Ministry of Higher Education and Scientific Research

Al-Muthanna University

College of Science

وزارة الـتعليم الـعالـي والـبحث الـعلمي

جـــامعــــــة الـــمثنــــــى

كليــــة الـعلـــــــــــوم

قـســــــــــم الــكـــيمـياء

Electrochemistry

Lecture (15)

Stage 3

Prof. Hassan Sabih

Electrochemistry - I

(Electrochemical Cells)

BASICS

Section - 1

Electrochemisrty deals with the inter-conversion of electrical energy and chemical energy. This part of Electrochemistry will deal with the conversion of chemical energy into electrical energy (Electrochemical Cells).

Electrochemical Cells :

Consider the following redox reaction :

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

In the above reaction, Zn displaces copper ions (Cu^{2+}) from aqueous solution. This reaction can be achieved very easily in practice. Put a Zn rod into a solution of $CuSO_4$ (containing Cu^{2+} ions). It is observed that blue colour of $CuSO_4$ solution disappears after sometime. What happens actually ? Zn loses $2e^-$s per atom and Cu^{2+} ions in the solution accepts them. Cu^{2+} ions from solution in this manner are deposited out in form of solid Cu and Zn goes into the solution as Zn^{2+} (colourless). The reaction can well be understood in terms of two half reactions :

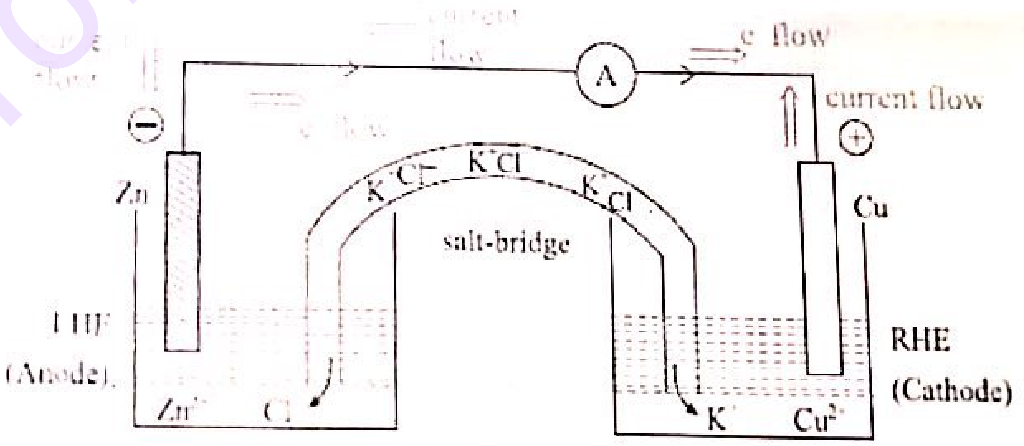
Oxidation : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Note : **(i)** In this reaction, Zn atoms are directly giving electrons to the copper ions.

(ii) Another aspect of this reaction is that it is an exothermic reaction. This means decrease in energy of the reacting system takes place which appears as heat.

Now, we can make the same reaction take place even if the copper ions and zinc rod are not in direct contact. If we put the Cu^{2+} ions and Zn rod in two separate containers and connect the two by a conducting metallic wire and introduce an inverted U shape instrument (called as salt-bridge), then electrons will still be transferred through the connecting wires. The electrons from Zn rod travel to Cu^{2+} ions through the connecting wires and the same reaction takes place.



Electrochemical Cell

In such an arrangement, the solution does not get heated up. The loss in energy now appears as the potential difference which is used to do the work in transferring the electrons from Zn to Cu^{2+} ions. Such an arrangement is called as electrochemical cell or Galvanic cell or Voltaic cell. The potential difference which drives the electrons from Zn to Cu^{2+} ions, is called as electromotive force (E.M.F.) of a cell.

An electrochemical cell (shown in diagram) mainly consists of two compartments : left hand electrode (LHE) and right hand electrode (RHE). In LHE, oxidation takes place and is called as anode. In RHE, reduction takes place and is called as cathode.

Anode is generally of that metal (or substance) which readily loses electrons (i.e., oxidised easily). A rod of that metal is prepared and put into one of its solution in LHE to get anode. In RHE, a rod of metal that loses electrons less easily as compared to the metal of LHE (in the diagram, Zn is taken in LHE and Cu is taken in RHE) is prepared and put into one of its solution to get cathode. LHE and RHE are also known as two half-cells. Now the electrons move from anode (LHE) to cathode (RHE) and hence a current flow is maintained in the external circuit.

