NERNST EQUATION

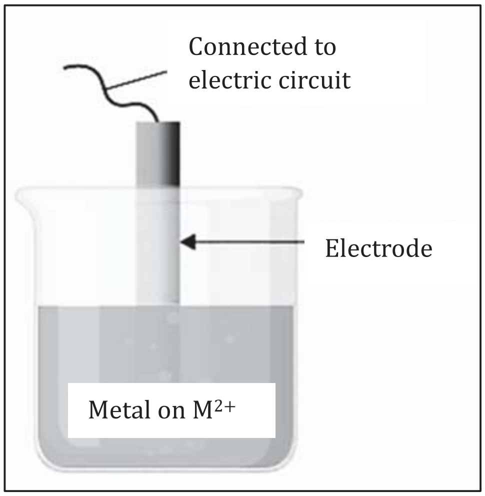
Standard Reduction Potential (Srp) And Standard Hydrogen Electrode

Reduction is characterized by the acquisition of electrons, and the inclination of an electrode to gain electrons is termed its reduction potential. The equilibrium potential difference existing between the metal electrode and the adjacent solution is referred to as the electrode potential. Alternatively, it is described as the predisposition of an electrode to either loss or gain electrons.

Reduction Potential Explanation

When a metal piece is placed in a solution containing its ions, a potential difference arises at the interface between the metal and the solution. The magnitude of this potential difference serves as an indicator of the electrodes' inclination toward oxidation or reduction, reflecting their propensity to either loss or gain electrons.

In this setup, the metal and its ions constitute the half-cell, and the corresponding reaction is referred to as a half-reaction. The metal immersed in the solution functions as an electrode, and the potential arising from the reaction at the electrode-solution interface is termed the electrode potential. Therefore, the electrode potential signifies the electrode's predisposition to either loss or gain electrons. If the electrode undergoes reduction, it is specifically known as reduction potential.



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

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

As metal ions begin to accumulate on the metal surface, a positive charge emerges on the metal rod. Given that oxidation is essentially the reverse of reduction, the reduction potential can be derived from the oxidation potential by merely 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

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

reduction potential for the standardized designation of electrode potential. When the half-cell reaction occurs at a temperature of 298K, and the electrode is immersed in a solution with a concentration of one molar, the resulting electrode potential is termed the standard electrode potential, denoted as E^o. The standard electrode potential, E^o, serves as a means to evaluate the thermodynamic activity of various chemical substances. However, there are currently no available methods to directly measure its absolute value. To determine the electrode potential of an electrode, it is measured in relation to a standard hydrogen electrode.

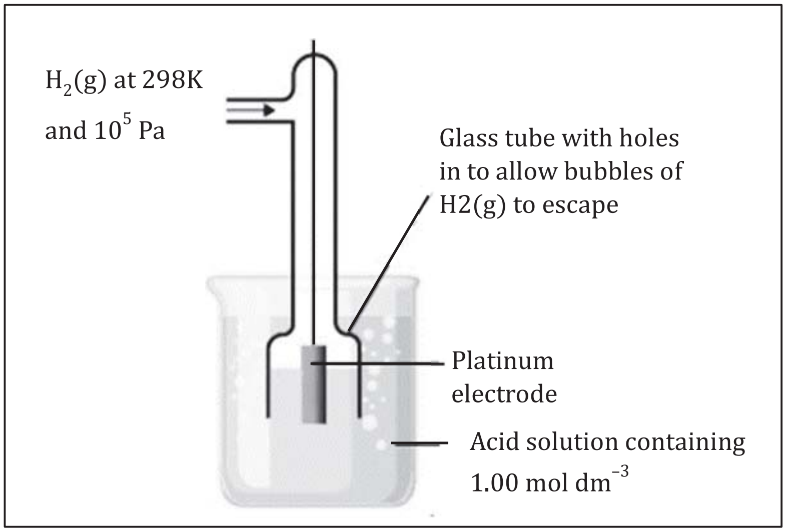
The electrode potential of an electrode is influenced by the concentration of ions in the solution in contact with the metal. Specifically, the oxidation potential of an electrode is inversely proportional to the concentration of ions, while the reduction potential is directly proportional to the concentration of ions.

Half cells

As a cellular device, a battery comprises two half-cells divided by an electrolyte. Electrodes play a crucial role in linking the half-cells to an external circuit. While each electrode may function as part of a redox couple, it is not a mandatory requirement. The standard conditions for the hydrogen half-cell include a concentration of hydrogen ions [H^+(AQ)], a hydrogen gas pressure of 10^5 Pa, and a temperature of 298 K.

