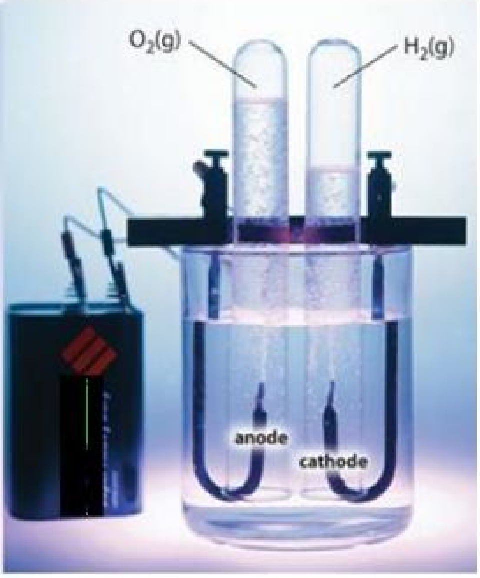


3. Electrochemistry

Content

Introduction

Electrochemistry, the study of the exchange between electrical and chemical energy, dealing with chemical reactions that produce electricity in which the energy released by a spontaneous reaction is converted to electricity and/ or electrical energy is used to cause a nonspontaneous reaction to occur. In these specific systems the reactions involve electron transfer, and so they are mainly a pair of reactions named oxidation-reduction (redox) reactions. An oxidation involves the loss of one or more electrons from a chemical species while a reduction involves the gain of one or more electrons by a chemical species. When an oxidation and a reduction are paired together in a redox reaction, electrons can flow from the oxidized species (the reducing agent or reductant) to the reduced species (the oxidizing agent or oxidant). That electron flow can either be spontaneously produced by the reaction and converted into electricity, as in a galvanic cell, or it can be imposed by an outside source to make a non-spontaneous reaction proceed, as in an electrolytic cell. The following descriptions on electrochemistry involve basics in redox reactions, galvanic cells, electrolytic cells, and the applications with electrolysis.

3.1 Conductivity

We encounter different materials in our day to day life such as paper, wood, glass, plastics, rubber, metals, and composite materials (i.e. mix of two different kind of materials). These materials have different properties thus differ in applications. One such important property is ability of a material to flow electricity through it. It is necessary to define a few terms before we consider the subject of conductance of electricity through electrolytic solutions. The electrical resistance is represented by the symbol *'R'* and it is measured in ohm (Ω) which in terms of SI base units is equal to (kg m^2). It can be measured with the help of a Wheatstone bridge. The electrical resistance of any object is directly proportional to its length, *l*, and inversely proportional to its area of cross section, *A*. That is,

$$R \propto l \quad \text{and} \quad R \propto \frac{1}{A}$$

$$\text{Therefore,} \qquad R \propto \frac{l}{A}$$

$$R = \rho \frac{l}{A}$$

The constant of proportionality, **ρ** (rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (Ω m) and quite often, ohm centimetre (Ω cm) is also used. That is, physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2. It can be seen that: 1 Ω m = 100 Ω cm.

The inverse of resistance, R, is called **conductance**, G, and we have the relation,

$$\textbf{Conductance } (\boldsymbol{G}) = \frac{\boldsymbol{1}}{\boldsymbol{R}}.$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}.

Further we can write,

$$\textbf{Conductance } (G) = \frac{1}{R} = \frac{A}{\rho\, l} = \kappa\,\frac{A}{l}$$

The inverse of resistivity, $\frac{1}{\rho} = \kappa$, called **conductivity** (specific conductance) is represented by the symbol, κ (Greek, kappa). The SI units of conductivity are S m^{-1} but quite often, κ is expressed in S cm^{-1}. Conductivity of a material in S m^{-1} is its conductance when it is 1 m long and its area of cross section is 1 m^2. It may be noted that $1\ \text{S cm}^{-1} = 100\ \text{S m}^{-1}$. These definitions can be depicted by Figure 3.1 as given below.

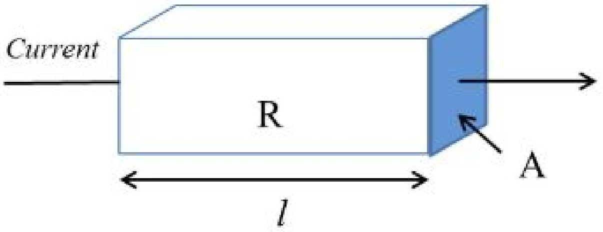


Figure 3.1 Resistance and resistivity

Conductivity and resistivity are constant for a particular substance (metal or an ionic solution with known concentration). However, it is important to provide the temperature at which conductivity or resistivity was measured as it varies with the temperature. In general, about 2% change in conductivity per one degree Celsius is observed for solutions.

Electricity can be conducted through materials (such as metals) as a flow of electrons in the metal. Such materials are known as **electrical conductors**. Electricity can also be conducted as a flow of ions in a solution or molten ionic compound. These are called **ionic conductors**. So, to conduct electricity through materials, it is essential to present electrons (or holes) which can move or ions in solid or liquid state when an electric field is applied.

Solutions can be categorized as **strong electrolytes, weak electrolytes and non-electrolytes (insulators)**. If a particular substance is fully ionized in solution, such as ionic solids and strong acids/ bases, it is called a **strong electrolyte**. Such solutions have concentration of ions proportional to the concentration of strong electrolytes used. Examples for strong electrolytes are aqueous solutions of NaCl, KNO_3, HCl. In the case where electrolytes added are partially ionized in aqueous solution, these are called **weak electrolytes**. Weak aqueous Bronsted acids and bases such as CH_3COOH, NH_3, H_2O are examples for weak electrolytes. The other extreme of electrolytes are the substances which do not produce ions in aqueous media. These are called ***non-electrolytes*** or insulators and these do not conduct electricity. Non polar organic compounds such as Benzene (C_6H_6) and Kerosene are examples for such non-electrolytes.

The conductivity and resistivity of an electrolyte solution can be measured using two oppositely charged metal electrodes placed in an imaginary cuboid shaped portion of a solution with dimensions, length (*l*) and area of cross section(A) as shown in Figure 3.2.

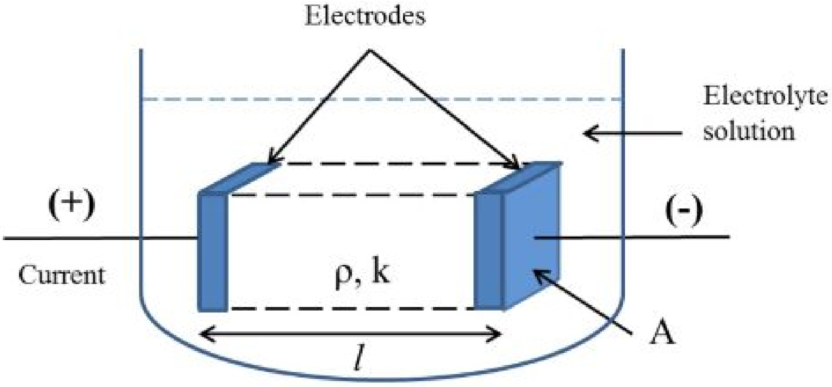


Figure 3.2 Conductivity and resistivity through a solution of electrolytes

3.1.1 Factors affecting conductivity of a solution

There are several factors which affect the conductivity of a solution. These are: **nature of the solute, concentration of the solute, and the temperature of the solution**. All of these factors affect conductivity because mobility of charge carriers is dependent on the above factors and as a result conductivity is dependent on the mobility of charge carriers.

The nature of the species plays important role as it determines presence of ions or mobile charge carriers. Aqueous solutions of strong electrolytes (e.g.: KCl, NaCl) can conduct electricity as these species produce ions due to complete dissociation. However, in the solid state these strong electrolytes do not conduct electricity due to absence of ions. If such a solid electrolyte is brought to the molten state, such as NaCl(l) then ions gain mobility thus conduct electricity. On the other hand, weak acids and bases are also able to conduct electricity as these will react with water to produce ionic species through partial dissociation.

Example 3.1

Which of the following substances once dissolved in water will conduct electricity?

(a) table salt (b) glucose (c) vinegar

Answer

(a) Chemical formula of table salt is NaCl. It is an electrolyte which fully dissolves in water to produce Na^+ and Cl^- ions. Since table salt is a substance that produces ions in water, it is capable of conducting electricity.

(b) Glucose is an organic compound with formula $C_6H_{12}O_6$. When glucose is dissolved in water it will not produce any ionic species. Therefore, a glucose solution cannot conduct electricity.

(c) Vinegar is mostly consists of acetic acid, CH_3COOH. Acetic acid is a weak acid which partially dissociates in water to produce H_3O^+ and CH_3COO^- ions. As a result vinegar solution is able to conduct electricity due to presence of ions.

Another important factor that affects the conductivity of a solution is concentration. When the concentration of dilute aqueous solution is decreased, the conductivity is also decreased. This is due to decreased amount and interactions of ions upon dilution. The Table 3.1 illustrates the effect of concentration on conductivity.

Table 3.1 Conductivities of various water samples and solutions at 298 K

Sample	**Conductivity / μS cm^{-1}**
Distilled water	1 – 2
0.01 mol dm^{-3} KCl solution	1,480
0.10 mol dm^{-3} KCl solution	12,400
1.0 mol dm^{-3} KCl solution	110,000
Well water	100 – 200
Pipe borne water	50 – 150
Sea water	40,000

μS: micro seimans

The temperature of the solution has a considerable influence on the conductivity values measured. When the temperature is increased, conductivity of the solution is also increased at a given concentration due to enhanced speed of ions. This effect is clearly demonstrated in the Table 3.2 below.

