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29

CHAPTER

Electromotive Force

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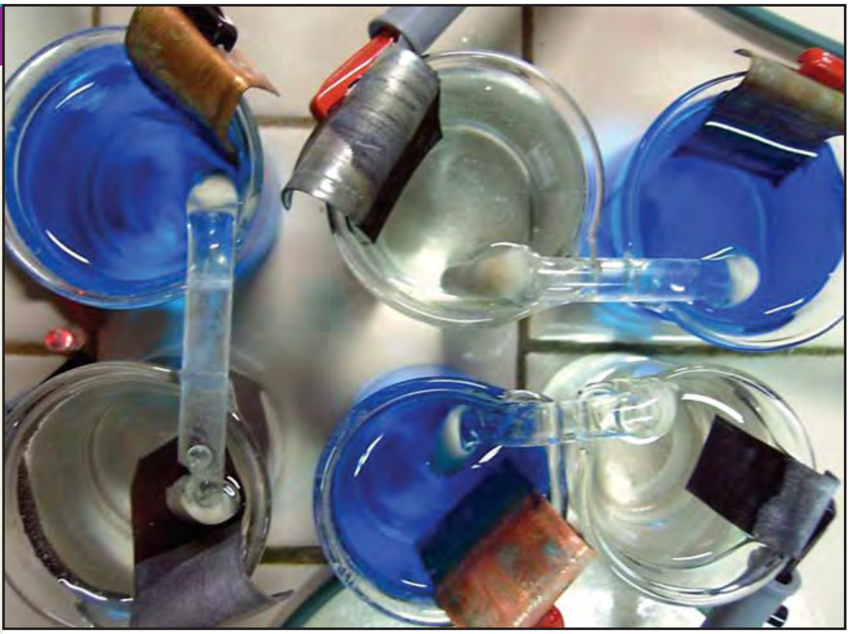

WHAT ARE HALF REACTIONS ?

Let us consider the reaction

$$2\,Na + Cl_2 \longrightarrow 2Na^+ + 2Cl^-$$

It occurs by the transfer of electrons from Na to Cl. Na loses an electron and is said to be oxidized to Na^+ ion. At the same time, Cl gains an electron and is reduced to Cl^- ion. Such a reaction which is brought about by loss of electrons (oxidation) and gain of electrons (reduction) simultaneously, is called an **Oxidation-Reduction reaction or Redox reaction** in brief. It may be noted that in the overall redox reaction no free electrons are generated.

The redox reaction can be considered as made up of two reactions. For example, the redox reaction

$$2Na + Cl_2 \longrightarrow Na^+ + 2Cl^-$$

is composed of two half-reactions :

$$2Na \longrightarrow 2Na^+ + 2e^- \qquad \textit{(oxidation)}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad \textit{(reduction)}$$

Each of the two reactions shows just its oxidation or just the reduction portion of the overall redox reaction. Being half components of the redox reaction, these reactions are called

Half-reactions. The first half-reaction that proceeds by oxidation is often referred to as the **Oxidation half-reaction.** The second half-reaction that occurs by reduction, is referred to as the **Reduction half-reaction.** When the two half-reactions are added together, the sum is the net redox reaction.

We will see presently how redox reactions are a source of electric current in electrochemical cells.

ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an **electrochemical cell.**

How a Redox reaction can produce an electrical current ?

When a bar of zinc is dipped in a solution of copper sulphate, copper metal is deposited on the bar (Fig. 29.1). The net reaction is

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$$

This is a redox reaction and the two half-reactions are :

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^-$$

$$\mathrm{Cu}^{2+} + 2e^- \longrightarrow \mathrm{Cu}$$

In this change, Zn is oxidized to give Zn^{2+} ions and Cu^{2+} ions are reduced to Cu atoms. The electrons released in the first half-reaction are used up by the second half-reaction. Both the half-reactions occur on the zinc bar itself and there is no net charge.

Now, let the two half-reactions occur in separate compartments which are connected by a wire (Fig. 29.2) The electrons produced in the left compartment flow through the wire to the other compartment. However the current will flow for an instant and then stop. The current stops flowing because of the charge build up in the two compartments. The electrons leave the left compartment and it would become positively charged. The right compartment receives electrons and becomes negatively charged. Both these factors oppose the flow of electrons (electrical current) which eventually stops.