The two half cells are connected by a inverted 'U' shaped tube called as salt-bridge. The salt-bridge contains solution of strong ionic salts like NaCl, $NaNO_3$, KNO_3 and KCl, etc., (salts of most reactive alkali metals) soaked in a colloidal solution of agar-gel which allows only the movement of ions of salts, not water. The role of a salt-bridge is very important as it allows the continuous discharge of the cell (i.e., the supply of voltage from cell). The salt-bridge keeps the two solutions (i.e., in LHE and RHE) electrically neutral to each other. In the Zn-$CuSO_4$ cell, in left hand cell as Zn loses electrons, excess of positive charge (in form of Zn^{2+} ions) is collected near LHE and as Cu^{2+} ions gets discharged (accepting electrons from Zn) in right hand cell, excess of negative charge (in form of SO_4^{2-} ions) is accumulated near RHE. Now the salt-bridge provides positive charge to RHE (in form of K^+, Na^+ ions) and negative charge to LHE (in form of Cl^-, NO_3^- etc) and thus bringing about the neutrality of two solutions. If this does not take place, a reverse potential difference is created in the two compartments and thus breaking the continuous supply of voltage (current), which is the purpose of the cell.

The efficiency of a cell is determined by the tendency of LHE to loose electrons and the tendency of RHE to accept electrons. A measure of cell efficiency is called as electromotive force (EMF) or the voltage or the difference in potentials of two electrodes. EMF is defined as the difference in the potential across LHE and RHE due to which electrons from anode travel to cathode.

EMF value of a cell made up of such two half-cells is a constant provided that the concentration of electrolyte, temperature and the pressure (if gases are involved) remains constant. It means that EMF values do change with concentration, temperature and pressure. EMF values are hence standardised at a temperature of 25°C (298 K), a pressure of 1 atm (if gases are involved) and at concentrations of 1.0 M for all solutes prevent as electrolytes. EMF value under these conditions is called as standard EMF and is denoted as E°.

EMF of a cell is measured as the difference of potentials of anode and cathode. The potential of a half-cell or EMF of a half-cell (i.e., a cathode or anode) is called as electrode potential. It is defined as the tendency of an electrode either to get oxidised or to get reduced i.e., to loose or gain electrons. electrode potentials are of two types :

Oxidation Potential :

It is the tendency of an electrode to get oxidised, i.e., to loose electrons.

Reduction Potential :

It is the tendency of an electrode to get reduced, i.e., to accept electrons.

Electrode potentials at standard conditions (1 atm, 298 K and 1.0 M) are called as standard electrode potentials.

Note :

- Anode is the negatively charged electrode in electrochemical cell and positively charged in electrolytic cell (to be discussed later) but it will always be the oxidation electrode (electrode on which oxidation take place).
- Cathode is the positively charged electrode in electrochemical cell and negatively charged in electrolytic cell (to be discussed later) but it will always be the reduction electrode (electrode on which reduction takes place).
- We can also define cathode and anode electrodes as :

  Anode : Electrode at which current enters.

  Cathode : Electrode at which current leaves.
- An important property for an ionic salt to act as a salt bridge is that ionic mobility (ease with which ions move in solution) of both cations anion should be similar. Also, it should not react with the contents of either anode or cathode.

Types of Electrodes :

1. Metal in contact with its ions :

Metal (M) in contact with its ion (M^{n+}) is represented as M/M^{n+} when it acts as oxidation electrode (anode) and M^{n+}/M when it acts as reduction electrode (cathode). Whether a given electrode acts as anode or cathode depends upon the other electrode with which it forms an electrochemical cell. So, it is necessary to define both oxidation and reduction potentials for an electrode.

M / M^{n+} is written as :

$$M(s) \longrightarrow M^{n+}\ (1.0M) + ne^- \qquad \text{(oxidation electrode)}$$

and its potential is called as oxidation potential and at standard state is represented as $E^0(M/M^{n+})$.

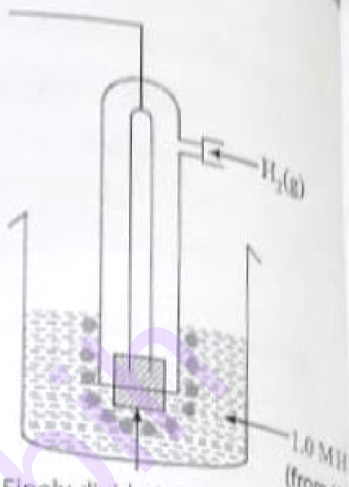
M^{n+} / M is written as :

$$M^{n+}\ (1.0M) + ne^- \longrightarrow M(s) \qquad \text{(reduction electrode)}$$

and its potential is called as reduction potential and at standard state is represented as $E^0(M^{n+}/M)$.

Note : Symbol "/" denotes the phase seperation between the two substances.

