# Study material for B.Sc Chemistry SEM-2 General (CC2/GE2)

STANDARD ELECTRODE POTENTIAL

According to IUPAC, the standard electrode potential of an electrode X is the EMF of a cell in which the negative electrode is a standard hydrogen electrode (SHE), arbitrarily assigned a potential of 0 V and the positive electrode is made up of the electrode X, its components being maintained at unit activity. If the electrode X is written as X^+/X, then its standard electrode potential is the EMF of the cell:

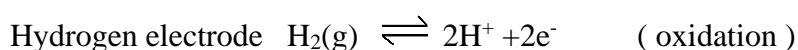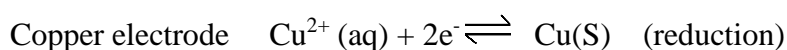$$Pt/H_2 \text{ (g, 1 atm) } /H^+ \text{ (a=1) } // X^+ \text{ (a=1) } /X$$
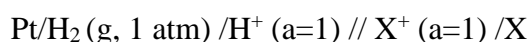
e.g., If we place the half-cell Zn^{2+}/Zn in place of electrode X, the EMF observed is -0.763 V, i.e., standard electrode potential or standard reduction potential for Zn^{2+}/Zn half cell is -0.763 V. It is represented as: $E^0_{Zn2+/Zn} = -0.763$ V.
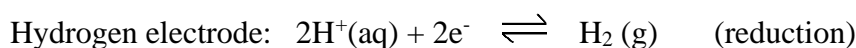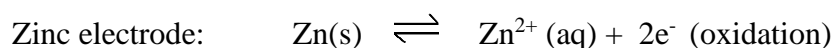

SIGN OF ELECTRODE POTENTIAL

According to the latest convention adopted by IUPAC (International Union Of Pure And Applied Chemistry), the electrode potential is given a positive sign if the electrode reaction involves reduction when connected to the standard hydrogen electrode reaction involves oxidation when connected to the standard hydrogen electrode whose potential is taken arbitrarily as zero.

Thus with copper electrode (copper rod dipped in a solution of copper salt) is connected with a standard hydrogen electrode, reduction takes place at the copper electrode. The electrode reactions are as follows:

Copper electrode $\quad Cu^{2+} \text{ (aq) } + 2e^- \rightleftharpoons Cu(S) \quad$ (reduction)

Hydrogen electrode $\quad H_2(g) \rightleftharpoons 2H^+ + 2e^- \qquad$ (oxidation)

Hence the potential of copper electrode is taken as positive. Thus $E^0_{Cu2+/Cu}$ is positive. If zinc electrode is connected with the standard hydrogen electrode, oxidation takes place at the zinc electrode. The electrode reaction are shown as follows,

Zinc electrode: $\qquad Zn(s) \rightleftharpoons Zn^{2+} \text{ (aq) } + 2e^-$ (oxidation)

Hydrogen electrode: $2H^+(aq) + 2e^- \rightleftharpoons H_2 \text{ (g) } \qquad$ (reduction)

Hence, the potential of zinc electrode is taken as negative. Thus $E^0\ _{Zn2+/Zn}$ is negative.

CELL DIAGRAM OR REPRESENTATION OF A CELL:

A cell diagram is a depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half cells. Each half-cell is again made of metal electrode in contact with metal ions in solution.

In 1953 IUPAC (International Union of Pure and Applied Chemistry) recommended the following conventions for writing cell diagrams. Let us illustrate these with reference to zinc copper cell.

(i) A single vertical line:

In this representation (/) represents a phase boundary between metal electrode and ion solution. These the two half cells in a voltaic cell are indicated as   phase boundary

$Zn\ /\ Zn^{2+}$ $Cu^{2+}\ /\ Cu$
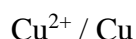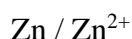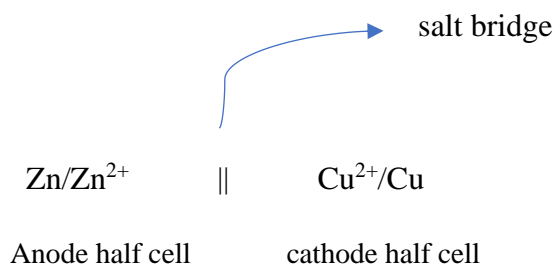
Anode half cell   Cathode half cell

It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half cell it is on the right of the metal ion.

(ii) A double vertical line:

The double vertical line represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.

(iii) Anode half cell is written on the left and cathode half cell on the right.

(iv) In the complete cell diagram, the two half cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as

salt bridge

Zn/Zn^{2+} || Cu^{2+}/Cu

Anode half cell   cathode half cell

CALCULATING THE STANDARD EMF (E⁰) OF A CELL:

The standard e.m.f. of a cell calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula:

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

Where E^0_R and E^0_L are the reduction potentials of the right-hand and left-hand electrodes respectively.