Table 3.2 Conductivities of KCl(aq) and solutions at different temperatures

Concentration / mol dm^{-3}	Conductivity / µS cm^{-1}		
	0 °C	13 °C	25 °C
1.00 KCl solution	6.5×10^4	9.8×10^4	1.1×10^5
0.10 KCl solution	7.2×10^3	1.1×10^4	1.3×10^4
0.01 KCl solution	7.8×10^2	1.2×10^3	1.4×10^3

Current carried by an ion at a given temperature and an electric field depends on the concentration of ions and their speed. The speed of an ion depends on it's charge, size, and potential gradient of the applied electric field. According to Table 3.3, H^+ and OH^- ions have the highest speeds due to relatively small size. Thus, these ions are major contributors for the conductance of an aqueous solution.

Table 3.3 Speeds of ions in an aqueous solution under the potential gradient 1 V cm^{-1} at 298 K

Ion	Speed/ mm min^{-1}	Ion	Speed/ mm min^{-1}
H^+	2.05	NO_3^-	0.40
OH^-	1.12	Cl^-	0.42
Na^+	0.29	SO_4^{2-}	0.88
K^+	0.42	Ca^{2+}	0.67

Conductivity of a solution plays an important role when analyzing ionic content of a water sample. In practice, conductivity meters are used to measure the conductivity of a solution. Such measurements can be used in evaluating salinity, calculating solubility products, and in many other applications.

3.2 Electrodes in equilibrium

3.2.1 Metal – metal ion electrode

Before discussing details about this *electrode equilibrium* it may be worth understanding the behaviour of reactivity of metals in solutions as that would be the basic concept of building up an electrode.

As we know, when metals react, they give away electrons and form positive ions. For example, $Mg^{2+}(aq)$, $Zn^{2+}(aq)$ or $Cu^{2+}(aq)$ ions are formed when the respective metals react in aqueous solutions of their ions and form positive and negative charges as shown by the following reaction.

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e$$

This occurs as follows; once a piece of solid magnesium is dipped in a beaker of Mg^{2+} solution there will be some tendency for the magnesium atoms to remove electrons and go into solution as $Mg^{2+}(aq)$ ions. The electrons will be left behind on the magnesium as depicted in the Figure 3.3.

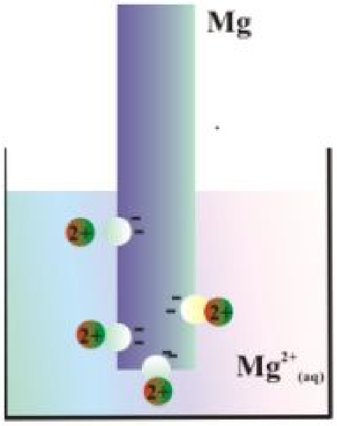


Figure 3.3 Behaviour of Mg metal in an aqueous solution of $Mg^{2+}(aq)$ ions

Once the Mg rod is dipped in Mg^{2+} solution, there will be a quick build-up of electrons on the magnesium, and it will be surrounded in the solution by a layer of positive Mg^{2+} ions. These will tend to stay close because they are attracted to the negative charge on the piece of metal. Some of them will be attracted enough that they will reclaim their electrons and stick back on to the piece of metal. A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again. At that point there will be a constant negative charge on the magnesium rod and a constant number of $Mg^{2+}(aq)$ ions surround the rode. This dynamic equilibrium is shown in Figure 3.4 in which the negative charge on the Mg rod is balanced by the positive charges surrounded by it in the solution. Once this situation is achieved, we consider and define such a system as an electrode.

A system where a metal is in dynamic equilibrium with its ions can be defined as an ***electrode****.*

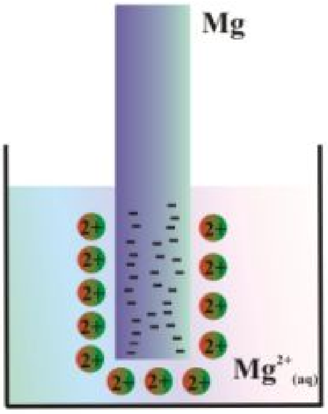


Figure 3.4 Behaviour of Mg metal in an aqueous solution at dynamic equilibrium

As with the above descriptions it is notable that the equilibrium exists in two ways; in one direction Mg solid is converted to $Mg^{2+}(aq)$ ions while in the other direction $Mg^{2+}(aq)$ ions in the solution are converted to Mg metal. In other words, Mg oxidizes in one direction and $Mg^{2+}(aq)$ reduces in the other direction indicating that the overall system exhibits an oxidation-reduction couple.

Accordingly, we can get the idea that a charge separation occurs at the interface between metal and the solution/water. The tendency of this charge separation depends on the activity of metal. For example if we use a rod of Cu metal, the charge separation will be less compared to that of Mg. This relates the activity of metals described in electrochemistry (detailed discussion of this will appear in a later section).

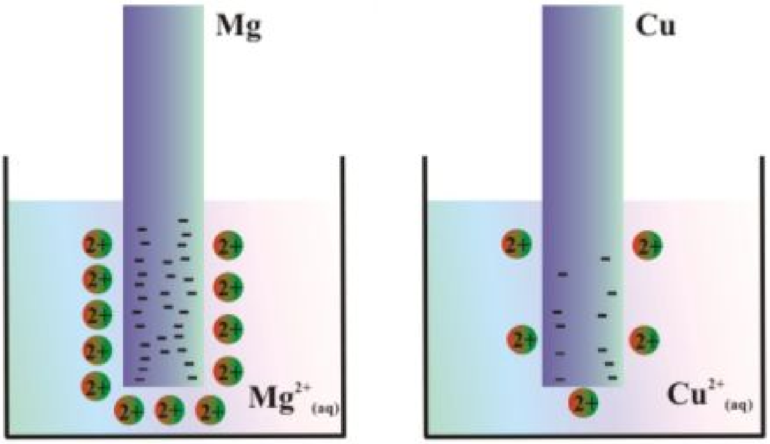


Figure 3.5 Behaviour of Mg and Cu metals in an aqueous solutions at dynamic equilibrium. As Cu is less reactive than Mg, Cu forms its Cu^{2+} ions less readily.

In general any ions which do break away are more likely to reclaim their electrons and stick back on to the metal again. The equilibrium position can still reachable, but there will be less charge on the metal, and fewer metal ions in solution as compared in Figure 3.5.

Once systems are in dynamic equilibrium, two reactions can be written as given below and it will also be possible to compare the positions of equilibrium of the two systems.

$$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s) \quad \dots\dots\dots\dots (1)$$

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s) \quad \dots\dots\dots\dots (2)$$

According to Figure 3.5, the position of the equilibrium (1) is further to the left than that of the equilibrium (2).

It has to be noted the way that the two equilibria are written. By convention, all these equilibria are usually written with the electrons on the left-hand side of the equation that is as a reduction reaction.

As the position of equilibrium is different in the above two cases, the ability to reach the equilibrium may be expressed by introducing some numbers and that can be directly related to the term **electrode potential** which is simply an attempt to attach some numbers to these differing positions of equilibria. In principle, that is quite easy to do. In the case of magnesium, there is a large difference between the negativeness of the metal and the positiveness of the solution around it. In the copper case, the difference is much less and this can be used to understand the potential which arises due to the charge separation at the interface of the particular electrode.

This **potential difference** can be recorded as a voltage meaning that the bigger the difference between the positiveness and the negativeness, the bigger the voltage. Unfortunately, that voltage is impossible to measure by connecting a device to the above mentioned systems.

Even though, it would be easy to connect a voltmeter to the piece of metal, the problem is how a connection is made to the solution. If any probe is put into the solution a similar sort of equilibrium would happen around it. Therefore, the best measure would be some sort of combination of the effects at the probe and the piece of metal of interest.

That means, it is not required to measure the absolute voltage between the metal and the solution. It is enough to compare the voltage with a standardized system called a **reference electrode** and the system used is called a *standard hydrogen electrode (SHE)* which is shown in Figure 3.6.

As we know from the unit 12 (Equilibrium), the position of any equilibrium can be changed by changing conditions. That means the conditions must be standardized so that you can make fair comparisons.

In the standard hydrogen electrode the following conditions are used: 101325 Pa ~100 kPa, 1 atm pressure of hydrogen gas, the temperature of 298 K (25 °C) and 1.0 mol dm^{-3} concentration of the hydrogen ions in the solution.

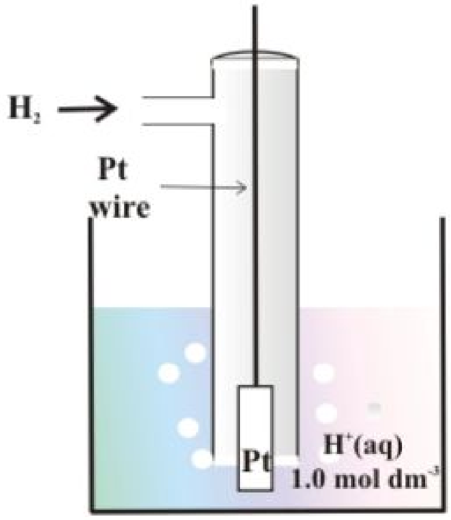


Figure 3.6 The standard hydrogen electrode

In this electrode, as the hydrogen gas flows over the porous platinum, an equilibrium is established between hydrogen molecules and hydrogen ions in solution which is catalyzed by platinum.

$$2H^+(aq) \ + \ 2e \rightleftharpoons H_2(g)$$

Now let us see how we would measure the potential of a given electrode. In this measurement, the standard hydrogen electrode is attached to the electrode system for example, a piece of magnesium in a solution containing magnesium ions as considered earlier; a conducting Pt wire is introduced to connect the voltmeter and a salt bridge is introduced as shown in Figure 3.7.

