICAL AND CHEMICAL ASPECTS OF BIOCHEMISTRY**

**UNIT -2 INTRODUCTION TO THERMODYNAMIC AND  
ELECTROCHEMISTRY**

Prepared by: kadchha jagruti.

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## UNIT:-2 Introduction to thermodynamic and electrochemistry

### **Introduction to thermodynamic system.**

- Thermodynamics deals with the concepts of heat and temperature and the inter-conversion of heat and other forms of energy.
- The four laws of thermodynamics govern the behaviour of these quantities and provide a quantitative description. William Thomson, in 1749, coined the term thermodynamics.
- To be specific, it explains how thermal energy is converted to or from other forms of energy and how matter is affected by this process.
- Thermal energy is the energy that comes from heat. This heat is generated by the movement of tiny particles within an object, and the faster these particles move, the more heat is generated.
- Thermodynamics applies to a wide variety of topic in science and engineering ,especially chemical engineering and mechanical engineering .

### **System and surroundings system**

- A thermodynamic system is a specific portion of matter with a definite boundary on which our attention is focused.
- The system boundary may be real or imaginary, fixed or deformable.
- System : A system in thermodynamic refers to that part of universe which is under consideration and properties of which are under observation .

**Surroundings:** The regions outside the boundaries of the system are called surroundings .

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Thus, Universe =system +surroundings.

## There are three types of systems:

- **Isolated System** – An isolated system cannot exchange energy and mass with its surroundings. The universe is considered an isolated system.
- **Closed System** – Across the boundary of the closed system, the transfer of energy takes place but the transfer of mass doesn't take place. Refrigerator, compression of gas in the piston-cylinder assembly are examples of closed systems.
- **Open System** – In an open system, the mass and energy both may be transferred between the system and surroundings. A steam turbine is an example of an open system.

## Law of thermodynamics

- Thermodynamics is principally based on a set of four laws which are universally valid when applied to systems that fall within the constraints implied by each.
- Thermodynamics laws define the fundamental physical quantities like energy, temperature and entropy that characterize thermodynamic systems at thermal equilibrium.
- These thermodynamics laws represent how these quantities behave under various circumstances.

There are four laws of thermodynamics and are given below:

- **Zeroth law of thermodynamics**
- **First law of thermodynamics**
- **Second law of thermodynamics**
- **Third law of thermodynamics**

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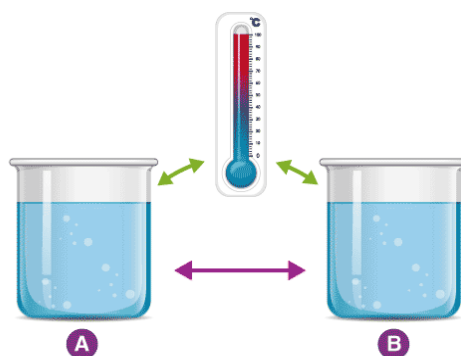
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## Zeroth law of thermodynamics

- If two systems are in thermal equilibrium with a third system, then they are also in thermal equilibrium with each other.
- It explains the principle of working of thermometer.
- This means that if system A is in thermal equilibrium with system C and system B is also in equilibrium with system C, then system A and B are also in thermal equilibrium.

### An example demonstrating the Zeroth Law



Consider two cups A and B, with boiling water.

When a thermometer is placed in cup A, it gets warmed up by the water until it reads 100 °C.

When it reads 100 °C, we say that the thermometer is in equilibrium with cup A. When we move the thermometer to cup B to read the temperature, it continues to read 100 °C.

The thermometer is also in equilibrium with cup B. By keeping in mind the zeroth law of thermodynamics, we can conclude that cup A and cup B are in equilibrium with each other.

The zeroth law of thermodynamics enables us to use thermometers to compare the temperature of any two objects that we like.