Example: $E^0_{Zn2+/Zn} = -0.763$ V, $E^0_{Cu2+/Cu} = +0.337$ V

From these values, it can be said that Zn is more powerful reducing agent than Cu. So, oxidation takes place at Zn^{2+}/Zn, so it will be anode. Reduction takes place at Cu^{2+}/Cu, so it will be cathode. So, the cell can be represented as: $Zn/Zn^{2+} \| Cu^{2+}/Cu$
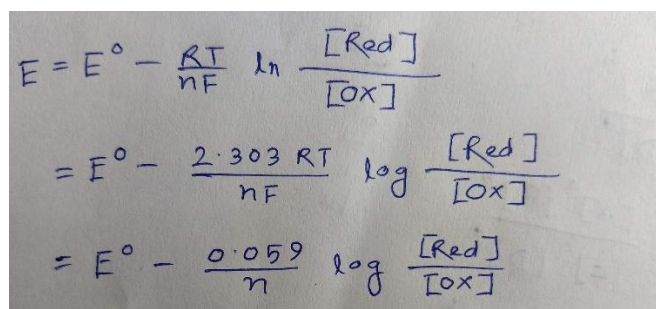
Therefore, $E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0.337 - (-0.763) = 1.1$ V.

NERST EQUATION

Let a redox system is represented by a general expression:

$$Ox + ne \rightleftharpoons Red$$
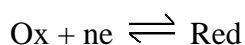
Where, Ox is the oxidising or oxidant species and Red is the reducing or reductant species. The observed potential E of this half-cell id represented by Nernst equation as:
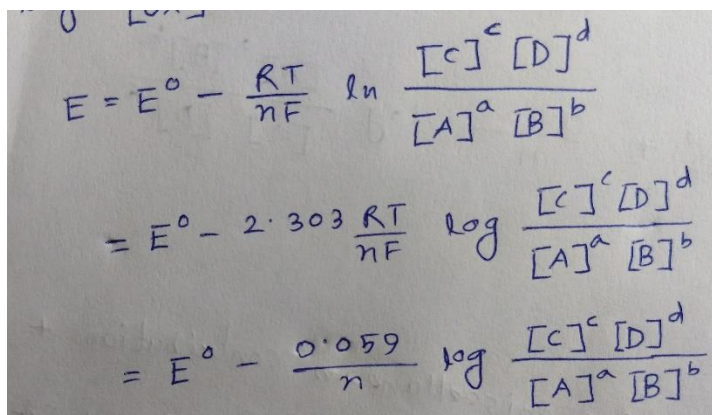
$$E = E^0 - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

$$= E^0 - \frac{2.303\ RT}{nF} \log \frac{[Red]}{[Ox]}$$

$$= E^0 - \frac{0.059}{n} \log \frac{[Red]}{[Ox]}$$

Where, R is gas constant, F is faraday.

If a cell reaction is: $aA + bB \rightleftharpoons cC + dD$

Then, Nernst equation will be:

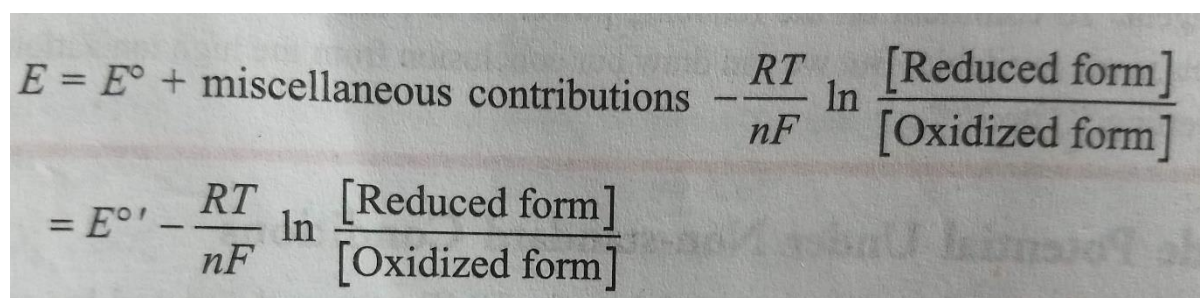$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$= E^0 - 2.303 \frac{RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$= E^0 - \frac{0.059}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

FORMAL POTENTIAL

Formal potential is the reduction potential that applies to a specified set of conditions (e.g., effect of pH, effect of complexation, effect of precipitation etc.) for a redox couple containing equal formal concentrations of the oxidised and reduced forms.

Under a specified set of conditions of pH, ionic strength, concentration of complexing agent etc, it is possible to tag all these effects to the E^0 term and Nernst equation is expressed as:

$$E = E^\circ + \text{miscellaneous contributions} - \frac{RT}{nF} \ln \frac{[\text{Reduced form}]}{[\text{Oxidized form}]}$$

$$= E^{\circ\prime} - \frac{RT}{nF} \ln \frac{[\text{Reduced form}]}{[\text{Oxidized form}]}$$

Where, E_0' (E zero prime) is termed as formal potential of the half-cell.