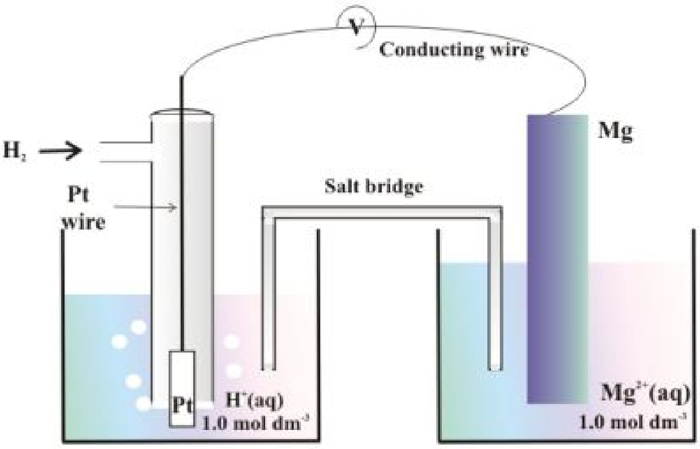


Figure 3.7 Measurement of electrode potential using the standard hydrogen electrode

The salt bridge is introduced to complete the electrical circuit making a liquid junction. It is just a glass tube filled with a solution of an electrolyte like potassium nitrate. The ends are "stoppered" by bits of cotton wool or sometimes with agar gel to prevent mixing of the contents in the salt bridge with the contents of the two beakers. Each electrode on one side is defined as a *half-cell*.

It has to be noted that the electrolyte in the salt bridge is chosen so that it doesn't react with the contents of either beaker.

Once the two electrodes are connected two equilibria are set up on the two electrodes as follows.

$$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$$

$$2H^{+}(aq) + 2e \rightleftharpoons H_2(g)$$

Magnesium has a much higher ability to form its ions than hydrogen does. Therefore, position of the Mg/Mg^{2+} equilibrium will be more to the left than that of the H_2/H^+ equilibrium. This means that there is a much greater build-up of electrons on the piece of magnesium than on platinum. Therefore, there is a major difference between the charges on the two electrodes and hence a potential difference which can be measured with a voltmeter.

The value of potential mentioned above for $Mg^{2+}(aq)$ / $Mg(s)$ is actually the standard electrode potential of the $Mg^{2+}(aq)$ / $Mg(s)$ system.

The potential difference measured when a metal / metal ion electrode is coupled to a hydrogen electrode under standard conditions is known as the standard electrode potential of that metal / metal ion combination. This means that each E° value shows whether the position of the equilibrium lies to the left or right of the hydrogen equilibrium. The difference in the positions of equilibrium causes the number of electrons built up on the metal electrode and the platinum of the hydrogen electrode to be different. Here, as a convention the number of electrons produced on the Pt surface is considered to be negligible. The standard cell potential E^0 of the standard hydrogen electrode is taken as 0.00 V at room temperature. The potential difference produced is measured as a voltage having units of volts (V).

As we know that magnesium has the greater amount of negativeness, the voltage measured would be 2.37 V and the voltmeter would show magnesium as the negative electrode and the hydrogen electrode as positive. Therefore, the standard electrode potential of the $Mg^{2+}(aq)$/ $Mg(s)$ electrode is recorded as $E^0 = -2.37$ V.

In the case when a similar measurement is done with the $Cu^{2+}(aq)/ Cu(s)$ electrode, copper forms its ions less readily than hydrogen does.

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$$

$$2H^{+}(aq) + 2e \rightleftharpoons H_2(g)$$

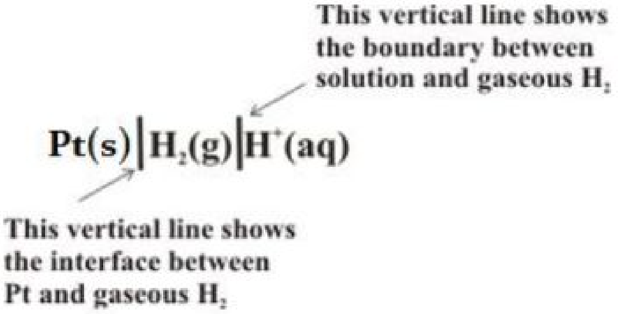
Therefore, the equilibrium in the hydrogen electrode lies further to the left. As a result there will be less build-up of electrons on copper than that is on the platinum of the hydrogen electrode. Therefore, there is less difference between the electrical charges on the two electrodes, so the voltage measured will be less (only +0.34 volts).

The other major change is that this time the copper is the more positive (less negative) electrode. The voltmeter will show the hydrogen electrode as the negative electrode and the copper electrode as the positive electrode and hence the electrode potential is recorded as + 0.34 V.

(If any current flows, the voltage measured drops. In order to make proper comparisons, it is important to measure the maximum possible voltage in any situation. This is called the ***electromotive force*** *or* ***e.m.f.*** *Details of this will be discussed in coming sections).*

Electrode notations

The hydrogen electrode is represented as below.



From the above descriptions we know that the standard electrode potential of a metal / metal ion combination is the potential difference measured when that metal / metal ion electrode is coupled to a hydrogen electrode under the standard conditions.

The measurement of electrode potentials allows us to determine the position of the metal/ metal ion equilibrium with respect to the equilibrium involving hydrogen.

A few typical standard electrode potentials are shown in the table below.

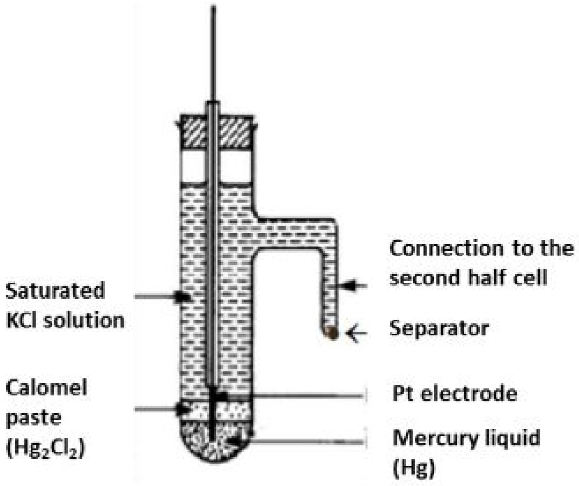
Metal / metal ion combination	$E°$/ V
Mg^{2+}(aq)/ Mg(s)	-2.37
Zn^{2+}(aq)/ Zn(s)	-0.76
Cu^{2+}(aq)/ Cu(s)	+0.34
Ag^{+}(aq)/ Ag(s)	+0.80

Comparing these with the $E°$ values, it can be seen that the ones whose positions of equilibrium lie furthest to the left have the most negative $E°$ values. That is because they form ions more readily leaving more electrons behind on the metal. Those which don't release electrons readily have positions of equilibrium further to the right. Their $E°$ values get progressively more positive.

In addition to these metal-metal ion electrodes, there are other types of electrodes as discussed below.

3.2.2 Metal – insoluble salt electrode

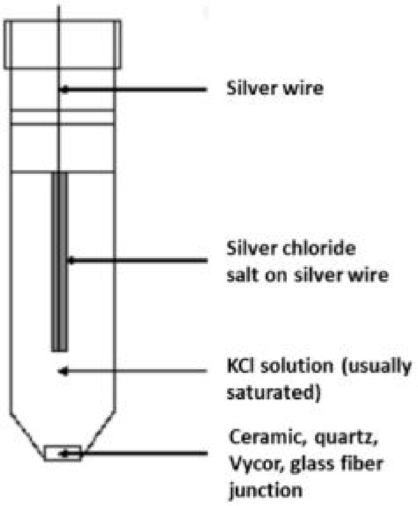
In order to define an electrode it is necessary to have oxidized and reduced species of the same element to be present. Accordingly, if a metal is in contact with the solid salt of the same metal, such electrodes are called **metal – insoluble salt type**. Examples for such electrodes are calomel electrode and silver-silver chloride electrode. Figure 3.8 shows details of the calomel electrode. A Pt wire is used to establish the electrical connection with an external circuit. A saturated solution of KCl is used for the electrical conductance.



$$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$$

Figure 3.8 Calomel electrode

Silver – silver chloride is another example for metal-insoluble salt type of an electrode. The essential components of this electrode comprise a silver wire coated with AgCl which is in contact with the KCl electrolyte. An important part of silver – silver chloride electrode is the tip (ceramic, quartz, vycor tip, glass fibre) that connects electrode with the external solution. Figure 3.9 illustrates silver-silver chloride electrode.



$$AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$$

Figure 3.9 Silver – silver chloride electrode

In general, calomel electrode and silver – silver chloride electrode are also known as **reference electrodes** as potential of these electrodes remains almost constant during experiment time.

3.2.3 Gas electrodes

Hydrogen electrode

Standard Hydrogen Electrode is an example for a gas electrode. The standard conditions used here are 1.0 mol dm^{-3} H^+ ion concentration, 1 atm pressure for H_2 gas, and temperature of the system is at 298 K. This hydrogen electrode is called the **standard electrode** as the potential of this electrode is defined as 0.00 V as described earlier.

$$2H^+_{(aq)} + 2e \rightleftharpoons H_2(g)$$

Chlorine electrode

Chlorine is well known as an oxidizing agent. Since the electrochemical series is about ranking substances according to their oxidizing or reducing ability, it makes some insights to the electrode reactions with gases like chlorine. Again, as has been done above, we can measure the position of this equilibrium relative to the hydrogen equilibrium.

$$Cl_2 (g) + 2e \rightleftharpoons 2Cl^-(aq)$$

Note that as usual, the equilibrium is still written with the electrons on the left-hand side of the equation. That's why the chlorine gas has to appear on the left-hand side rather than on the right indicating the reduction during the reaction. For this chlorine electrode, a half-cell can be built as similar to the hydrogen electrode by bubbling chlorine gas over a platinum electrode, which is immersed in a solution containing chloride ions with a concentration of 1.0 mol dm^{-3}.

The notation of writing the cell looks like this.

$$Pt(s)|Cl_2(g) \mid Cl^-(aq)$$

It can be noted that the chloride ions are losing electrons and hence the cell has a positive potential difference.

