ELECTROCHEMISTRY
NERNST EQUATION

❖ STANDARD REDUCTION POTENTIAL (SRP) AND STANDARD HYDROGEN ELECTRODE: -

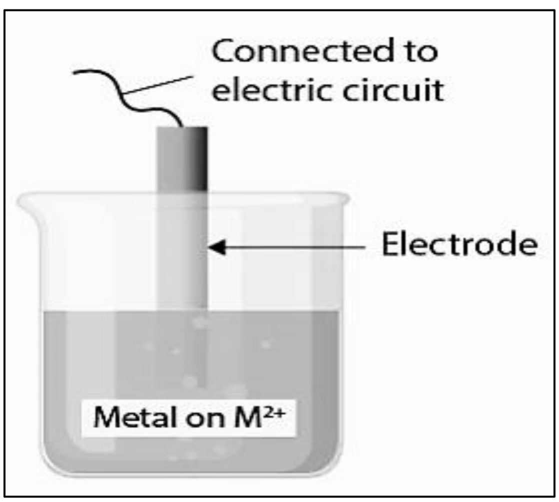
Reduction Potential?

Reduction involves gain of electrons, so the tendency of an electrode to gain electrons is called its reduction potential. The equilibrium potential difference between the metal electrode and the solution surrounding it is called the electrode potential. It is also defined as the tendency of an electrode to lose or gain electrons

Reduction Potential Explanation

When a piece of metal is immersed in a solution of its own ions, a potential difference is created at the interface of the metal and the solution. The magnitude of the potential difference is a measure of the tendency of electrodes to undergo oxidation or reduction or the tendency to lose or gain electrons.

The metal and ion represent the half cell and the reaction is half-reaction. The immersed metal is an electrode and the potential is due to reaction at the interface of the electrode and the solution is called the electrode potential. Thus, electrode potential is the tendency of an electrode to lose or gain electrons. If the reduction takes place at the electrode, it is termed reduction potential.



If the oxidation takes place at the electrode, it is called the oxidation potential

$M \rightarrow M^{2+} + 2e^-$

As metal ions start depositing on the metal surface this develops a positive charge on the metal rod. Since oxidation is just a reverse of reduction therefore reduction potential is obtained from the oxidation potential by simply changing the sign.

In general, for an electrode

Oxidation potential = – Reduction potential

For example, in a zinc electrode, the standard oxidation potential is represented as

$E^o (Zn/Zn^{2+}) = 0.76V$

and standard reduction potential as

$E^o (Zn^{2+}/Zn) = -0.76V$

It is a common practice to express all the electrode potentials as reduction potentials.

More recently the reduction potential has been adopted by the International Union of Pure and Applied Chemistry (IUPAC) for the designation of electrode potential.

When the half-cell reaction is carried out at a temperature of 298K and the electrode is suspended in a solution of one molar concentration, the electrode potential is termed the standard electrode potential and is represented by E^o. The Standard electrode potential E^o enables one to assess the thermodynamics activity of various chemical substances. But there are no methods available by which we can measure its absolute value. The electrode potential of an electrode is measured with respect to a standard hydrogen electrode.

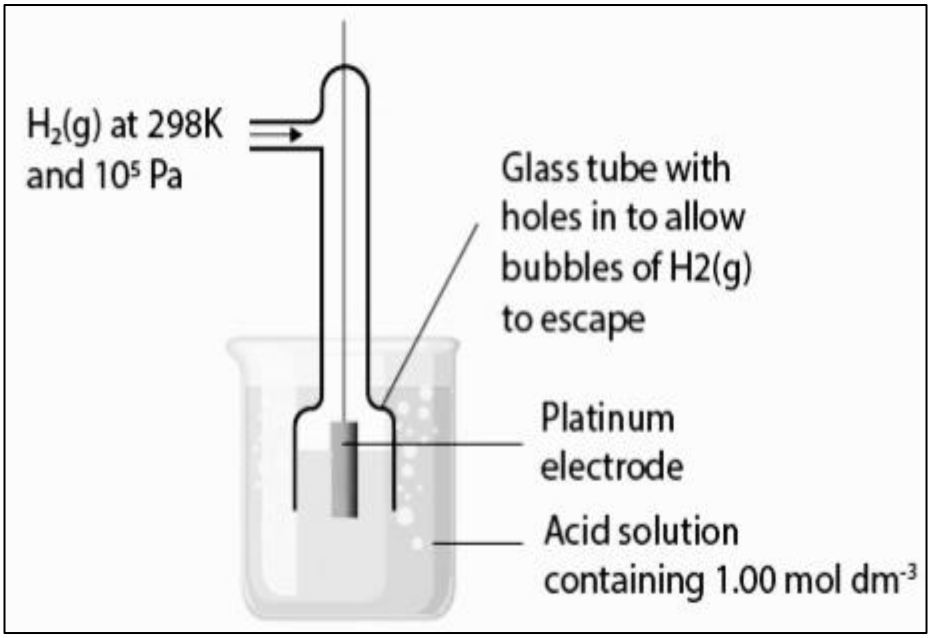
The electrode potential of an electrode depends upon concentration of ions in solution in contact with metal. Simply oxidation potential of an electrode is inversely proportional to the concentration of ions and the reduction potential is directly proportional to the concentration of ions.