2. Gaseous electrode :



Finely divided Pt coated on Platinum foil

Gases like $H_2(g)$ can loose electrons to form H^+ ions and hence can act as anode and also H^+ ion can add up electrons to form H_2 (g) and hence can act as cathode. Similarly gases like Cl_2 (g) can add electrons to form Cl^- ions and Cl^- ions can loose electrons to form Cl_2(g). The concentration of electrolytes is the value for $[H^+]$ ions and we take pressure of gas in atm. A hydrogen electrode is made by passing H_2 (g) at 1 atm near an electric conductor made up of platinum (for conduction of e^-s) dipped in an aqueous solution containing H^+ ions (generally HCl) as shown in figure.

Electrode representation : Pt, H2/H+
or H+/H2, Pt

Its electrode potentials are represents as :

$E(H_2/H^+)$:	$\frac{1}{2}H_2(g) \longrightarrow H^+(aq.) + e^-$	(oxidaion potential)
$E(H^+/H_2)$:	$H^+(aq.) + e^- \longrightarrow \frac{1}{2}H_2(g)$	(reduction potential)
$E^0(H_2/H^+)$:	$\frac{1}{2}H_2(1\ atm) \longrightarrow H^+(1M) + e^-$	(standard oxidation potential)
$E^0(H^+/H_2)$:	$H^+(1M) + e^- \longrightarrow \frac{1}{2}H_2(1atm)$	(standard reduction potential)

Similarly, Cl_2/Cl^- electrode is prepared by passing Cl_2 gas and taking HCl (aq) or KCl (aq) as electrolyte

3. Redox Electrodes :

In this type of electrode, an inert wire (e.g. Platinum) is placed in a solution (electrolyte) containing ions of a element in more than one oxidation states. e.g. Pt wire dipped in an electrolyte of Fe^{2+} and Fe^{3+} ions. Th electrode (inert material wire) acts as a source / sink for electrons.

Electrode representation : $Pt/Fe^{3+}, Fe^{2+}$

Electrode reaction : As cathode : $Fe^{3+}(aq.) + e^- \longrightarrow Fe^{2+}(aq.)$

As anode : $Fe^{2+}(aq.) \longrightarrow Fe^{3+}(aq.) + e^-$

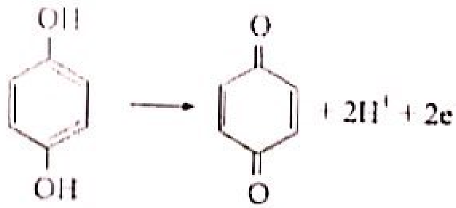
Another example : $Pt/MnO_4^-, Mn^{2+}, H^+$

As cathode : $MnO_4^-(aq.) + 8H^+(aq.) + 5e^- \longrightarrow Mn^{2+}(aq.) + 4H_2O(\ell)$

Redox electrodes can also be made using substances that exist in two different oxidation states. Quinhydrone is an equimolar mixture of benzoquinone (Q) and hydroquione (H_2Q)

Electrode representation : $Pt/H_2Q, Q, H^+$

Electrode reaction : As anode :



(H_2Q) (Q)

> ***Note :*** If two substances are in same solution then in the cell or electrode representation, they are separated by comma (',').

4. Calomel Electrode :

It consists of mercury covered with mercurous chloride (calomel) in contact with a solution of KCl :

Electrode representation : $Hg / Hg_2Cl_2 / Cl^-$

Electrode reaction : As cathode : $Hg_2Cl_2\,(s) + 2e^- \rightleftharpoons 2\,Hg\,(\ell) + 2Cl^-\,(aq.)$

As anode : $2\,Hg(\ell) + 2Cl^-\,(aq.) \rightleftharpoons Hg_2Cl_2\,(s) + 2e^-$

Most common calomel electrode is the saturated catomel electrode (SCE) in which the concentration of KCl is at its saturation (about 3.5 M). $E^0_{SCE} \approx 0.24\ V$ (w.r.t. SHE)

5. Silver - Silver Chloride Electrode :

It consists of a pure silver wire in a solution of KCl saturated with solid silver chloride.