3.2.4 Redox electrodes

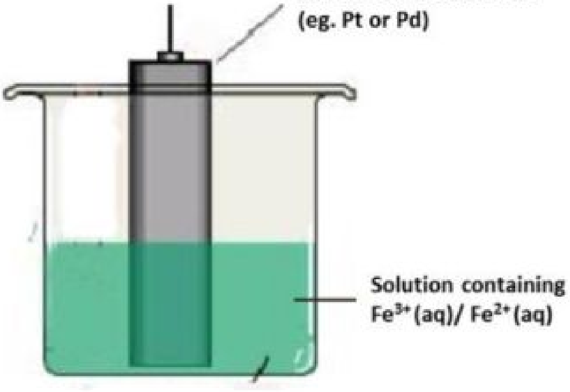
These types of electrodes are frequently observed in redox reactions. Both oxidized and the reduced species must be present in the solution when defining a particular redox electrode. A Pt wire can be used to establish the electrical connection with the external circuit. Such a redox type of electrode is given in Figure 3.10.

Fe^{2+}/ Fe^{3+} redox electrode system

Iron(II) ions can easily be oxidized to iron(III) ions, and iron(III) ions are fairly easily reduced to iron(II) ions. The equilibrium for this can be written as follows.

$$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$$

To measure the redox potential of this, a platinum electrode can be inserted into a beaker containing a solution of both iron(II) and iron(III) ions (1.0 mol dm^{-3} with respect to each), and couple this to a hydrogen electrode.



$$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$$

Figure 3.10 The Fe^{2+}/ Fe^{3+} redox electrode system

- When writing electrode in standard notation, phase boundaries are separated by a vertical line "|"

  E,g. Gas electrodes: $Pt(s)|O_2(g)|OH^-(aq)$
- Physical states must be included next to each chemical species and conditions should be included where possible.

  E.g. Redox electrodes: $Pt(s)|Fe^{2+}(aq,1\ mol/dm^3),\ Fe^{3+}(aq,1\ mol/dm^3)$

The following table summarizes the types of different electrodes with some examples.

Table 3.4 Summary of different types of electrodes

Type of electrode	Standard notation	Redox couple	Reduction half reaction
Metal – metal ion	**$M(s)\vert M^{n+}(aq)$**	**$M(s)/M^{n+}(aq)$**	**$M^{n+}(aq) + ne \rightarrow M(s)$**
	$Zn(s)\vert Zn^{2+}(aq)$	$Zn(s)/Zn^{2+}(aq)$	$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$
Metal – insoluble salt	**$M(s)\vert MX_n(s)\vert X^-(aq)$**	**$M(s)/MX_n(s)$**	**$MX(s) + ne \rightarrow nM(s) + X^- (aq)$**
	$Ag(s)\vert AgCl(s)\vert Cl^-(aq)$	$Ag(s)/Ag^+(aq)$	$AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$
	$Pt(s)\vert Hg(l)\vert Hg_2Cl_2(s)\vert Cl^-(aq)$	$Hg(l)/Hg_2Cl_2(s)$	$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$
Gas	**$Pt(s)\vert X_2(g)\vert X^+(aq)$**	**$X_2(g)/X^+(aq)$**	**$X^+(aq) + e \rightarrow \frac{1}{2}X_2(g)$**
	$Pt(s)\ \vert X_2(g)\ \vert X^-(aq)$	$X^-(aq)/X_2(g)$	$\frac{1}{2}X_2(g) + e \rightarrow X^-(aq)$
	$Pt(s)\vert H_2(g)\vert H^+(aq)$	$H_2(g)/H^+(aq)$	$H^+(aq) + e \rightarrow \frac{1}{2}H_2(g)$
	$Pt(s)\vert O_2(g)\vert OH^-(aq)$	$OH^-(aq)/O_2(g)\vert$	$2O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^-(aq)$
Redox	**$Pt(s)\vert M^+(aq),M^{2+}(aq)$**	**$M^+(aq)/M^{2+}(aq)$**	**$M^{2+}(aq) + e \rightarrow M^+(aq)$**
	$Pt(s)\vert Sn^{2+}(aq),Sn^{4+}(aq)$	$Sn^{2+}(aq)/Sn^{4+}(aq)$	$Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq)$

Note: *When writing any electrode reaction, a single arrow is used when there is a current passing through (not in equilibrium) and an equilibrium arrow is used when the electrode is isolated. Also, it is compulsory to mention the physical state of the chemical species whenever electrode reactions are written.*

As indicated in above examples it is necessary to note that the electrode potentials of half-cells are given as redox potentials (the potential of the redox reaction).

Therefore, by arranging various redox equilibria in the order of their standard electrode potentials (redox potentials) we can build up the **electrochemical series**. The most negative E° values are placed at the top of the electrochemical series, and the most positive at the bottom as summarized in Table 3.5.

Table 3.5 Standard reduction potentials of selected electrodes at 298K

Reduction half reaction	**Standard reduction potential ($E^\ominus$ / V)**
$Li^+(aq) + e \rightarrow Li(s)$	-3.05
$K^+(aq) + e \rightarrow K(s)$	-2.93
$Ca^{2+}(aq) + 2e \rightarrow Ca(s)$	-2.87
$Na^+(aq) + e \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$	-2.36
$Al^{3+}(aq) + 3e \rightarrow Al(s)$	-1.66
$Mn^{2+}(aq) + 2e \rightarrow Mn(s)$	-1.18
$2H_2O\ (l) + 2e \rightarrow H_2\ (g) + 2OH^-\ (aq)$	-0.83
$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$	-0.76
$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	-0.44
$Ni^{2+}(aq) + 2e \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$	-0.13
$H^+(aq) + e \rightarrow 1/2H_2(g)$	**0.0**
$Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq)$	+0.15
$AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$	+0.27
$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	+0.34
$O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^-(aq)$	+0.40
$I_2(s) + 2e \rightarrow 2I^-\ (aq)$	+0.54
$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e \rightarrow Ag(s)$	+0.80
$Br_2(l) + 2e \rightarrow 2Br^-(aq)$	+1.09
$O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l)$	+1.23
$Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$	+1.36
$Au^{3+}(aq) + 3e \rightarrow Au(s)$	+1.40
$S_2O_8^{2-}(aq) + 2e \rightarrow 2SO_4^{2-}(aq)$	+2.05
$F_2(g) + 2e \rightarrow 2F^-(aq)$	+2.87

Reducing agents and oxidizing agents

As we know, a **reducing agent** reduces some other chemical species. That means that a **reducing agent** gives electrons to another chemical species. Conversely, an **oxidizing agent** oxidizes something else by accepting electrons.

According to the above electrochemical series, magnesium is good at giving away electrons to form its ions. Hence Magnesium is a good reducing agent. On the other hand, copper doesn't form its ions very readily, and its ions easily pick up electrons to convert to metallic copper. Hence, copper(II) ions must be a good as an oxidizing agent.

It is with this idea we notice that the metals at the top of the series (with negative standard electrode potential) are good at giving away electrons hence act as good reducing agents. The reducing ability of the metal increases going up the series.

Metal ions at the bottom of the series are good at picking up electrons. These are good oxidizing agents. The oxidizing ability of the metal ions increases down the series.

In other words, the more negative the E° value, the position of the equilibrium to the left and the tendency of the metal to lose electrons. Therefore, the more negative the value, a particular species is stronger reducing agent. The situation is opposite for the species at the bottom of the electrochemical series as these are good oxidizing agents. Therefore, metals such as Na, Mg, Zn, etc. with negative reduction potential prefer to be in ionic state rather elemental state and shows higher reactivity. The opposite is true for the species listed below the potential of standard hydrogen electrode. When two metals are in contact, metals with higher negative standard potential prefer to be in ionic state, thus can be used to reduce ions of the other metal in contact.

3.3 Electrochemical cells

3.3.1 Construction of an electrochemical cell

So far we have considered combinations of a hydrogen electrode with the different electrodes as we measure standard reduction potential. It is interesting to consider what happens if a zinc half-cell is combined with a copper half-cell through a voltmeter and the solutions are connected via a salt bridge as shown in Figure 3.11.

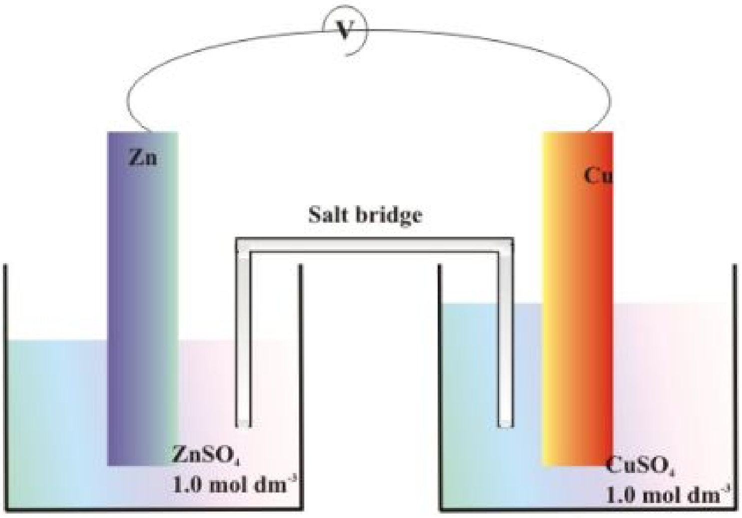


Figure 3.11 An electrochemical cell prepared by connecting two half-cells of Zn and Cu

This type of set up is defined as an **electrochemical cell** which **consists of two electrodes in contact with an electrolyte**. In an electrochemical cell, there can be a common electrolyte or may be in different electrolytes. In the latter case, electrodes in two different electrolytes are connected via a salt bridge. The potential generated due to presence of two different electrolytes in the electrode compartments is called "liquid junction potential". However, this potential can be minimized if two electrolytes are joined using a salt bridge. A salt bridge is essentially a medium consisting of an electrolyte such as KCl or KNO_3 which is jellified with agar in an inverted "U" shaped tube. The two ends of liquid junction are dipped in respective electrode units. This liquid junction can also be made by a permeable membrane/ diaphragm/ porous partitioning which allows ions to pass through it.