Half cells

Being a cell, a battery contains two half cells separated by an electrolyte. The electrodes are needed to connect the half cells to an external circuit. Each electrode may act as part of a redox couple, but neither has to be. The standard conditions for the hydrogen half-cell are concentration of hydrogen [H^+(AQ)], pressure of hydrogen gas 10^5Pa and temperature 298K.

The standard hydrogen half-cell is used as a reference half-cell and all other half-cells are measured against it. A list of electrode potentials has been generated relative to the standard hydrogen half-cell. The half-reaction in this half-cell is

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$



Electrodes potentials vary with temperature and so a standard temperature is defined. This is 298K. Altering the concentration of any ions appearing in the half-reactions also affects the voltages, so a standard concentration of 1.00 mol dm^{-3} is chosen. Standard pressure is 10^5Pa.The potential of a standard hydrogen half-cell is defined as 0.0V a value chosen for convenience.

The standard electrode potential of a half-cell E^o is defined as the potential difference between the half cell and a standard hydrogen half-cell. Eo Values have a sign depending on whether the half-cell is at a higher or lower positive potential than the standard hydrogen half-cell. Measurements are made at 298K with the metal dipping into a 1.00 mol dm^{-3} solution of a salt of the metal.

STANDARD HYDROGEN ELECTRODE: -

Electrode potential is a measure of reducing power of any element. It is also called standard reduction potential. Standard Hydrogen Electrode is used as a reference electrode when calculating the standard electrode potential of a half cell.

The Standard Hydrogen Electrode is often abbreviated to SHE, and its standard electrode potential is declared to be 0 at a temperature of 298K. This is because it acts as a reference for comparison with any other electrode.

The half-cell reaction of SHE can be written as follows:

- $2H^+ (aq) + 2e^- \rightarrow H_2 (g)$
- The reaction given above generally takes place on a platinum electrode. The pressure of the hydrogen gas present in this half-cell equals 1 bar.
- Uses of Platinum in the Standard Hydrogen Electrode

Platinum is used in the Standard Hydrogen Electrode due to the following reasons:

- Platinum is a relatively inert metal which does not corrode easily.
- Platinum has catalytic qualities which promote the proton reduction reaction.
- The surface of platinum can be covered with platinum black, a fine powder of platinum. This type of platinum electrode is called a platinized platinum electrode.
- Platinum also improves the reaction kinetics by adsorbing hydrogen at the interface.

Standard Hydrogen Electrode Construction

The parts that make up a Standard Hydrogen Electrode are listed below.

A platinum electrode is covered in finely powdered platinum black (platinized platinum electrode).