FACTORS AFFECTING THE EMF OF HALF CELLS

1. Effect of concentration

The concentration of the reacting species in a half-cell greatly influences the potential of a system. A half-cell reaction is generally expressed as

$$\text{Oxidized form} + ne^- = \text{Reduced form}$$

For this reaction, the Nernst reaction is

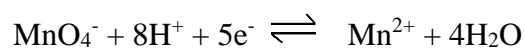$$E = E° - \frac{0.059}{n} \log \frac{[\text{reduced form}]}{[\text{oxidized form}]}$$

Example: $E^0_{Fe3+/Fe2+}$ = +0.77 V; But when $[Fe^{3+}]$ = 1 mol/lit and $[Fe^{2+}]$ = 0.0001 mol/lit, we have:

$$E = E° - \frac{0.059}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.77 + 0.059 \log \frac{1}{10^{-4}} = +1.006 \text{ V}.$$

2. Effect of pH

When hydrogen or hydroxyl ions are involved in a half-cell reaction, their concentrations appear in the Nernst equation and accordingly the potential is influenced by the pH of the medium.

Example: MnO_4^-/Mn^{2+} (E^0 = +1.51 V) system in acid medium involves oxidation as:

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

The Nernst equation is:

$$E = E^\circ - \frac{0.059}{5} \log \frac{\left[Mn^{2+}\right]}{\left[MnO_4^-\right]\left[H^+\right]^8}$$

$$= +1.51 - 0.094 \times pH - \frac{0.059}{5} \log \frac{\left[Mn^{2+}\right]}{\left[MnO_4^-\right]}$$

At pH = 6, the reduction potential falls to +0.95 V.

3. Effect of precipitation

Precipitation is due to change of concentration of the oxidized and reduced form and precipitation of one product is happened due to low solubility i.e. it depend upon the solubility product of that compound, $e.g.$ due to low reduction potential of Cu^+/Cu^{2+} (+0.15 volt), it is not expected to oxidize iodide to iodine ($E^\circ = +0.54\ volt$) but in practice due to low solubility of CuI, the concentration of Cu^+ ion reduces in such a way that the reduction potential is substantially increased.

$$Cu^{2+} + e = Cu^+$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\left[Cu^+\right]}{\left[Cu^{2+}\right]}$$

The concentration of cuprous ion (Cu^+) is determined by the solubility product (k) of CuI,

$$k = \left[Cu^+\right]\left[I^-\right] = 10^{-12}$$

$$\text{So, } E = E^\circ - \frac{RT}{nF} \ln \frac{10^{-12}}{\left[Cu^{2+}\right]\left[I^-\right]}$$

$$E = 0.15 + 12 \times 0.059 + 0.059 \log\left[Cu^{2+}\right]\left[I^-\right]$$

$$= +0.86 + 0.059 \log\left[Cu^{2+}\right]\left[I^-\right]$$

The effective potential thus rises above the reduction potential of the iodide-iodine system and iodide ion is oxidized by cupric ion in solution. In fact, the reaction proceeds almost toward the right.

$$2Cu^{2+} + 4I^- = 2CuI \downarrow + I_2$$

Copper may be estimated by treating the liberated iodine with a solution of sodium thiosulfate.

4. Effect of complex formation

Complex formation may also bring down the effective concentration of one of the species involved in an electrode process, thereby altering the potential of the system. Fe^{3+} ion normally oxidises I^- ion to I_2 in aqueous solution (as $E^0_{Fe3+/Fe2+} = 0.77$ V, $E^0_{I2/I-} = +0.54$V). But in presence of excess F^- ion, Fe^{3+} ion is removed as the complex ion $[FeF]^{2+}$.

$$Fe^{3+} + F^- \rightleftharpoons FeF^{2+} \; ; \; K_{eq} = 10^5 = \frac{\left[[FeF]^{2+}\right]}{\left[Fe^{3+}\right]\left[F^-\right]}$$
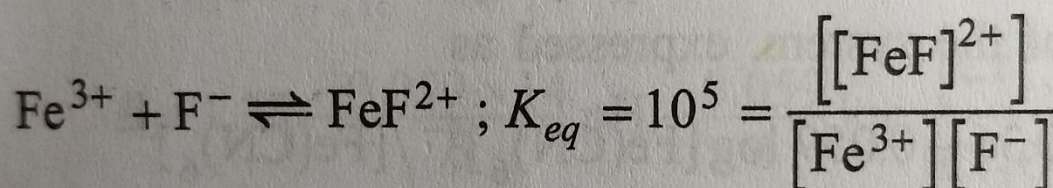
The value of $[Fe^{3+}]$ from this relation is now substituted in the expression for the reduction potential for Fe^{3+}/Fe^{2+} system:

$$E = E° - 0.059 \log \frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]} = +0.77 - 0.059 \log \frac{10^5 \left[F^-\right]\left[Fe^{2+}\right]}{\left[[FeF]^{2+}\right]}$$

$$= +0.475 - 0.059 \log \frac{\left[Fe^{2+}\right]\left[F^-\right]}{\left[[FeF^{2+}]\right]}$$

As the reduction potential decreases, the oxidising power of Fe^{3+} decreases and it can no longer oxidise I^-.