The two equilibria which are set up in the above half cells are as follows.

$$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s) \qquad E^0 = -0.76\ V$$

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s) \qquad E^0 = +0.34\ V$$

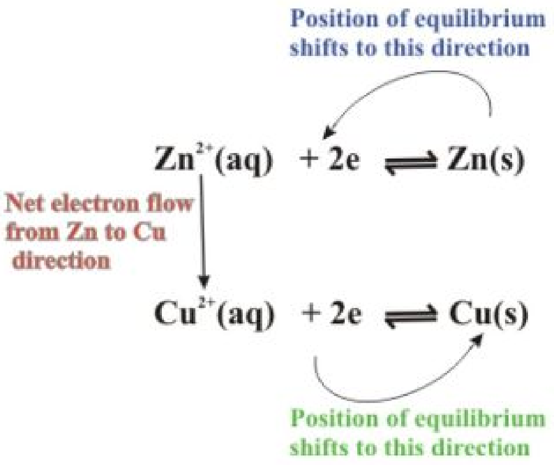
The negative sign of the E° value for zinc shows that it releases electrons more readily than hydrogen does. The positive sign of the copper E° for copper shows that it releases electrons less readily than hydrogen.

This allows us to compare the two electrode equilibria directly. The position of the zinc equilibrium lies further to the left than the copper equilibrium. Therefore, the voltmeter will show that the zinc as the negative electrode and copper is the (relatively) positive one. It will indicate a voltage showing the difference between them.

Usually the high resistivity voltmeter is used stop any current flow in the circuit. If the circuit is constructed without a voltmeter but two half-cells still connected, then electrons will flow from where there are lot of them (on zinc) to where there are fewer (on copper). The movement of the electrons is thus an electrical current. At this situation the equilibrium is disturbed, hence we may apply Le Chatelier's Principle to understand the changes in the system due to current flow. Here following two opposing effects are noticed.

On one side, electrons are flowing away from the zinc equilibrium, according to Le Chatelier's principle; the position of equilibrium will move to replace the lost electrons.

On the other side of copper, electrons are added onto the piece of copper in the copper equilibrium. According to Le Chatelier's Principle, the position of equilibrium will move to remove these extra electrons. As a result, the changes occur as shown in the following sketch and can be illustrated by Figure 3.12.



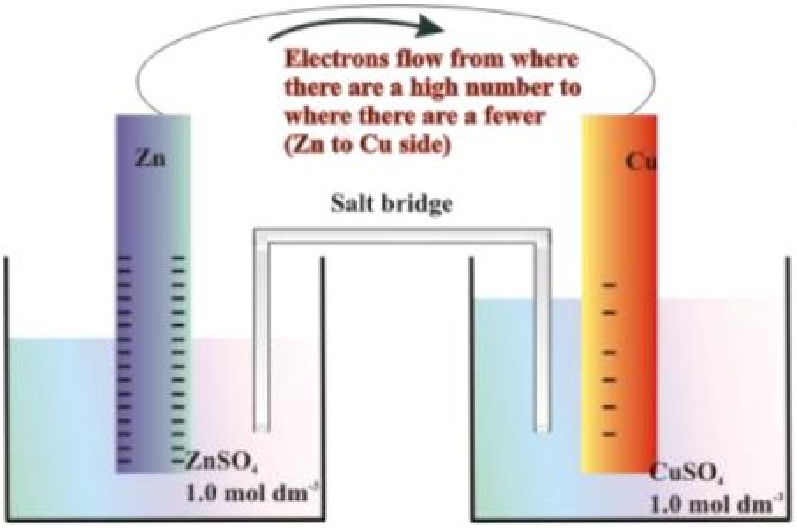


Figure 3.12 A Galvanic cell prepared by combining two half-cells of Zn and Cu without a voltmeter

In the above system, if electrons continue to flow from Zn side to Cu side, the positions of equilibrium keeps on shifting. Therefore, the two equilibria essentially turn into two one-direction (side) reactions. The zinc continues to ionize, and the copper(II) ions keep on collecting up electrons and the two reactions can be written as follows.

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

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$

Therefore, on the whole we can see that there is a **net chemical reaction going on** in which zinc is going into solution as zinc ions, and is giving electrons to copper(II) ions to turn them into metallic copper. The overall reaction can be obtained by adding the above two reactions which are called half-cell reactions.

In the above, it is seen that the current is produced in the cell due to the occurrence of a spontaneous chemical reaction. Therefore, it is possible to categorize electrochemical cells into two types. If the cell is able to produce electricity through a spontaneous reaction, then it is called a **galvanic cell** or a **voltaic cell**. If the reaction is not spontaneous then an external source of current is required to operate the cell. Such a cell is called an **electrolytic cell.**

In a galvanic cell, oxidation and reduction reactions are responsible for the operation of the cell. When the cell is in operation, electrons released at one electrode due to oxidation travels to the other electrode resulting in reduction of the chemical species in that compartment. The electrode at which *oxidation* takes place is called the **anode** and the electrode at which *reduction* takes place is called the **cathode**. The overall cell reaction is obtained as combination of reduction and oxidation half reactions. Therefore, for the galvanic cell consisting of Zn and Cu electrodes which is named as Daniel cell, the overall reaction is given by the sum of the two half reactions.

Cathode (reduction half reaction): $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ (Right hand side electrode, RHE)

Anode (oxidation half reaction) : $\underline{Zn(s) \rightarrow Zn^{2+}(aq) + 2e}$ (Left hand side electrode, LHE)

Cell reaction : $\mathbf{Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)}$

It has to be noted that, if an external opposite potential is applied to the galvanic cell described above and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V at which the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction ($\mathbf{Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)}$).

It now functions as an **electrolytic cell**, a device which uses electrical energy to carry non-spontaneous chemical reactions. Here, it is important to pay attention to the voltage of 1.1 V stated above and how it arises for the presently considered Daniel cell. This can be understood as follows.

The oxidation and reduction half reactions occur in two different parts of the Daniell cell. The reduction half reaction occurs at the copper electrode while the oxidation half reaction occurs at the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples** as mentioned earlier. The copper electrode may be called the reduction half-cell and the zinc electrode, the oxidation half-cell.

In a galvanic cell, the half-cell in which oxidation takes place (**anode**) has a **negative potential** with respect to the solution. The other half-cell in which reduction taking place (**cathode**) has a **positive potential** with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of the electron flow. The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. The ***cell potential*** is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the *cell* **electromotive force (emf)** of the cell *when no current is drawn through the cell.* It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing a galvanic cell. If there is an electrochemical cell where two electrodes are in two different electrolyte solution, there is an additional potential difference arise across the boundary. This is termed as "***liquid junction potential***". The contribution of liquid junction potential can be minimized using a salt bridge to join two electrolyte solutions.

A Galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Following points are important in writing the **cell notation.**

- *Electrode corresponding to the oxidation half reaction in a cell is always written on the left hand side and electrode where reduction half reaction take place is written on the right hand side.*
- *Phase boundaries are represented by a vertical bar "|"*
- *If there is a liquid junction potential present then a " ⁝ " is used between two electrodes*
- *If there is a salt bridge (i.e. no liquid junction potential), two electrodes are separated by a double vertical bars "||"*
- *Indication of the physical state is compulsory for all species and indication of conditions such as concentration, pressure, temperature must be in cooperated if known.*

According to the cell notation, the Daniel cell above can be written as,

$$Zn(s)|Zn^{2+}(aq,\ 1.0\ mol\ dm^{-3}))||Cu^{2+}(aq,\ 1.0\ mol\ dm^{-3})|Cu(s)$$

Other examples are:

$$Mg(s)|\ Mg^{2+}(aq,\ 1.0\ mol\ dm^{-3})\ ||\ H^{+}(aq,\ 1.0\ mol\ dm^{-3})\ |\ H_2(g)\ |Pt(s)$$

$$Pt(s)|H_2(g)\ |H^{+}(aq)\ ||\ Cl^{-}(aq)\ |Cl_2(g)\ |Pt(s)$$

When a common electrolyte HCl is used for both electrodes,

$$Pt(s)|H_2(g)\ |H^{+}(aq),\ Cl^{-}(aq)\ |AgCl(s)\ |Ag(s)$$

Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side i.e.,

$$E_{cell} = E_{right} - E_{left}$$

or

$$E_{cell} = E_{cathode} - E_{anode}$$

Thus, for the cell that we are considering,

$$E_{cell} = E_{Cu^{2+}(aq)/Cu(s)} - E_{Zn^{2+}(aq)/Zn(s)}$$

$$E_{cell} = 0.34\ V - (-0.76\ V)$$

$$E_{cell} = +1.10\ V$$

This can further be understood by the following example.