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## First Law of Thermodynamics

- First law of thermodynamics, also known as the law of conservation of energy, states that energy can neither be created nor destroyed, but it can be changed from one form to another.
- The first law of thermodynamics may seem abstract, but we will get a clearer idea if we look at a few examples of the first law of thermodynamics.

### **First Law of Thermodynamics Examples:**

- Plants convert the radiant energy of sunlight to chemical energy through photosynthesis. We eat plants and convert the chemical energy into kinetic energy while we swim, walk, breathe, and scroll through this page.
- Switching on light may seem to produce energy, but it is electrical energy that is converted.

## Second law of thermodynamic

*Heat cannot spontaneously flow from a colder location to a hotter location.*

The second law of thermodynamic state that ....

- 'A process can occur spontaneously only if the sum of the entropies of the system and its surroundings increases.
- The second law also states that the changes in entropy of the universe can never be negative.
- Entropy is the measure of the degree of randomness or disorderliness of a system.
- First law of thermodynamics is fundamental law of nature which deals with the conversion of energy but it does not state the conditions for conservation and direction of flow of energy.
- The second law of thermodynamic accounts for both.it is very fundamental law of nature and can be stated in a number of ways .

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## Third Law of thermodynamics

- The third law of thermodynamics states that the entropy of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero.
- Entropy, denoted by 'S', is a measure of the disorder/randomness in a closed system.
- It is directly related to the number of micro states (a fixed microscopic state that can be occupied by a system) accessible by the system, i.e. the greater the number of microstates the closed system can occupy, the greater its entropy. The micro state in which the energy of the system is at its minimum is called the ground state of the system.

## Concept of free energy

- **Gibbs free energy**, also known as the **Gibbs function, Gibbs energy, or free enthalpy**, is a quantity that is used to measure the maximum amount of work done in a thermodynamic system when the temperature and pressure are kept constant.
- Gibbs free energy is denoted by the symbol 'G'.
- Its value is usually expressed in Joules or Kilojoules. Gibbs free energy can be defined as the maximum amount of work that can be extracted from a closed system.
- The energy that is absolutely available for work is referred to as free energy.
- $\Delta G$  represents the change in free energy and is also termed as Gibbs free energy. It will be positive for endergonic reactions and negative for exergonic reactions.

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## Gibbs Free Energy Equation

Gibbs free energy is equal to the enthalpy of the system minus the product of the temperature and entropy. The equation is given as:

$$G = H - TS$$

Where,

G = Gibbs free energy

H = enthalpy

T = temperature

S = entropy

## Variations of the Equation

Gibbs free energy is a state function; hence it doesn't depend on the path. So, change in Gibbs free energy is equal to the change in enthalpy minus the product of temperature and entropy change of the system.

$$\Delta G = \Delta H - \Delta(TS)$$

If the reaction is carried out under constant temperature  $\{\Delta T=0\}$

$$\Delta G = \Delta H - T\Delta S$$

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This equation is called the Gibbs-Helmholtz equation.

$\Delta G > 0$ ; the reaction is non-spontaneous and endergonic

$\Delta G < 0$ ; the reaction is spontaneous and exergonic

$\Delta G = 0$ ; the reaction is at equilibrium

## Standard free energy

- It is the free energy change of a reaction under standard conditions. it is denoted by  $\Delta G$ .

**What is meant by standard free energy?**

- Standard free energy of formation is the free energy change that occurs when 1 mole of a compound forms from its component elements at standard conditions.

