5.2 Electrode Potential

Standard electrode potential is a measurement of the potential for equilibrium. There is a potential difference between the electrode and the electrolyte called the potential of the electrode. When unity is the concentrations of all the species involved in a semi-cell, the electrode potential is known as the standard electrode potential.

Electrode Potential Definition

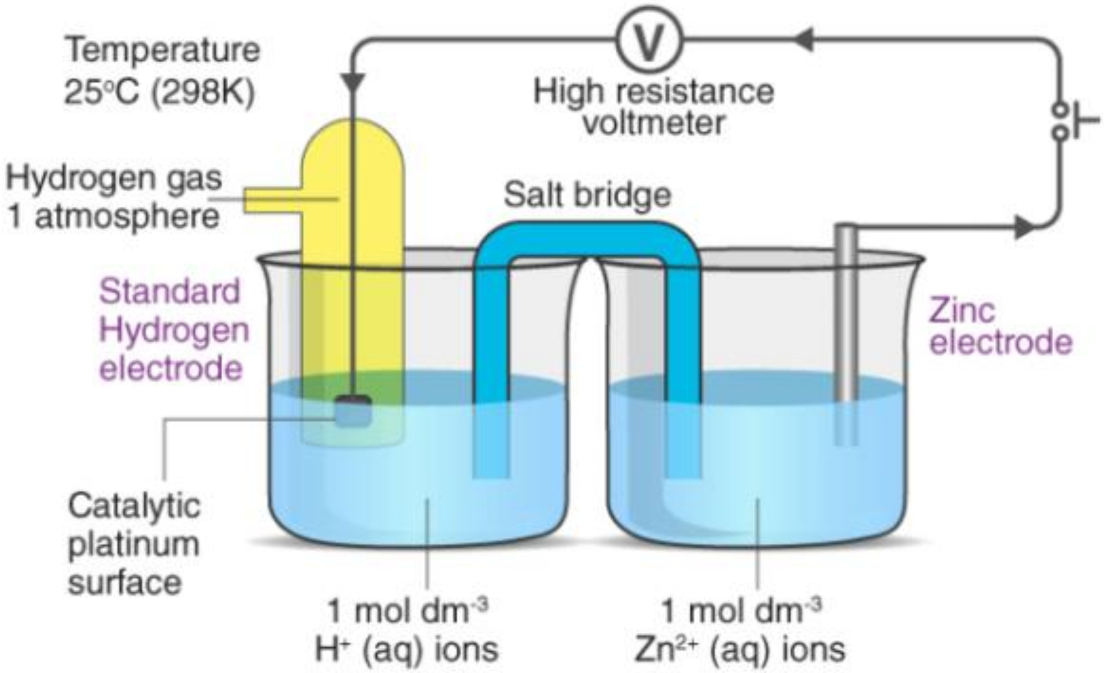
Under standard conditions, the standard electrode potential occurs in an electrochemical cell say the temperature = 298K, pressure = 1atm, concentration = 1M. The symbol 'E^o_{cell}' represents the standard electrode potential of a cell.

Significance of Electrode Potential

- All electrochemical cells are based on redox reactions, which are made up of two half-reactions.
- The oxidation half-reaction occurs at the anode and it involves a loss of electrons.
- Reduction reaction takes place at the cathode, involving a gain of electrons. Thus, the electrons flow from the anode to the cathode.
- The electric potential that arises between the anode and the cathode is due to the difference in the individual potentials of each electrode *(which are dipped in their respective electrolytes)*.
- The cell potential of an electrochemical cell can be measured with the help of a voltmeter. However, the individual potential of a half-cell cannot be accurately measured alone.
- It is also important to note that this potential can vary with a change in pressure, temperature, or concentration.
- In order to obtain the individual reduction potential of a half-cell, the need for standard electrode potential arises.
- It is measured with the help of a reference electrode known as the standard hydrogen electrode (abbreviated to SHE). ***The electrode potential of SHE is 0 Volts.***
- The standard electrode potential of an electrode can be measured by pairing it with the SHE and measuring the cell potential of the resulting galvanic cell.
- The oxidation potential of an electrode is the negative of its reduction potential. Therefore, the standard electrode potential of an electrode is described by its standard reduction potential.
- Good oxidizing agents have high standard reduction potentials whereas good reducing agents have low standard reduction potentials.
- For example, the standard electrode potential of Ca^+ is -3.8V and that of F_2 is +2.87V. This implies that F_2 is a good oxidizing agent whereas Ca is a reducing agent.

Electrode Potential Example

The calculation of the standard electrode potential of a zinc electrode with the help of the standard hydrogen electrode is illustrated below.



It can be noted that this potential is measured under standard conditions where the temperature is 298K, the pressure is 1 atm, and the concentration of the electrolytes is 1M.

Spontaneity of Redox Reactions

If a redox reaction is spontaneous, the ΔG^o (Gibbs free energy) must have a negative value. It is described by the following equation:

$$\Delta G^o_{cell} = -nFE^0_{cell}$$

Where n refers to the total number of moles of electrons for every mole of product formed, F is Faraday's constant (approximately 96485 $C.mol^{-1}$).

The E^0_{cell} can be obtained with the help of the following equation:

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

Therefore, the E^0_{cell} can be obtained by subtracting the standard electrode potential of the anode from that of the cathode. For a redox reaction to be spontaneous, the E^0_{cell} must have a positive value (because both n and F have positive positive values, and the ΔG^o value must be negative).

This implies that in a spontaneous process,

$$E^0_{cell} > 0\text{; which in turn implies that } E^0_{cathode} > E^0_{anode}$$

Thus, the standard electrode potential of the cathode and the anode help in predicting the spontaneity of the cell reaction. It can be noted that the ΔG^o of the cell is negative in galvanic cells and positive in electrolytic cells.