Consider the cell reaction:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

Half-cell reactions:

Cathode (*reduction*): $2Ag^{+}(aq) + 2e \rightarrow 2Ag(s)$

Anode (*oxidation*): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e$

It can be seen that the sum of half reactions leads to the overall reaction in the cell and that silver electrode acts as the cathode and copper electrode acts as the anode. The cell can be represented as:

$$Cu(s)|Cu^{2+(}aq)||Ag^{+}(aq)|Ag(s)$$

and we have ,

$$E_{cell} = E_{right} - E_{left} = E_{Ag^{+}/Ag} - E_{Cu^{2+}/Cu}$$

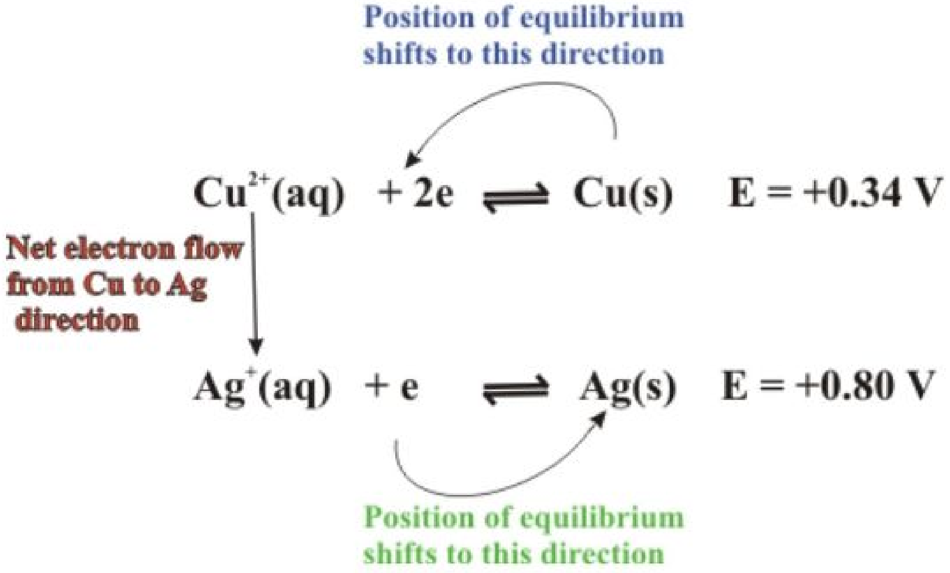
Therefore, by substituting corresponding reduction potentials of the half-cells the value of the emf of the cell can be estimated.

$$E_{cell} = +0.80\ V - (0.34\ V) = +0.46\ V$$

This reaction can also be treated like below.

Both of these E° values are positive. $E_{Ag^+/Ag} = +0.80$ V and $E_{Cu^{2+}/Cu} = +0.34$ V indicating that neither copper nor silver produces ions and releases electrons as easily as hydrogen does.

However, of the two, copper releases electrons more readily as it has a less positive E^0 value. In a cell, copper would have the greater buildup of electrons, and is the negative electrode. If copper and silver are connected by a bit of a wire, electrons would flow from the copper to silver as described below.

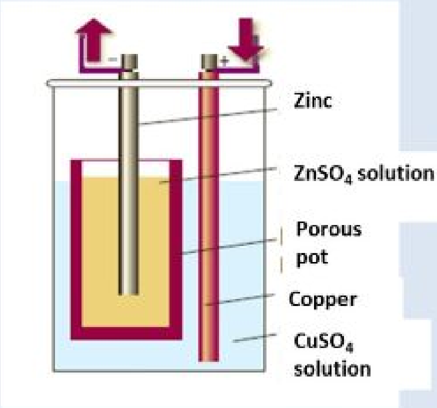


Therefore, it can be confirmed that the given cell reaction is feasible.

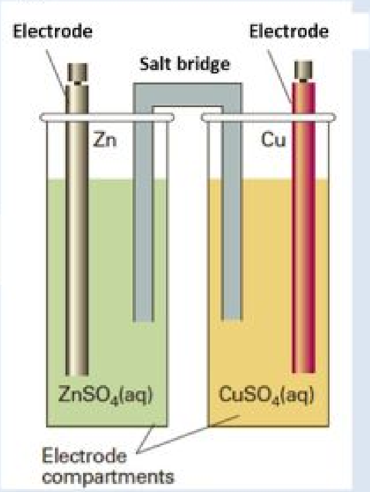
Example 3.2

Following diagrams indicate different versions of Daniel cells. Write the cell in standard notation.

(a)



(b)



Answer

(a) In this diagram, there is a liquid junction between the two different electrolytes. Therefore, cell notation is $Zn(s)|Zn^{2+}(aq)\vdots Cu^{2+}(aq)|Cu(s)$.

(b) In this diagram, the presence of liquid junction potential is minimized using a salt bridge. Therefore, cell notation is $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$.

3.3.2 Factors affecting the electrode potential

The potential of an electrode depends on several factors as listed below.

- temperature
- concentration of the electrolyte
- nature of the electrolyte
- pressure of the gas
- type of electrolyte

For an electrochemical reaction to take place, metal ions must collide with the electrode surface with proper orientation and energy. Therefore, temperature and concentration of the electrolyte are important when determining the electrode potential. The nature of the electrolyte is also important when considering charge transport during the operation of the cell. This is discussed under section 3.1.1. When gas electrodes are used, it is very important to mention the pressure of the gas as it can be used to define number of molecules in a unit volume.

The electrode potential of silver-silver chloride measured with respect to SHE is 0.220 V. However, if the concentration of KCl electrolyte used is 0.10 mol dm^{-3}, then the electrode potential is changed to 0.288 V and in the case of 1.00 mol dm^{-3} KCl it is further changed to 0.235 V.

3.3.3 Different types of electrochemical cells

Electrochemical cells are used to convert chemical energy to electrical energy. Therefore, such electrochemical cells are employed in many aspects of daily life where electrical items are operated with 'batteries'. In these cells chemical reactions occur when two electrodes are connected externally using a conductor to generate the current. When the cell reaction cannot be reversed by providing electrical energy, such electrochemical cells are called "**primary cells**" (i.e. non rechargeable). Normal Leclanche cell in Figure 3.11(a) and Daniel cell in Figure 3.11 (b) are examples for primary cells.

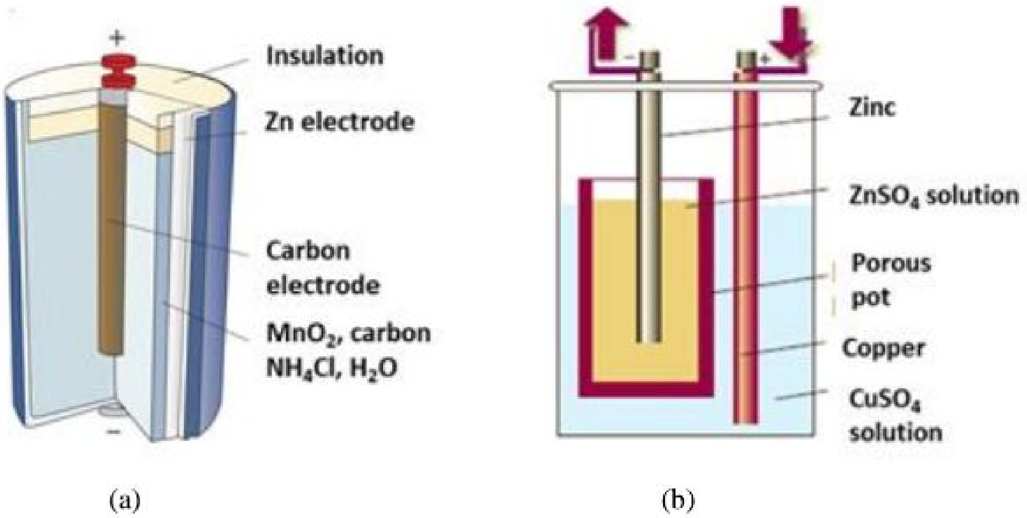
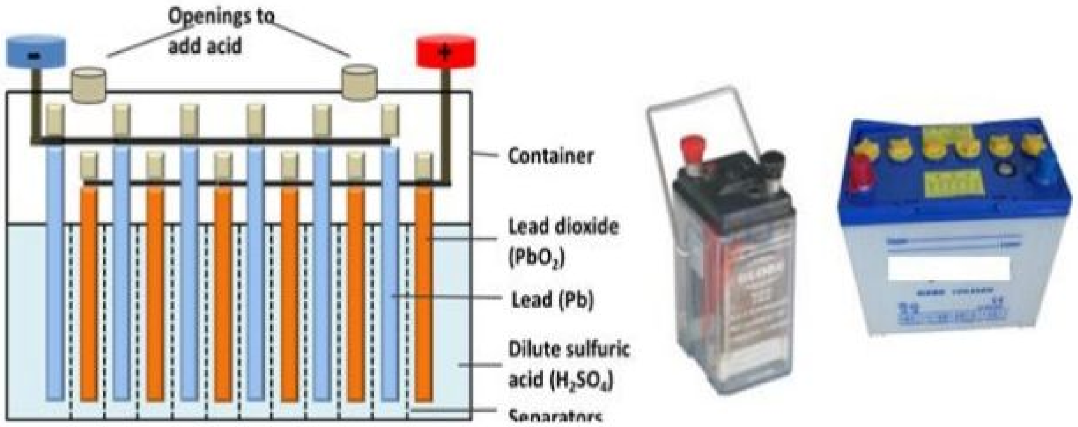


Figure 3.11 (a) Normal Leclanche cell (b) Daniel cell



(a) (b) (c)

Figure 3.12 (a) Schematic diagram of a lead accumulator (b) Lead accumulator (c) Commercial lead accumulator (car battery)

Another type of cell that is used in daily life is the lead accumulator. This is more commonly known as the "car battery". These cells can be recharged by reversing the cell reaction (rechargeable), so these cells are referred as "**secondary cells**". Figure 3.12 illustrates a lead accumulator.

Table 3.6 Summary on different types of electrochemical cells

Electrochemical cell	Normal Leclanche cell (primary cell)	Daniel cell (primary cell)	Lead accumulator (secondary cell)
Electrolyte	NH_4Cl / $ZnCl_2$	$ZnSO_4$ (aq)/ $CuSO_4$ (aq)	Dil. H_2SO_4
(+) pole	C/ MnO_2	Cu	PbO_2
(-) pole	Zn	Zn	Pb
Reaction at (+) pole (Cathode reaction)	$2NH_4^+(aq) + 2MnO_2(s) + 2e \rightarrow Mn_2O_3(s) + H_2O(l) + 2NH_3(g)$	$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	(During discharging) $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \rightarrow PbSO_4(s) + 2H_2O(l)$
Reaction at (-) pole (Anode reaction)	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$	(During discharging) $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(aq) + 2e$
Cell reaction	$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l) + 2NH_3(g)$	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	(During discharging) $PbO_2(s) + 4H^+(aq) + Pb(s) \rightarrow 2\,PbSO_4(s) + 2H_2O(l)$

3.4 Electrolysis

In Galvanic cells, a spontaneous chemical reaction can convert chemical energy to electrical energy. However, in daily life we come across situations where non-spontaneous redox reactions must be carried out to produce useful items. Examples are electroplating where precious metals like silver (Ag) can be coated on a less expensive metal to get a more appealing cover or can be used to coat a protective metal layer. In such a situation, the corresponding non-spontaneous chemical reaction can be driven forward giving electrical energy from outside. Conducting a non-spontaneous chemical reaction using electrical energy from outside is known as **electrolysis**. A direct current is passed through a molten substance or substance dissolved in a suitable solvent when conducting electrolysis. Chemical reactions at electrodes will result in the desired product.

