Chapter two

Electrochemical cells

2.1. Introduction

An electrochemical system is comprised of a vessel containing an electrolyte into which two electrodes are dipped. The electrodes are connected by first-class conductors either with a source of electric current. During electrolysis, chemical reactions of ions occur at the electrodes due to the passage of electric current. In an electrolytic cell, a flow of current produces a chemical reaction; electrical energy from an external source is converted into chemical energy. In a galvanic cell, on the other hand, electric current is generated in consequence of chemical reactions proceeding at the electrodes.

The *cathode* is an electrode at which reduction occurs. *Reduction* is a reaction during which electrons are consumed. An example of a reduction is the reaction

$$Cu^{2+} + 2e^{-} \rightarrow Cu.$$

The *anode* is an electrode at which oxidation proceeds. *Oxidation* is a reaction during which electrons are released. An example of an oxidation is the reaction:

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

2.2. Basic Concepts of Electrochemistry

Oxidation and reduction

The term "**redox**" stands for **reduction-oxidation**. It refers to electrochemical processes involving **electron** transfer to or from a molecule or **ion** changing its **oxidation state**. This reaction can occur through the application of an external **voltage** or through the release of chemical energy. Oxidation and reduction describe the change of oxidation state that takes place in the atoms, ions or molecules involved in an electrochemical reaction. Formally, oxidation state is the hypothetical **charge** that an atom would have if all bonds to atoms of different elements were 100% **ionic**. An atom or ion that gives up an electron to another atom or ion has its oxidation state increase, and the recipient of the negatively charged electron has its oxidation state decrease.

For example, when atomic **sodium** reacts with atomic **chlorine**, sodium donates one electron and attains an oxidation state of +1. Chlorine accepts the electron and its oxidation state is reduced to −1. The sign of the oxidation state (positive/negative) actually corresponds to the value of each ion's electronic charge. The attraction of the differently charged sodium and chlorine ions is the reason they then form an **ionic bond**.

Oxidation and reduction always occur in a paired fashion such that one species is oxidized when another is reduced. For cases where electrons are shared (covalent bonds) between atoms with large differences in **electronegativity**, the electron is assigned to the atom with the largest electronegativity in determining the oxidation state.

The atom or molecule which loses electrons is known as the **reducing agent**, or **reductant**, and the substance which accepts the electrons is called the **oxidizing agent**, or **oxidant**. Thus, the oxidizing agent is always being reduced in a reaction; the reducing agent is always being oxidized. Oxygen is a common oxidizing agent, but not the only one. Despite the name, an oxidation reaction does not necessarily need to involve oxygen. In fact, a **fire** can be fed by an oxidant other than oxygen; **fluorine** fires are often unquenchable, as fluorine is an even stronger oxidant (it has a higher **electronegativity** and thus accepts electrons even better) than oxygen. For reactions involving oxygen, the gain of oxygen implies the oxidation of the atom or molecule to which the oxygen is added (and the oxygen is reduced). In organic compounds, such as **butane** or **ethanol**, the loss of hydrogen implies oxidation of the molecule from which it is lost (and the hydrogen is reduced). This follows because the hydrogen donates its electron in covalent bonds with non-metals but it takes the electron along when it is lost. Conversely, loss of oxygen or gain of hydrogen implies reduction.

Electrochemical cells

An **electrochemical cell** is a device capable of either generating electrical energy from chemical reactions or facilitating chemical reactions through the introduction of electrical energy. There are two types of electrochemical cells.

- ✓ Electrolytic cells and

- ✓ Galvanic (voltaic) cell.

In electrolytic cell, **nonspontaneous chemical reactions** ($\Delta G > 0$) are forced to occur by the input of **electrical energy**. This process is called **electrolysis**. An **electrolytic cell** consists of **two electrodes**, an **electrolyte** and **external power source.**

- ✓ **Electrodes** are surfaces on which oxidation or reduction half-reactions occur.
- ✓ They may or may not participate in the reactions. Those that do not react are called **inert electrodes**.
- ✓ Inert electrodes are **often used** so that they do not affect product of electrolysis.
- ✓ The external power source acts as an "*electron pump*"; the electric energy is used to do work on the electrons to cause an electron transfer
- ✓ Electrons are pulled from the anode and pushed to the cathode by the battery or power supply.
- ✓ Regardless of the kind of cell, electrolytic or voltaic, the electrodes are identified as follows.
- ✓ The **cathode** is defined as the electrode at which reduction occurs as electrons are gained by some species.
- ✓ The **anode** is the electrode at which oxidation occurs as electrons are lost by some species.

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

$$Cu(s) \leftrightarrow Cu^{+2} + 2e^{-} \text{ (oxidation)}$$

$$Zn^{+2} + 2e^{-} \leftrightarrow Zn(s) \text{ (reduction)}$$

- ✓ Each of these can be either the positive or the negative electrode.
- ✓ In electrolytic cell, anode is positive while cathode is negative.