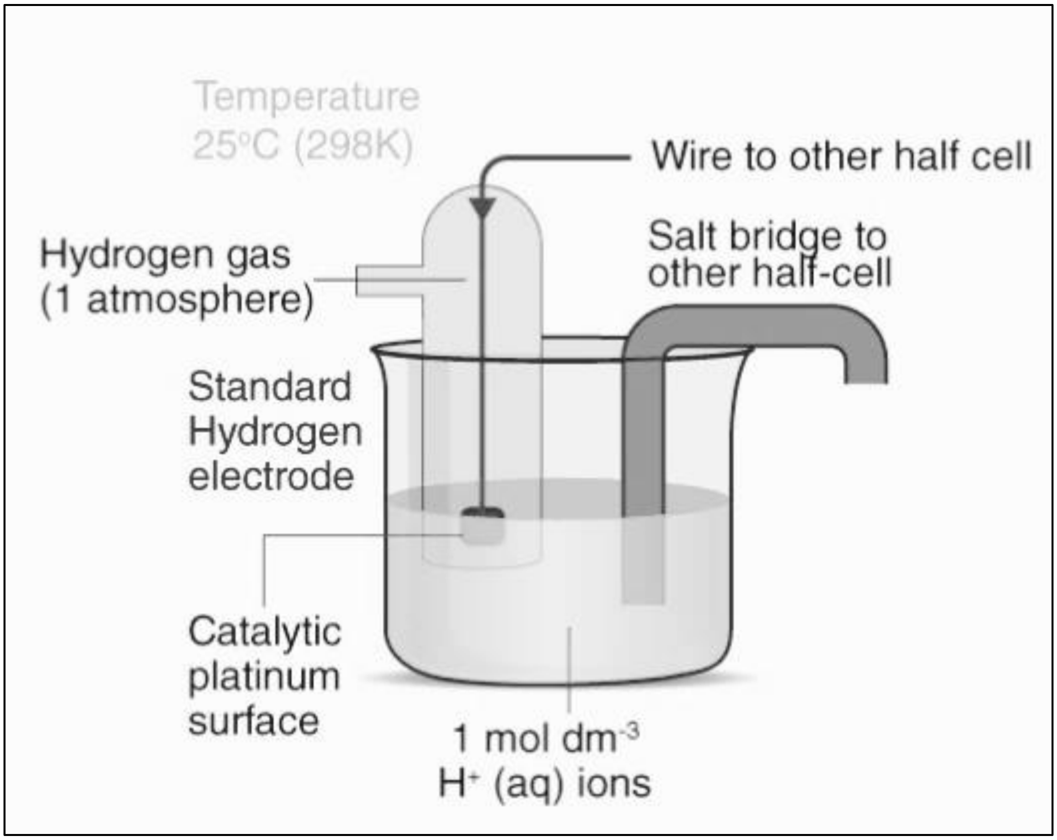
A hydrogen blows. A solution of acid having an H^+ molarity of 1 mole per cubic decimeter.

SHE also contains a hydro seal which is used to prevent the interference of oxygen.

The other half-cell of the entire Galvanic cell must be attached to the Standard Hydrogen Electrode through a reservoir in order to create an ionically conductive path. This can be done through a direct connection, through a narrow tube, or even through the use of a salt bridge.

Standard Hydrogen Electrode Diagram

A labelled diagram of a standard hydrogen electrode is provided below. In SHE, a salt bridge is used to link SHE with the other half cell.



The platinized platinum surface has a very high adsorption activity. Therefore, this surface must be protected from atmospheric oxygen as well as from organic substances. Substances such as arsenic and sulphur compounds can deactivate or poison the catalyst.

NERNST EQUATION: -

The Nernst equation provides a 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 named Walther Hermann Nernst.

Expression of Nernst Equation: -

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 298K and one molar or one atmospheric pressure.

With the help of Nernst equation,

we can calculate the electrode potential of electrode or EMF of cell.

Where - E^0 = standard electrode potential

R = gas constant

T = temperature (in K)

F = Faraday (96500 coulomb mol^{-1})

n = no. of e^- gained or loosed in balanced equation.

or = E° –

Let, in the cell :

at Anode : $M_1 \rightarrow M_1^{+n} + ne^-$

for this reaction – ....(1)

at Cathode : $M_2^{+n} + ne^- \rightarrow M_2$

for this reaction – ....(2)

Note : Concentration of solid taken as unity.

so $[M_1] = [M_2] = 1$

We know that EMF of cell is

$$EMF = \underset{(Anode)}{E_{oxi}} + \underset{(Cathode)}{E_{red.}}$$

By adding equation (1) & (2) we get :

$$(E^0_{axi} + E^0_{rad}) - \frac{0.0591}{n}[\log[M_1^{--1}] - \log[M_2^{-0}]]$$

$$EMF = E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[M_1^{-n}]}{[M_2^{-n}]}$$

Ex. The 0.1M copper sulphate solution in which copper electrode is dipped at 25°C. Calculate the electrode potential of copper electrode [Given E^0 Cu^{+2} / Cu = 0.34V]

Sol. $Cu^{+2} + 2e^{-} \rightarrow Cu$

$$E_{red} = E^0_{red} - \frac{0.0591}{n} \log \frac{[Product]}{[Reactant]}$$

here n = 2

so $E = 0.34 \quad \frac{0.0591}{2} \quad - \log 10$

$= 0.34 - 0.03 = 0.31$ Volts

Ex. The EMF of the cell