When conducting electrolysis, the electrode connected to the positive terminal of the external source of electricity (battery) is the **positive electrode (anode)**. The electrode connected to the negative terminal is the **negative electrode (cathode).** When conducting electrolysis, positive ions in the solution are attracted towards the negative electrode (cathode) and undergo reduction. The opposite happens at the anode where negatively charged ions in the solution are oxidized.

3.4.1 Electrolysis of water

Water is a very stable chemical substance. Therefore, electrolysis of water to produce hydrogen gas and oxygen gas is not a spontaneous chemical reactions under atmospheric conditions (1 atm, 25 °C, ΔG^{θ} is 474.4 kJ mol^{-1}). In order electrolyse water, external electrical energy must be supplied to carry out the redox reaction.

Electrolysis of water can be performed using the setup given in the Figure 3.14.

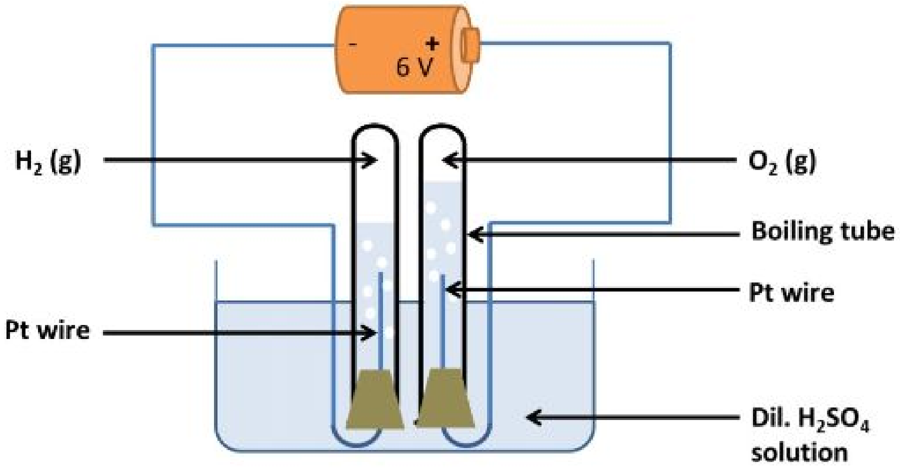


Figure 3.14 Experimental set up for electrolysis of water

The main ionic species in pure water are H^+(aq) ion and OH^-(aq) ions each having a concentration of 1×10^{-7} mol dm^{-3}. Therefore, dilute H_2SO_4 (0.10 mol dm^{-3}) is added to water to enrich $H^+(aq)$ ions in solution. This facilitates conducting electricity due to the presence of sufficient number of ionic species than in pure water.

The overall reaction is given by

Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode (reduction): $\underline{4H^+(aq) + 4e^- \rightarrow 2H_2(g)}$
Overall: $\mathbf{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$

It is clear from the overall reaction of electrolysis that H_2SO_4 concentration has no effect on the electrolysis.

Example 3.3

Using standard electrode potentials listed in Table 3.5, calculate the minimum voltage required for the electrolysis of water.

Answer

Standard electrode potentials for the electrolysis of water is given below.

Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $(E^\circ = 1.23\ V)$
Cathode (reduction): $\underline{4H^+(aq) + 4e^- \rightarrow 2H_2(g)}$ $(E^\circ = 0.00\ V)$
Overall: $\mathbf{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$

$E^\ominus$cell = $E^\ominus$cathode - $E^\ominus$anode = 0 V – (1.23 V) = **-1.23 V**

Since $E^\ominus$cell is negative, ΔG° is positive. Therefore, reaction is not spontaneous. In order to conduct this reactions external electrical supply must give a minimum voltage of 1.23 V.

3.4.2 Electrolysis of $CuSO_4(aq)$ using copper electrodes

Electrolysis of $CuSO_4$ (aq) solution using Cu electrodes is a method practiced commercially to purify copper. In general raw copper is extracted from the ore using carbon. However, copper produced in this way comprises many impurities. Therefore, pure Cu can be obtained when $CuSO_4$ (aq) solution is electrolysed with a positive electrode (anode) made of impure Cu and a negative electrode (cathode) of pure Cu. When the system is connected to an electrical source (e.g. 9V battery), impure Cu rod (anode) will dissolve providing Cu^{2+} ions to the solution while more Cu will deposit on the pure Cu rod (cathode) growing it's size.

Anode (oxidation): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

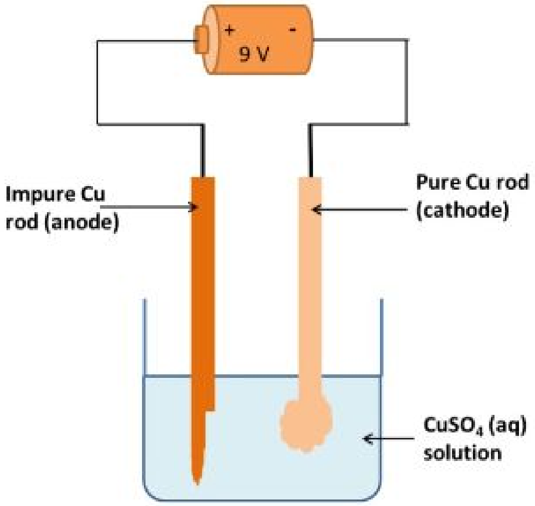


Figure 3.15 Experimental set up for electrolysis of $CuSO_4(aq)$

3.4.3 Electrolysis of $CuSO_4(aq)$ using inert electrodes

A scenario different from above is observed when electrolysis of $CuSO_4$ solution is conducted using inert electrodes such as Pt or graphite. In this case, at the anode O_2 gas is released and deposition of Cu is observed at the cathode. The experimental set up used here is much similar to Figure 3.15. The only change is the use of inert electrodes.

Anode (oxidation):	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode (reduction):	$\underline{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$
Overall reaction:	$\mathbf{2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq)}$

In this experiment if ions that are present near the cathode (negative electrode) are considered, reduction of Cu^{2+} ions to Cu metal (+0.34 V) is easier compared to reduction f H^+ ions to H_2 gas (0.00 V) according to the values of standard reduction potentials listed in **Table 13.5.** Similarly, when anode (positive electrode) is concerned, SO_4^{2-} and OH^- ions are attracted. Among these ions, oxidation of water (+1.23V) is more feasible than the oxidation of $SO_4^{2-}(aq)$ ion (+2.05 V). Therefore, at the anode, O_2 gas is released by oxidation of water.

3.4.4 Electrolysis of NaCl(aq) using inert electrodes

When considering electrolysis of NaCl(aq) solution, it is important to analyze oxidation and reduction reactions that can happen at the corresponding electrodes first. Then comparison of standard reduction potentials of competing reactions can be used to predict final products. Following are competing reduction reactions taking place near the cathode.

$$2H^+(aq) + 2e \rightarrow H_2(g) \qquad E^\circ = 0.00\ V \qquad (1)$$

$$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.83\ V \qquad (2)$$

$$Na^+(aq) + e \rightarrow Na(s) \qquad E^\circ = -2.71\ V \qquad (3)$$

When considering standard reduction potentials, the most probable reduction is reaction (1). However, this reaction requires standard conditions and also, [$H^+(aq)$] in water is too low (10^{-7} mol dm^{-3}). Hence it is not possible under ordinary laboratory conditions. The reaction (3) which involves reduction of $Na^+(aq)$ ion cannot happen due to large negative potential. Therefore, when electrolysis of $NaCl(aq)$ solution is considered, the most possible reduction reaction that can happen at the cathode is (2) which involves reduction of water to produce $H_2(g)$ and $OH^-(aq)$ ions.

In order to determine the most possible oxidation reactions that happen at the anode, first it is important to list all oxidation reactions.

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e \qquad (4)$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e \qquad (5)$$

Then we can write the standard reduction potentials for the reduction of above reactions before predicting the most possible reaction.

$$Cl_2(g) + 2e \rightarrow 2Cl^-(aq) \qquad E^\circ = +1.36\ V \qquad (4')$$

$$O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l) \qquad E^\circ = +1.23\ V \qquad (5')$$

According to above data, reduction reaction of *(4')* is more feasible than *(5')* i.e. oxidation of (5) is more feasible than (4). Therefore, according to standard reduction potentials, most favourable oxidation reaction is (5). However, when this experiment is conducted the gas evolved is Cl_2 and NOT O_2! That is because the actual potential that needs to be supplied for the reaction to take place is sometimes greater than the standard reduction potential. This extra potential is termed **over potential** (Detailed discussion of over potential is beyond the scope of G. C. E. (A/L) Chemistry syllabus). In other words, standard reduction potentials can be used to obtain minimum voltage values that can be supplied to drive the reaction of interest; however, actual voltage may be higher due to presence of over potentials. Therefore, Cl_2 (g) is observed, because over potential for reaction (5) (release of $O_2(g)$) could be much greater than for the reaction (4). Thus reaction (4) requires less potential to be supplied than for reaction (5).

Finally, the reactions taking place at the cathode and anode when electrolyzing $NaCl(aq)$ solution using inert electrodes can be written as follows.