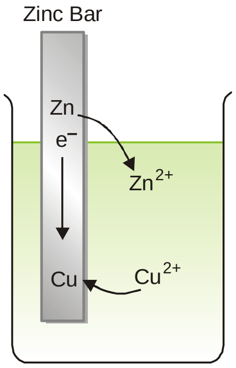

Figure 29.1

Redox reaction taking place on zinc bar itself.

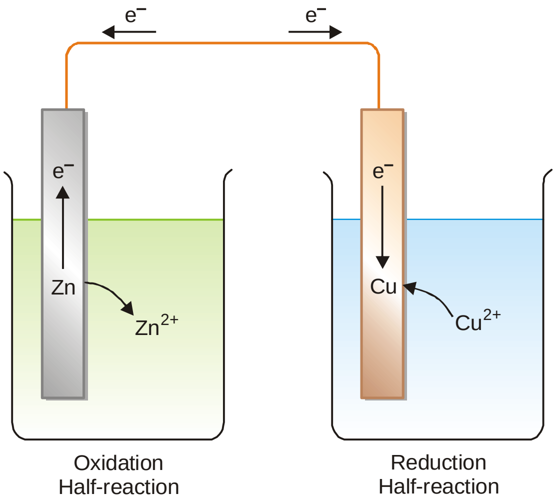

Figure 29.2

Separate half-reactions cause flow of electrons (current) in the wire connecting them.

This problem can be solved very simply. The solutions in the two compartments may be connected, say, by a **salt bridge.** The salt bridge is a U-tube filled with an electrolyte such as NaCl, KCl, or

K_2SO_4. It provides a passage to ions from one compartment to the other compartment without extensive mixing of the two solutions. With this ion flow, the circuit is complete and electrons pass freely through the wire to keep the net charge zero in the two compartments.

Voltaic Cells

A **Voltaic cell,** also known as a **galvanic cell** is one in which electrical current is generated by a spontaneous redox reaction. A simple voltaic cell is shown in Fig. 29.3. Here the spontaneous reaction of zinc metal with an aqueous solution of copper sulphate is used.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution interconnects the solutions in the anode compartment and the cathode compartment.

The oxidation half-reaction occurs in the anode compartment.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The reduction half-reaction takes place in the cathode compartment.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

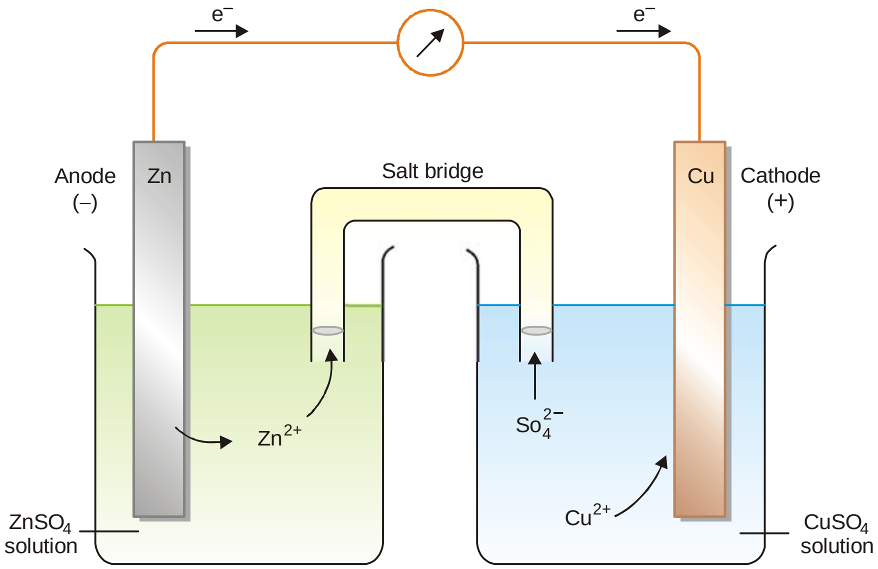

Figure 29.3
A simple voltaic (galvanic) cell.

When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode. At the same time, SO_4^{2-} ions from the cathode half-cell migrate to the anode half-cell through the salt bridge. Likewise, Zn^{2+} ions from the anode half-cell move into the cathode half-cell. This flow of ions from one half-cell to the other completes the electrical circuit which ensure continuous supply of current. The cell will operate till either the zinc metal or copper ion is completely used up.