Voltaic or **galvanic cells** are electrochemical cells in which **spontaneous (**$\Delta G < 0$**)** redox reaction produce electrical energy.

- ✓ In all voltaic cells, electrons flow spontaneously from the negative electrode (anode) to the positive electrode (cathode).
- ✓ Composed of two separated half-cells; which each consist of a metal rod or strip immersed in a solution of its own ions or an inert electrolyte.

- ✓ The electrodes are connected by wire and the circuit b/n the two cells is completed by *salt bridge*. This can be any medium through which ions can slowly pass.
- ✓ The electrons *flow* from the *anode to the cathode* through an electrical circuit rather than passing directly from one substance to another.

A ***salt bridge*** (e.g., filter paper soaked in KNO_3 or some other electrolyte) is often employed to provide ionic contact between two half-cells with different electrolytes, yet prevent the solutions from mixing and causing unwanted side reactions.

- ✓ An alternative to a salt bridge is to allow direct contact (and mixing) between the two half-cells, for example in simple electrolysis of water.
- ✓ A salt bridge allows the flow of negative or positive ions to maintain a steady-state charge distribution between the oxidation and reduction vessels, while keeping the contents otherwise separate.

Difference between Electrolytic and galvanic cell

Electrolytic cell	**Electrochemical / Galvanic cell**
It requires EMF	It produces EMF
Electric energy is converted into chemical energy	Chemical energy is converted into electrical energy
Anode is +ve and cathode '-' ve	Anode is –ve cathode is '+' ve
Oxidation takes place at anode and reduction at cathode	Oxidation takes place at anode and reduction at cathode.
Electrodes are just metal rods graphite electrode can be used	Atoms in contact with ion (graphite electrodes can be used) (Pt, O_2 , OH^-)
Discharges of ion occur at both electrodes.	Discharges of ions occur only at cathode.
Non – spontaneous reaction occurs.	Spontaneous reaction occurs
These are irreversible.	These may be reversible
Flow of electrons is from anode to cathode.	Flow of electrons is from anode to cathode
Electrons leave the cell at anode and enter the cell at cathode.	Electrons leave the cell at anode and enter the cell at cathode

Reactions occurring during electrolysis

During electrolysis, the *anode carries a positive charge and the cathode a negative charge* due to the influence of an external source. Anions travel through the electrolyte toward the anode, cations travel toward the cathode. Electrochemical reactions take place at the electrodes.

Electrochemical reactions depend primarily on the *nature of the electrolyte*, *on temperature*, *the current density, and on the material of the electrodes*. In terms of the material used, we classify electrodes as inert and active. Inert electrodes do not participate in electrochemical reactions proceeding at them- a platinum electrode is a typical example of an inert electrode. At these electrodes, the products of oxidation or reduction are either discharged or they participate in further reactions, most often with the solvent. Active electrodes take part in electrochemical reactions. They may either dissolve or their material may react with the corresponding ions.

Faraday’s Law of Electrolysis

Micheal faraday studied electrolysis using through experiment and found that there is a relation between the quantity of electricity flowing and the amount of chemical change occuring at the electrodes.

The quantitative relation made by him are known as **faradays law**

i) Faraday’s First law of electrolysis

The amount of chemical change occuring at any electrode is strictly proportional to the quantity of electricity passed through electrolyte.

$m \alpha Q \quad \Rightarrow m = zQ$

Where m = mass of chemical change

Q = quantity of electricity and z = proportionality constant

But $Q = I \times t \Rightarrow m = zIt$ where I = current passed and t = time used.

ii) Faraday's second law of electrolysis

When different compounds are decomposed by the same quantity of electricity, the amounts of products obtained at different electrode are proportional to their chemical equivalents.

i.e., $\frac{m_1}{m_2} = \frac{E_1}{E_2}$

$$\frac{m_1}{m_2} = \frac{z_1 Q}{z_2 Q} \Rightarrow \frac{m_1}{m_2} = \frac{z_1}{z_2} = \frac{E_1}{E_2}$$

Therefore the chemical equivalents of the atoms are proportional to its electrochemical equivalents.

2.3. Reversible electrodes

Reversible electrode is the electrode at which the small change in potential can reverse the direction of the net current flow at this electrode.

A metallic electrode that will dissolve when a current is passed from it into a solution and that will have plated on metal from the solution when the current is passed in the reverse direction

When current is led through a Daniell cell (***Zn / $ZnSO_4$ (aq)//$CuSO_4$ (aq)/ Cu***) from the zinc to the copper the direction in which it naturally flows, more ions of zinc are formed from the solid electrode; if by means of another battery current be sent the reverse way through the cell, it will carry some of the zinc ions with it, and deposit them in the metallic state on the electrode. The two processes are the precise converse of one another, and no new substances are formed in them. This, then, is a case of a reversible electrode, and in particular it is reversible with respect to a cation, that is Zn^{+2}.