Anode (oxidation): $2Cl^-(aq) \rightarrow Cl_2(g) + 2e$
Cathode (reduction): $\underline{2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)}$
Overall reaction: $\mathbf{2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)}$

3.4.5 Electrolysis of NaCl(l) (molten NaCl) using inert electrodes

NaCl exits in solid form at room temperature, thus does not conduct electricity due to absence of mobile ionic species. However, if the temperature is raised to more than the melting point of $NaCl(s)$ (i.e. > 801 °C), molten $NaCl(l)$ consists of mobile Na^+ ions and

Cl^- ions. Therefore, electrolysis of molten NaCl will result in reduction of Na^+ ion to produce Na metal and Cl_2 gas as the oxidation product.

Anode (oxidation): $2Cl^-(l) \rightarrow Cl_2(g) + 2e$
Cathode (reduction): $\underline{Na^+(l) + e \rightarrow Na(l)}$
Overall reaction: $\mathbf{2Cl^-(l) + 2Na^+(l) \rightarrow Cl_2(g) + 2Na(l)}$

According to the standard reduction potentials listed in Table 3.5, the minimum voltage that should be supplied for the overall reaction to take place is 4.07 V. However, in practice, much higher voltage is required to drive the reaction due to the presence of a large over potential associated with the reaction. Industrially Na metal is extracted by this method by electrolyzing molten NaCl solution. The industrial set up is known as the **Downs cell**.

Example 3.4
Predict the gases evolved at the cathode and anode when Na_2SO_4 (aq) solution is electrolyzed using inert electrodes.

Answer
Step 1: Identify possible oxidation reactions that can happen near the anode (Hint: Anions are likely to be oxidized at the anode) and write standard reduction potentials using **Table 13.5**.

$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e$ (Standard reduction potential = +2.05 V) .....(1)
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ (Standard reduction potential = +1.23 V) .....(2)

When over potential is not considered, the lower the standard reduction potential easier is to oxidize when the direction of oxidation is concerned.
At the anode O_2 gas will be evolved.

Step 2: Identify possible reduction reactions that can happen near the cathode (Hint: cations are likely to be reduced at the cathode) and write standard reduction potentials using **Table 3.5**.

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ (Standard reduction potential = -0.83 V) ......(3)
$Na^+(aq) + e \rightarrow Na(s)$ (Standard reduction potential = -2.71 V) ......(4)

The higher the negative value of standard reduction potential of a species, it is more likely to be in the oxidized form. Reduction of Na^+ has a higher negative value compared to reduction of water as listed above. Therefore, Na^+ tends to stay in the Na^+ state while H_2O will be reduced at the **cathode to produce H_2 gas.**

Both half reactions involve oxidation and reduction of water instead of OH^- ions and H^+ ions. That it is because Na_2SO_4 is a neutral salt which keeps the solution at a pH of approximately 7. Therefore, H_2O oxidize and reduce itself due to the absence of high concentrations of OH^- and H^+ ions.

Step 3: Write the overall reaction combining cathode and anode reactions.

Anode (oxidation):	$2\ H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$
Cathode (reduction):	$\underline{4\ H_2O(l) + 4e \rightarrow 2H_2(g) + 4OH^-(aq)}$
Overall reaction:	$\mathbf{2\ H_2O(l) \rightarrow O_2(g) + 2H_2\ (g)}$

3.4.6 Quantitative aspects of electrolysis

Michael Faraday was the first scientist who described the quantitative aspects of electrolysis. Faraday's laws stem from what has been discussed earlier.

Faraday's laws of electrolysis

The following well known Faraday's two laws of electrolysis is mainly used for quantitative analysis in electrolysis.

(i) First Law: *The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).*

(ii) Second Law: *The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal / Number of electrons required to reduce the cation).*

The quantity of electricity Q, passed is given by

$$Q = It$$

Q is in coloumbs when I is in ampere and t is in second. That is **1 C = 1 A × 1 s**

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:

$$Ag^+(aq) + e \rightarrow Ag(s)$$

one mole of electrons is required for the reduction of one mole of silver ions. We know that charge on one electron is equal to 1.6021×10^{-19}C.

Therefore, the charge on one mole of electrons is equal to:

$N_A \times 1.6021 \times 10^{-19}\ C = 6.02 \times 10^{23}\ mol^{-1} \times 1.6021 \times 10^{-19}\ C = 96487\ C\ mol^{-1}$

This quantity of electricity is called **Faraday (constant)** and is represented by the symbol **F**.

For approximate calculations we use 1F ≃ 96500 C mol^{-1}.

For the electrode reactions:

$$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$$

$$Al^{3+}(aq) + 3e \rightarrow Al(s)$$

it is obvious that one mole of Mg^{2+} and Al^{3+} require 2 moles of electrons (2F) and 3 moles of electrons (3F) respectively.

Application of Faraday constant to electrochemical calculations

When electrolysis experiments are conducted, it is important to know quantitatively the yield of the products at the cathode and the anode. The yield is associated with the current passed through the cell for a known period of time. For example, consider following reduction reactions.

$$Na^{+}(aq) + e \rightarrow Na(s)$$

$$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^{-}(aq)$$

In order to produce 1 mole of Na(s) metal, 1 mole of electrons must be used to reduce Na^{+}. Similarly, to produce 1 mole of H_2 gas, 2 moles of electrons are required.

The charge in coulombs for a one mole of electrons is given by the **Faraday constant** which is **96485 C mol^{-1}**. Therefore, if the charge in coulombs passed through the cell is known, then the amount product of consumption of reactants can be calculated. In general, the current passed though the electrolytic cell for given period of time is known. Then the following relationship can be used to calculate the charge associated during that period of time when the current passed through is given in amperes (A) and time in seconds (s).

Current(A) × time(s) → coulombs(C) → moles of electrons → moles of product or reactant

Example 3.5

Calculate the volumes of gases evolved at the cathode and anode when dil. $H_2SO_4(aq)$ solution is electrolyzed using inert electrodes for a period of 5 h passing a current of 1.5 A under 25 °C and 1 atm pressure.

Answer

Step 1: Identify possible oxidation reactions that can happen near the anode (Hint: anions are likely to be oxidized at the anode) and write standard reduction potentials using **Table 13.5**.

$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e$ (Standard reduction potential = +2.05 V) .....(1)

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ (Standard reduction potential = +1.23 V) .....(2)

As illustrated in **Example 3.4**, the reaction at the cathode is (2). Therefore, **at the anode O_2 gas is evolved**.

Step 2: Identify possible reduction reactions that can happen near the cathode (Hint: Cations are likely to be reduced at the cathode) and write standard reduction potentials using **Table 3.5**.

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ (Standard reduction potential = -0.83 V) .....(3)

$H^+(aq) + e \rightarrow H_2(g)$ (Standard reduction potential = 0.00 V) .....(4)

Since it is a dilute H_2SO_4 solution, there is sufficient H^+ concentration present for reaction (4) to take place preferably at the cathode. Therefore, **the gas evolved at the cathode is H_2 gas**.

Step 3: Write the overall reaction combining cathode and anode reactions.

Anode (oxidation):	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$
Cathode (reduction):	$\underline{4H^+(aq) + 4e \rightarrow 2H_2(g)}$
Overall reaction:	$\mathbf{2H_2O(l) \rightarrow O_2(g) + 2H_2(g)}$

Step 4: Calculate the amount of charge passed through during electrolysis period.

Charge = current (A) × time (s) =1.5A × (5 ×60 ×60) s = **27000 C**

Amount of moles of electrons = 27000 C × (1/96485 C mol^{-1})

= **0.28 moles of electrons**

Step 5: Calculate volume of O_2 gas evolved at the anode
According to the oxidation half reaction,

4 moles of electrons → 1 mole of $O_2(g)$

Amount of moles of O_2 (g) produced

$$= 0.28 \text{ moles of electrons} \times \frac{1 \text{ mole of } O_2(g)}{4 \text{ moles of electrons}}$$

$$\mathbf{= 0.07 \text{ moles of } O_2 \text{ (g)}}$$

Apply ideal gas equation to calculate volumes of O_2 (g) produce, $V = nRT/P$

Volume of $O_2(g) = (0.07 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) / 1\times10^5 \text{ Pa}$

$= 173.4 \times 10^{-5} \text{ m}^3 =$ **1.734 dm^3**

Step 5: Calculate the volume of H_2 gas evolved at the cathode.
According to the reduction half reaction,

2 moles of electrons → 1 moles of $H_2(g)$

Amount of moles of H_2 (g) produced

$$= 0.28 \text{ moles of electrons} \times \frac{1 \text{ mole of } H_2 \text{ (g)}}{2 \text{ moles of electrons}}$$

$$\mathbf{= 0.14 \text{moles of } H_2 \text{ (g)}}$$

Apply ideal gas equation to calculate volumes of H_2 (g) produce, $V = nRT/P$

Volume of $H_2(g) = (0.14 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) / 1\times10^5 \text{ Pa}$

$= 346.8 \times 10^{-5} \text{ m}^3 =$ **3.47 dm^3**

3.4.7 Comparison of galvanic cells and electrolytic cells

The main difference between the two types of cells is the spontaneous nature of the cell reaction. In Galvanic cells, the cell reaction is spontaneous and chemical energy is converted to electrical energy. Therefore, electricity is produced in galvanic cells. The anode in a Galvanic cell is negatively charged due to electrons left behind during oxidation. The cathode is positively charged due to taking up of electrons for the reduction half reaction.

The opposite is taking place during electrolysis or in electrolytic cells. The overall cell reaction is not spontaneous. Therefore, it is necessary to pump electrons from an external source to proceeds the reaction. Therefore, a battery is used in electrolysis to supply electricity for the chemical reaction to take place. Here, the anode is connected to the positive terminal of the battery. The oxidation reaction taking place at the anode will generate electrons that are attracted towards the positive terminal of the battery. Therefore, the anode is positively charged. The opposite is true for the cathode and it is connected to the negative terminal of the battery. So the cathode in electrolytic cell is negatively charged.

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