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## HIGH-ENERGY COMPOUNDS

### What are high energy compounds?

- High energy compounds are also called energy-rich compounds.
  - Compounds present in the biological system that when hydrolysed, produce free energy that is greater or equal to that of ATP ( $\Delta G$  is  $-7.3$  kcal/mol) are termed high energy compounds.
  - Low-energy compounds have an energy yield of less than  $-7.3$  kcal/mol.
  - High-energy bonds are found in the majority of high-energy compounds that produce energy upon hydrolysis.
  - Most of the high energy compounds contain phosphate groups and thus they are also termed high-energy phosphates.
- These high energy compounds are mainly classified into five groups:
1. Pyrophosphates
  2. Acyl phosphate
  3. Enol phosphate
  4. Thiol phosphate
  5. Phosphagens or guanido phosphates

### Types of High Energy Compounds

The energy released during catabolism is captured in the form of a group of compounds called high energy phosphates. There are also high energy compounds belonging to the sulphur group like acetyl CoA, succinyl CoA and fatty acyl CoA.

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## High Energy Compounds Examples

- **Pyrophosphates**

Pyrophosphate energy bonds are nothing but acid anhydride bonds. Condensation of acid groups (primarily phosphoric acid) or their derivatives results in the formation of these bonds. **ATP** ( $\Delta G = -7.3$  kcal/mol) is an example of a pyrophosphate. It has two phosphoanhydride diphosphate bonds.

- **Acyl phosphates**

The reaction between the carboxylic acid group and the phosphate group forms a high energy bond in this compound. **1,3-bisphosphoglycerate** ( $\Delta G = -11.8$  kcal/mol) is an example of acyl phosphate.

- **Enol phosphates**

The enol phosphate bond is present here. It is formed when a phosphate group binds to a hydroxyl group that is bound to a double-bonded carbon atom. As an example, consider **phosphoenolpyruvate** ( $\Delta G = -14.8$  kcal/mol).

- **Thiol phosphates**

There is no high energy phosphate bond here. Instead, a high energy thioester bond is found here. Thioester bonds are formed by the reaction of thiol and carboxylic acid groups. **Acetyl CoA** ( $\Delta G = -7.7$  kcal/mol) is an example.

- **Phosphagens**

Guanidine phosphate bonds are present in phosphagens or guanido phosphates. The phosphate group is attached to the guanidine group to form it. **Phosphocreatine** ( $\Delta G = -10.3$  kcal/mol) is the most important compound with this type of bond.

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## High energy compounds application in biochemistry

### High energy compounds

- (a) Are compounds that release a large amount of energy during respiration.
- (b) Are produced when ATP loses two terminal phosphate groups.
- (c) Are produced in respiration only
- (d) Are referred to as those compounds which link exergonic and endergonic reactions.



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## Introduction to electrochemistry

### • **What Is Electrochemistry?**

- **Electrochemistry** is the subdiscipline of Chemistry that deals with the study of the relationship between electrical energy and chemical changes.
- Chemical reactions that involve the input or generation of electric currents are called electrochemical reactions. Such reactions are broadly classified into two categories.

- A. Production of chemical change by electrical energy, i.e., the phenomenon of electrolysis .
- B. Conversion of chemical energy into electrical energy, i.e., the generation of electricity by spontaneous redox reactions.

- Electricity can be produced when electrons move from one element to another in certain types of reactions (such as redox reactions).
- Typically, electrochemistry deals with the overall reactions when multiple redox reactions occur simultaneously, connected via some external electric current and a suitable electrolyte.
- In other words, electrochemistry is also concerned with chemical phenomena that involve charge separation (as seen commonly in liquids such as solutions).
- The dissociation of charge often involves charge transfer that occurs homogeneously or heterogeneously between different chemical species.

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## Electrochemical cells

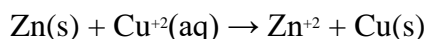
- A spontaneous chemical process is one which can take place on its own, and in such a process, the Gibbs free energy of a system decreases.
- In electrochemistry, spontaneous reaction (redox reaction) results in the conversion of chemical energy into electrical energy.
- The reverse process is also possible where a non-spontaneous chemical reaction occurs by supplying electricity.
- These interconversions are carried out in equipment called an electrochemical cell.