Reversible electrodes may be divided into three groups:

Electrodes of the first kind: These include cationic electrodes (metal, amalgam, gas electrodes, the hydrogen electrode), at which equilibrium is established between atoms or molecules of the substance and the corresponding cations in solution and anionic electrodes.

Electrodes of the second kind: These electrodes consist of three phases. The metal is covered by a layer of its sparingly soluble salt and is immersed in a solution containing the anions of this salt. The solution contains a soluble salt of this anion. Because of the two interfaces, equilibrium is established between the metal atoms and the anions in solution through two partial equilibria: between the metal and its cation in the sparingly soluble salt and between the anion in the solid phase of the sparingly soluble salt and the anion in solution.

Oxidation-reduction electrodes: An inert metal (usually Pt, Au, or Hg) is immersed in a solution of two soluble oxidation forms of a substance. Equilibrium is established through electrons, whose concentration in solution is only hypothetical and whose electrochemical potential in solution is expressed in term of the appropriate combination of the electrochemical potentials of the reduced and oxidized forms, which then correspond to a given energy level of the electrons in solution. This type of electrode differs from electrodes of the first kind only in that both oxidation states can be present in variable concentrations, while, in electrodes of the first kind, one of the oxidation states is the electrode material.

Cell Diagrams and IUPAC Conventions

Galvanic cells are schematically recorded in a line, with the following conventions applied:

- ✓ The anode is written on the left, the cathode on the right.
- ✓ The phase interface is marked by a single vertical bar”|”.
- ✓ If there is a salt bridge suppressing the diffusion potential at the place of contact of two electrolytes, we write a double vertical bars”||” instead of a single one.
- ✓ With the electrolyte we note its molality or activity in brackets.
- ✓ For gas electrodes, the gas pressure or fugacity is given in brackets.
- ✓ A dash (—) is written between a gas electrode and its carrier.

- ✓ In the case of electrodes of the second type, the symbol (**s**) is written with the chemical formula of undissolved salt, emphasizing that it is not salt in a solution.

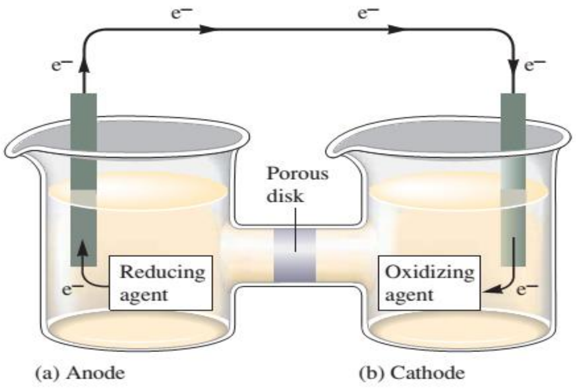


Figure1: An electrochemical process involves electron transfer at the interface between the electrode and the solution. (a) The species in the solution acting as the reducing agent supplies electrons to the anode. (b) The species in the solution acting as the oxidizing agent receives electrons from the cathode.

Example: Describe the following galvanic cell:

a) $(-)Zn\left|ZnSO_4(m_1)\right|\left|CuSO_4(m_2)\right|Cu(+)$

Solution

a) The cell is formed by a zinc anode dipped into a solution of zinc sulfate of the molality m_1.This half-cell is separated by a salt bridge from another half-cell formed by a solution of copper sulfate of the molality m_2 into which a copper cathode is dipped.

2.4. Thermodynamics of electrochemical cells

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1s.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential ($E°_{cell}$) and the total charge transferred during the reaction (nF):

$$w_{\max} = -nFE_{cell}$$

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of $E°_{cell}$. When both reactants and products are in their standard states, the relationship between $\Delta G°$ and $E°_{cell}$ is as follows:

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

A spontaneous redox reaction is characterized by a negative value of $\Delta G°$, which corresponds to a positive value of $E°_{cell}$.

Identifying the non-expansion work for the system as the work done on a reversible electrochemical cell gives an expression for dG in terms of electromotive force of an electrochemical cell

$$dG = -nFE$$

To obtain expressions for ΔS and ΔH, recall that:

$$dG = (\frac{\partial G}{\partial P})_T dP + (\frac{\partial G}{\partial T})_P dT \quad \text{and} \quad dG = VdP - SdT$$

Equating coefficients implies that:

$$(\frac{\partial G}{\partial T})_P = -S \quad \textbf{or} \quad \Delta S = -(\frac{\partial \Delta G}{\partial T})_P$$

Recalling the expression for dG yields:

$$\boxed{\Delta S = nF(\frac{\partial \Delta E}{\partial T})_P}$$

Thus, D*S* depends on the temperature dependence of the electromotive force of an electrochemical cell.