CELL TERMINOLOGY

Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current is the flow of electrons through a wire or any conductor.

Electrode is the material : a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (–) in cell diagrams.

Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is shown as (+) in cell diagrams.

Electrolyte is the salt solutions in a cell.

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

Cathode compartment is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.

Half-cell. Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

Daniel Cell

It is a typical voltaic cell. It was named after the British chemist John Daniel. It is a simple zinc-copper cell like the one described above.

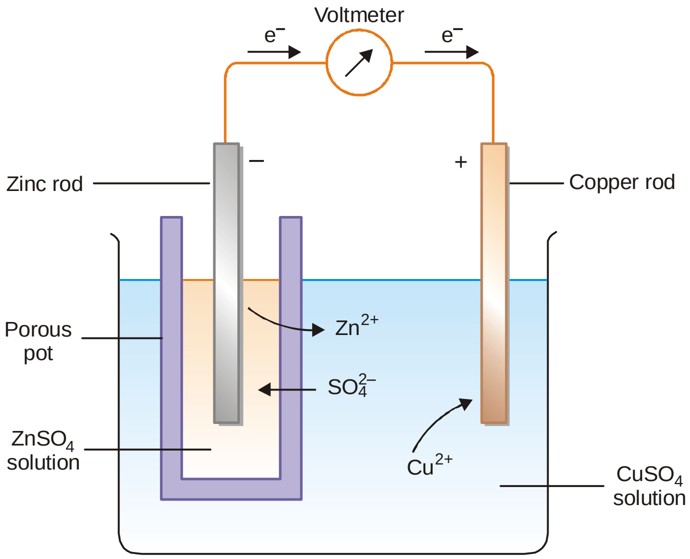

Figure 29.4
Daniel Cell.

In this cell the salt-bridge has been replaced by a porous pot. Daniel cell resembles the above voltaic cell in all details except that Zn^{2+} ions and SO_4^{2-} ions flow to the cathode and the anode respectively through the porous pot instead of through the salt-bridge. Inspite of this difference, the cell diagram remains the same.

$$\underset{\text{Anode}}{\mathrm{Zn}\,|\,\mathrm{Zn}^{2+}}\ \overset{\text{Porous Pot}}{\|}\ \underset{\text{Cathode}}{\mathrm{Cu}^{2+}\,|\,\mathrm{Cu}}$$

Cell reaction

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the **cell reaction.** Thus, for a simple voltaic cell described above, we have

(*a*) Half-reactions :

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

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

(*b*) Cell reaction by adding up the half-reactions :

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

Cell potential or emf

In a Zn-Cu voltaic cell, electrons are released at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electrical repulsions. The copper electrode gets positive charge due to the discharge of Cu^{2+} ions on it. Thus electrons from the outer circuit are attracted into this electrode. The flow of current through the circuit is determined by the 'push', of electrons at the anode and 'attraction' of electrons at the cathode. These two forces constitute the 'driving force' or 'electrical pressure' that sends electrons through the circuit. This driving force is called the **electromotive force** (abbreviated **emf**) or **cell potential.** The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage.**

Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic 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 a metal electrode contact with metal ions in solution.

IUPAC Conventions. In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) a **single vertical line** (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as

$$\underset{\substack{\text{Anode}\\ \text{Half-Cell}}}{\mathrm{Zn}\,|\,\mathrm{Zn}^{2+}} \qquad \underset{\substack{\text{Cathode}\\ \text{Half-Cell}}}{\mathrm{Cu}^{2+}\overset{\substack{\text{Phase}\\ \text{Boundary}}}{|}\mathrm{Cu}}$$

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.

(2) A **double vertical line** (||) represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.

(3) **Anode half-cell is written on the left** and **cathode half-cell on the right.**

(4) 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

$$\underset{\substack{\text{Anode}\\ \text{Half-Cell}}}{\mathrm{Zn}\,|\,\mathrm{Zn}^{2+}}\ \overset{\text{Salt Bridge}}{\|}\ \underset{\substack{\text{Cathode}\\ \text{Half-Cell}}}{\mathrm{Cu}^{2+}\,|\,\mathrm{Cu}}$$