## Types of Electrochemical Cell

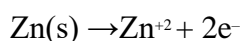
**Electrochemical cells are of two types: galvanic cells and electrolytic cells**

### Galvanic Cell

- The galvanic cell converts chemical energy into electrical energy, i.e., electricity can be obtained with the help of a redox reaction.
- The oxidation and reduction take place in two separate compartments. Each compartment consists of an electrolyte solution and a metallic conductor, which acts as an electrode.
- The compartment containing the electrode and the solution of the electrolyte is called half cells.
- For example, the Daniell cell is a galvanic cell in which zinc and copper are used for a redox reaction to take place.



**At anode (oxidation half),**



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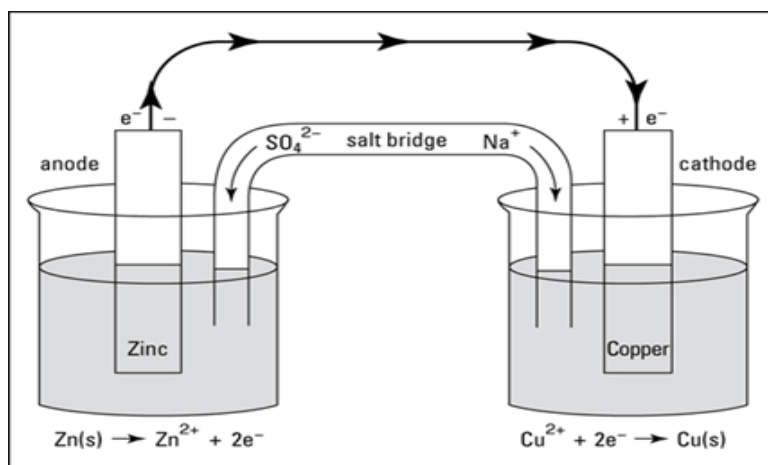
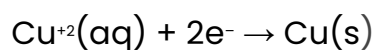
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At cathode( reduction half),



## Salt bridge:

- The salt bridge is usually an inverted U-tube filled with a concentrated solution of inert electrolytes.
- It is used to maintain the charge balance and to complete the circuit by allowing the flow of ions through it. It contains a gel in which inert electrolytes like  $\text{KNO}_3$  or  $\text{K}_2\text{SO}_4$  are mixed.
- Through the salt bridge, negative ion flows towards the anode and positive ion flows to the cathode, and the charge balance is maintained, and the cell keeps on functioning.

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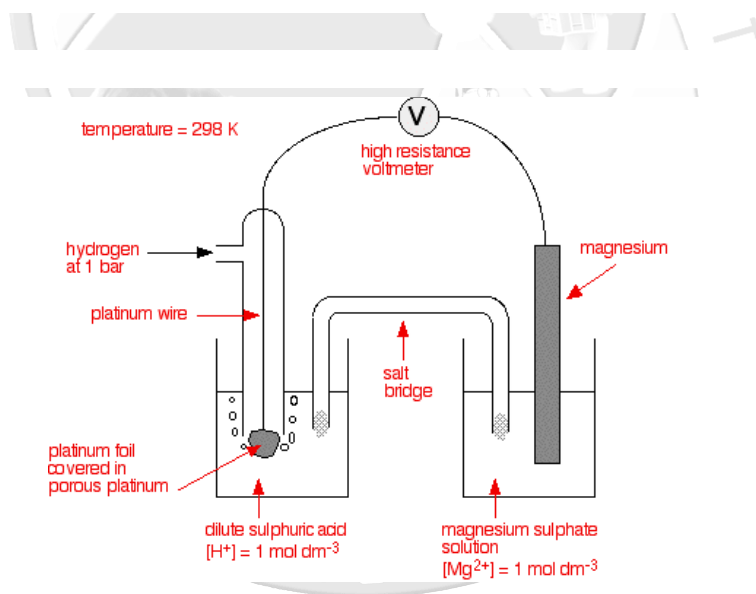
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## Electrode potential:

- In a galvanic cell, when two-electrode are dipped in their respective ion, there is a tendency for one of the electrodes (anode) to undergo oxidation, whereas the ion of the other electrode (cathode) has the tendency to gain an electron.
- This tendency of losing of electrons (oxidation) or gaining of electrons (reduction) is called electrode potential.