Electrode representation : $Ag/AgCl/Cl^-$

Electrode reaction : As cathode: $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq.)$ $E^0_{Reduction} = 0.222\ V$

As anode : $Ag(s) + Cl^-(aq) \rightleftharpoons AgCl(s) + e^-$

If saturated KCl solution, $E^0_{reduction}$ become 0.197 V (w.r.t. SHE)

6. Mercury - Mercurous Sulphate Electrode :

In this electrode, the metal is mercury, the sparingly soluble compound is mercurons sulphate (Hg_2SO_4) and the source of SO_4^{2-} anions is H_2SO_4 or K_2SO_4. It represented as :

Electrode representation : Hg / Hg_2SO_4 / SO_4^{2-}

Electrode reaction : As cathode : $Hg_2SO_4(s) + 2e^- \longrightarrow 2Hg(\ell) + SO_4^{2-}(aq.)$

$E^0_{Reduction} = 0.616\ V$ (w.r.t. SHE

As anode : $2Hg(\ell) + SO_4^{2-}(aq.) \longrightarrow Hg_2SO_4(s) + 2e^-$

Note : [1] Calomel electrodes, Silver - Silver Chloride electrodes and Mercury - Mercurons Sulphate electrod are secondary reference electrodes. Silver - Silver electrodes and calomel electrodes are the most commonly used (practically) as a reference electrode rather than SHE / NHE due to practical difficulti associated with its (SHE) used and maintenance.

[2] The potential of metal - metal ion electrode and metal-metal insoluble salt-slat anion electrode is sam while their standard potentials are not same. Statndard potential are related by the following equatio

$$E^\circ_{X^-/MX/M} = E^\circ_{M^+/M} + \frac{2.303RT}{F} \log K_{sp}(MX)$$ [Refer example - 4]

7. Amalgam electrodes :

This is the modified version of Metal / Metal - ion electrode in which metal strip is replaced by metal amalgam.

e.g. Na (in Hg at c_1 M) / Na^+ (c_2 M)

Electrode Potentials :

It is impossible to measure the absolute EMF's (electrode potentials) for half electrodes. This is done by arbitrarily selecting one half cell and setting its electrode potential as '0' volts. The electrode potentials o other half cells can then be measured by combining them with the standard reference electrodes in a cell arrangement.

The reference electrode against which all other half cells are generally measured is the hydrogen electro half-cell at a concentration of H^+ ions equal to 1.0 M and $H_2(g)$ at 1 atm pressure kept at 25°C (298 K). is also known as SHE (standard hydrogen electrode) or NHE (normal hydrogen electrode). Its potential taken as '0' volts.

$$E^0(H_2 / H^+) = 0 = E^0(H^+ / H_2)$$

Now other half cells can be divided into two categories : One which will act as anode and other which w act as cathode in a cell arrangement with SHE. Each type of cell arrangement will give an EMF value whi will be actually the EMF value of known electrode as EMF value of SHE is 'zero' volts (whether SHE a as anode or cathode).

For example : Cu electrode (half cell) acts as cathode with SHE, i.e., as :

Cu^{2+}/Cu : $Cu^{2+}(aq)_{(1.0M)} + 2e^- \longrightarrow Cu_{(s)}$.

The experimental measurement of EMF value for this cell arrangement give 0.34 volts. Since Cu electrode shows reduction with SHE, the given value of EMF represents the reduction potential of Cu half-cell.

$$E^0(Cu^{2+}/Cu) = 0.34 \text{ volts}$$

The oxidation potential of Cu half-cell is just the negative of this value.

$E^0(Cu/Cu^{2+}) = -0.34$ volts [Note : $E_{reduction} = -E_{oxidation}$]

Note : Reduction potential is taken as a standard potential i.e. if electrode potential is given (and nothing is mentioned whether it is oxidation or reduction), it is taken as the reduction potential, by default.

Rules for assigning sign (+ve or –ve) to electrode potentials :

1. The oxidation potential of half-cell (or an electrode) is given a positive sign if the given electrode acts as anode in a cell arrangement with SHE and its reduction potential is given a negative sign with the same magnitude. For example : oxidation potential of active metals like Na, Mg, Al, Zn, Fe etc. is given a positive sign.

2. The reduction potential of half-cell (or an electrode) is given positive sign if the given electrode acts as cathode in a cell arrangement with SHE and its oxidation potential is given a negative sign with the same magnitude.

   For example : reduction potential of less active metals like Cu, Ag etc is given a positive sign.

Note : Electrode potential measured in this manner are called as standard hydrogen scale potentials.

Standard EMF of a Cell (E^0_{cell}) :

E^0_{cell} can be defined in two ways as :

(i) $$E^0_{cell} = \left\{ \text{standard reduction potential of cathode} - \text{standard reduction potential of anode} \right\}$$

$$E^0_{cell} = \left(E^0_{reduction}\right)_{cathode} - \left(E^0_{reduction}\right)_{anode}$$

(ii) $$E^0_{cell} = \left\{ \text{standard oxidation potential of anode} - \text{standard oxidation potential of cathode} \right\}$$

$$E^0_{cell} = \left(E^0_{oxidation}\right)_{anode} - \left(E^0_{oxidation}\right)_{cathode}$$