The standard hydrogen half-cell serves as a reference point, against which all other half-cells are measured. A compilation of electrode potentials has been established with reference to the standard hydrogen half-cell.

The half-reaction in this half-cell is: $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$



Electrode potentials exhibit temperature dependence, necessitating the establishment of a standard temperature, which is set at 298K. To ensure consistency, a standard concentration of 1.00 mol dm^{-3} for ions involved in half-reactions is selected, and the standard pressure is maintained at 10^5 Pa. The potential of a standard hydrogen half-cell is arbitrarily defined as 0.0V for convenience.

The standard electrode potential (E^o) of a half-cell is defined as the potential difference between that half-cell and a standard hydrogen half-cell. The sign of E^o values indicates whether the half-cell possesses a higher or lower positive potential compared to the standard hydrogen half-cell. Measurements are conducted at 298K, with the metal immersed in a 1.00 mol dm^{-3} solution of a salt of the metal.

Standard Hydrogen Electrode

Electrode potential serves as an indicator of the reducing power of an element and is commonly referred to as standard reduction potential. The Standard Hydrogen Electrode, abbreviated as SHE, is employed as a reference electrode in determining the standard electrode potential of a half-cell.

The standard electrode potential of the SHE is defined as 0 at a temperature of 298K, making it a benchmark for comparing with other electrodes.

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.

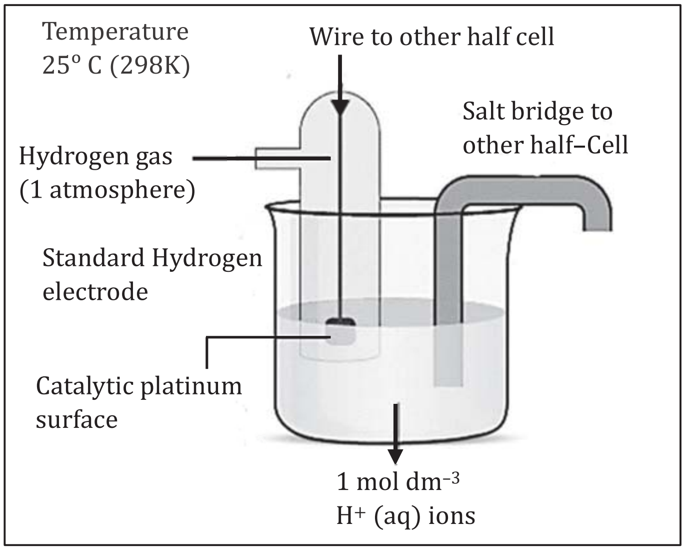
Standard Hydrogen Electrode Construction

The components constituting a Standard Hydrogen Electrode are detailed below:

1. A platinum electrode coated with finely powdered platinum black, forming a platinized platinum electrode.
2. A stream of hydrogen gas.
3. An acidic solution with an H^+ molarity of 1 mole per cubic decimeter.
4. The SHE includes a hydroseal designed to prevent interference from oxygen.
5. To establish an ionically conductive pathway, the other half-cell of the Galvanic cell must be connected to the Standard Hydrogen Electrode via a reservoir. This connection can be established directly, through a narrow tube, or by utilizing a salt bridge.

Standard Hydrogen Electrode Diagram

Below is a labeled diagram of a Standard Hydrogen Electrode. In the SHE setup, a salt bridge is employed to connect the SHE with the other half-cell.



The surface of platinized platinum exhibits a notably high adsorption activity. Consequently, it is imperative to shield this surface from atmospheric oxygen and organic substances. Catalyst deactivation or poisoning can occur in the presence of substances like arsenic and sulfur compounds.

Nernst Equation

Nernst Equation for cell

The Nernst equation establishes a connection between the cell potential of an electrochemical cell, the standard cell potential, temperature, and the reaction quotient. It allows for the determination of electrochemical cell potentials even when operating under non-standard conditions. Frequently applied to calculate the cell potential under specific temperatures, pressures, and reactant concentrations, the Nernst equation was introduced by the German chemist Walther Hermann Nernst.

Expression of Nernst Equation

The Nernst equation establishes a relationship between the electron-accepting capacity of an atom or ion (reduction potential) measured under specific conditions and its measurement under standard conditions (standard reduction potentials) at 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

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

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

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

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

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

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

here $n = 2$

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

$= 0.34 - 0.03 = 0.31$ Volts