## Standard electrode potential ( $E^{\circ}$ ):

- Standard electrode potential is defined as the electrode potential of an electrode relative to a standard hydrogen electrode under standard conditions. The standard conditions taken are as follows:
  - 1 molar concentration of each ion in the solution.
  - A temperature of 298 K.
  - 1 bar pressure.



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## NERNST EQUATION : (Derivation of Nernst equation)

### What Is Nernst Equation?

- The **Nernst equation** provides the relation between the cell potential of an electrochemical cell, the standard cell potential, temperature, and the reaction quotient.
- Even under non-standard conditions, the cell potentials of electrochemical cells can be determined with the help of the Nernst equation.
- The **Nernst equation is often used to calculate the cell potential** of an electrochemical cell at any given temperature, pressure, and reactant concentration. The equation was introduced by a German chemist, Walther Hermann Nernst.

### Expression of Nernst Equation

- The Nernst equation is an equation relating the capacity of an atom/ion to take up one or more electrons (reduction potential) measured at any conditions to that measured at standard conditions (standard reduction potentials) of 298 K and one molar or one atmospheric pressure.

### Nernst Equation for Single Electrode Potential

$$E_{\text{cell}} = E^{\circ} - [RT/nF] \ln Q$$

Where,

- $E_{\text{cell}}$  = cell potential of the cell
- $E^{\circ}$  = cell potential under standard conditions
- R = universal gas constant
- T = temperature
- n = number of electrons transferred in the redox reaction
- F = Faraday constant
- Q = reaction quotient

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- The calculation of single electrode reduction potential ( $E_{\text{red}}$ ) from the standard single electrode reduction potential ( $E^{\circ}_{\text{red}}$ ) for an atom/ion is given by the Nernst equation.
- $\Rightarrow$  **Also Read:** Redox Reactions
- For a reduction reaction, the Nernst equation for a single electrode reduction potential for a reduction reaction
- $M^{n+} + ne^{-} \rightarrow nM$  is;
- $E_{\text{red}} = E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} - [2.303RT/nF] \log [1/[M^{n+}]]$

Where,

- R is the gas constant = 8.314 J/K Mole
- T = absolute temperature,
- n = number of mole of electron involved,
- F = 96487 ( $\approx$ 96500) coulomb/mole = charge carried by one mole of electrons.
- $[M^{n+}]$  = active mass of the ions. For simplicity, it may be taken as equal to the molar concentration of the salt.
- 

## Nernst Equation at 25°C

For measurements carried out 298 K, the Nernst equation can be expressed as follows:

$$E = E^{\circ} - 0.0592/n \log_{10} Q$$

Therefore, as per the Nernst equation, the overall potential of an electrochemical cell is dependent on the reaction quotient.

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## Derivation of Nernst Equation

Consider a metal in contact with its own salt-aqueous solution. Reactions of metal losing an electron to become an ion and the ion gaining an electron to return to the atomic state are equally feasible and are in an equilibrium state.



In the reduction reaction, 'n' moles of an electron is taken up by the ion against a reduction potential of  $E_{red}$ .

1. The work done in the movement of electron

$$W_{red} = nFE_{red}$$

Where,

- **F is Faraday = 96487 coulomb = electrical charge carried by one mole of electrons .**

2. Change in the Gibbs free energy is an indication of spontaneity, and it is also equal to the maximum useful work (other than volume expansion) done in a process.

Combining work done and Gibbs free energy change:

$$W_{red} = nFE_{red} = -\Delta G \text{ or } \Delta G = -nFE_{red}$$

3. Change in the free energy at standard conditions of 298 K and one molar /one atmospheric pressure conditions is  $\Delta G^{\circ}$ . From the above relation, it can be written that

$$\Delta G^{\circ} = -nFE^{\circ}_{red}$$

Where,

- **$E^{\circ}_{red}$  is the reduction potential measured at standard conditions.**

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4. During the reaction, concentration keeps changing, and the potential also will decrease with the rate of reaction.

To get the maximum work or maximum free energy change, the concentrations have to be maintained the same. This is possible only by carrying out the reaction under a reversible equilibrium condition.

For a reversible equilibrium reaction, Van't Hoff isotherm says:

$$\Delta G = \Delta G^\circ + RT \ln K$$

Where,

- K is the equilibrium constant
- $K = \text{Product/Reactant} = [M]^n/[M^{n+}]$
- R is the Gas constant = 8.314J/K mole
- T is the temperature on the Kelvin scale.

5. Substituting for free energy changes in Van't Hoff equation,

$$-nFE_{\text{red}} = -nFE_{\text{red}}^\circ + RT \ln [M]/[M^{n+}] = -nFE_{\text{red}}^\circ + 2.303 RT \log [M]^n/[M^{n+}]$$

Dividing both sides by  $-nF$ ,

$$E_{\text{red}} = E_{\text{red}}^\circ - \frac{2.303RT}{nF} \log \frac{[M]^n}{[M^{n+}]}$$

or,

$$EM^{n+}/M = E^\circ M^{n+}/M - \frac{2.303RT}{nF} \log \frac{[M]^n}{[M^{n+}]}$$

The activity of the metal is always considered as equal to unity.

$$E_{\text{red}} = E_{\text{red}}^\circ \text{ - OR}$$

$$EM^{n+}/M = E^\circ M^{n+}/M - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

This relation connecting reduction potential measurable at conditions other than standard conditions to the standard electrode potential is the Nernst equation.

For reactions conducted at 298 K but different concentrations, the Nernst equation is:

$$\begin{aligned} EM^{n+}/M &= E^\circ M^{n+}/M - \frac{2.303 \times 8.314 \times 293}{n \times 96500} \log \frac{1}{[M^{n+}]} \\ &= E^\circ M^{n+}/M - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \end{aligned}$$

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Shree H.N. Shukla College Campus Nr. Lalpari lake, Behind old Marketing Yard,

Amargadh, Bhichari, Rajkot-360001, Ph. No-9727753360

## Nernst Equation Applications

The Nernst equation can be used to calculate the following:

- Single electrode reduction or oxidation potential at any conditions .
- Standard electrode potentials .
- Comparing the relative ability as a reductive or oxidative agent .
- Finding the feasibility of combining such single electrodes to produce an electric potential .
- Emf of an electrochemical cell .
- Unknown ionic concentrations .
- The pH of solutions and solubility of sparingly soluble salts can be measured with the help of the Nernst equation.

## Limitations of Nernst Equation

- The activity of an ion in a very dilute solution is close to infinity and can, therefore, be expressed in terms of the ion concentration.
- However, the ion concentration is not equal to the ion activity for solutions having very high concentrations.
- In order to use the Nernst equation in such cases, experimental measurements must be conducted to obtain the true activity of the ion.
- Another shortcoming of this equation is that it cannot be used to measure cell potential when a current flows through the electrode.
- This is because the current flow affects the ions' activity on the surface of the electrode.
- Also, additional factors such as resistive loss and overpotential must be considered when a current flows through the electrode.

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## Oxidation and reduction reaction

- The chemical reactions which involve the transfer of electrons from one chemical substance to another.
- These electron-transfer reactions are termed as oxidation-reduction reactions or **redox** reactions.

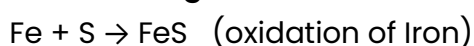
### What is Oxidation?

- According to Classical or earlier concept oxidation is a process which involves the addition of oxygen or any electronegative element or the removal of hydrogen or any electropositive element.
- According to electronic concept oxidation is defined as the process in which an atom or ion loses one or more electrons.
- Oxidation reactions involve:

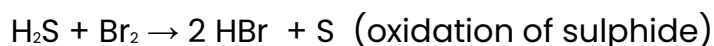
#### 1. Addition of oxygen:



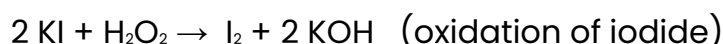
#### 2. Addition of electronegative element:



#### 3. Removal of hydrogen:



#### 4. Removal of electropositive elements:



**Oxidising agent** is a substance which brings about oxidation. In the above examples  $\text{O}_2$ , S,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{H}_2\text{O}_2$  are **oxidising agents**.

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## What is Reduction?

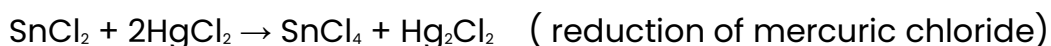
- According to Classical or earlier concept reduction is a process which involves the addition of hydrogen or any electropositive element or the removal of oxygen or any electronegative element.
- According to electronic concept reduction is defined as the process in which an atom or ion gains one or more electrons.

Reduction reactions involve:

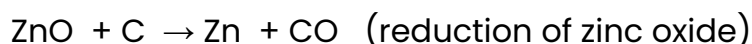
### 1. Addition of hydrogen:



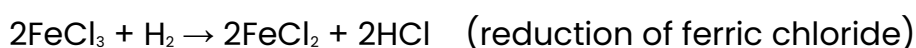
### 2. Addition of electropositive element:



### 3. Removal of oxygen



### 4. Removal of electronegative element



- **Reducing agent** is a substance which brings about reduction. In the above examples H<sub>2</sub>, HgCl<sub>2</sub> and C **are Reducing agents.**
- **Note:** A substance, which undergoes oxidation, acts as a reducing agent while a substance, which undergoes reduction, acts as an oxidising agent.

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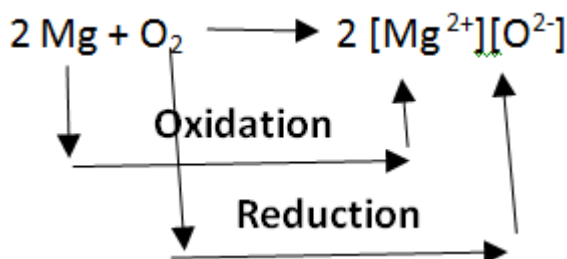
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## Redox potential reaction

- Oxidation and Reduction reactions are always interlinked. Because electrons are neither created nor destroyed in a chemical reaction, oxidation and reduction always occur in pairs, it is impossible to have one without the other.
- In the below reaction Magnesium gets oxidized by losing two electrons to oxygen which gets reduced by accepting two electrons from magnesium.



- Since oxidation and reduction cannot occur individually, they as a whole are called 'Redox Reactions'.
- The reactant that oxidizes the other reactants is called as the Oxidizing agent and reactant that reduces is called Reducing agent.
- There is quite some confusion about the aspect of whether oxidizing agents accept or giveaway electron

**The three common redox reactions are discussed below:**

**1. Combustion reaction** – It is a type of redox reaction which occurs between molecular oxygen and compound to form oxygen-containing products.



**2. Disproportionation reaction** – It is a type of redox reaction where a single reactant is reduced and oxidized. It is also known as an auto-oxidation reaction .



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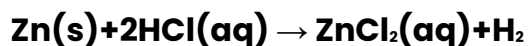
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### 3. Single replacement reaction

- It is a type of redox reaction that involves two elements switching places within a compound. It is also known as a single displacement reaction.



### Role in biological reaction

- cellular respirations .
- photosynthesis



**THANK YOU**

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