Finally, D*H* = D*G* + *T*D*S* at constant *T* and the previous results imply:

$$\boxed{\Delta H = -nFE + nFT(\frac{\partial \Delta E}{\partial T})_P}$$

Example:

The following reaction proceeds at the electrodes in a Daniell cell

$$Zn = Zn^{+2} + 2e^- \qquad Cu^{+2} + 2e^- = Cu$$

The equilibrium potential of the cell is 1 V.

a) Calculate the work done by the cell at one mole of reaction turnovers.

b) Calculate the work done by the cell at one mole of reaction turnovers if the reaction is written in the form: $\frac{1}{2}Zn = \frac{1}{2}Zn + 2 + e^-$, $\frac{1}{2}Cu + 2 + e^- = \frac{1}{2}Cu$

Solution

a) From the reactions record it follows that $z = 2$. By substituting into $W_{el} = -zFE$, we obtain $W_{el} = -2 \times 96485.3 \times 1 = -192\ 970.6\ J\ mol^{-1}$.
b) The work done has an opposite sign and it is equal to $192\ 970.6\ J\ mol^{-1}$. From the reactions record it follows that $z = 1$. The work done is half, **96 485.3 J/mol**.

Electrochemical Equilibrium in a Galvanic Cell

When an open-circuit reversible cell is assembled from its component phases, tiny amounts of charge are transferred between phases until electrochemical equilibrium is reached. In the open-circuit *Daniell cell* of Figure 2, electrochemical equilibrium exists between the ***Zn*** electrode and the ***ZnSO₄*** solution, between the ***Cu*** electrode and the ***CuSO₄*** solution, and between the ***Cu***’ terminal and the ***Zn*** electrode. However, the liquid junction (*the interface between two miscible electrolyte solutions*.) introduces irreversibility and there is no electrochemical equilibrium between the two solutions.

In the reversible ***cell 1***, there is no liquid junction and all adjacent phases are in electrochemical equilibrium.

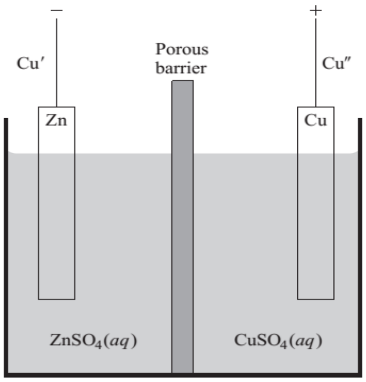


Figure 2: The Daniell cell, Open-circuit state.

Nernst equation

Let the following overall chemical reaction proceed in a galvanic cell

$$aA + bB + \ldots = sS + tT \ldots \qquad (1)$$

$$\Delta_r G = \Delta_r G^{st} + RT \ln \prod_{i=1}^{k} a_i^{v_i} \qquad (2)$$

(Equation 2 is the change in the Gibbs energy at one mole of reaction if substances involved in the reaction are in a standard state). The symbol $\prod_{i=1}^{k} a_i^{v_i}$ denotes the product of the activities of substances from ***1*** to ***k***, raised to the power of their stoichiometric numbers.

Combining the *equation 3 and 5* we obtain for the cell potential

$$\boxed{E = E^{\circ} - \frac{RT}{zF}\ln\frac{aS^{s}aT^{t}\ldots}{aA^{a}aB^{b}\ldots}} \qquad (3)$$

Where a_i is the activity of substance ***i***. This equation is called the ***Nernst equation*** for the equilibrium cell potential (electromotive force of the cell).

The quantity E° is called ***the standard equilibrium cell potential***. It is the potential of a cell in which the above reaction proceeds with the activities of all substances involved in the reaction being ***equal to one***.

If the cell is in the state of thermodynamic equilibrium, $\boldsymbol{E = 0}$ and we write

$$E^{\circ} - \frac{RT}{zF}\ln K \qquad (4)$$

Where K is the equilibrium constant of the reaction.

Equation 6 applies on condition that the cell diffusion potential, $\boldsymbol{E_d}$, is zero (either the electrodes share an electrolyte or the diffusion potential is suppressed, e.g. by a salt bridge). If it is not so, then;

$$E = E^{\circ} - \frac{RT}{zF}\ln\frac{aS^{s}aT^{t}\ldots}{aA^{a}aB^{b}\ldots} + E_d \qquad (5)$$

2.5. Determination of Standard cell potential (E^0)

The potential of the cell under standard conditions (1 M soln, 1 atm for gases, or a pure solids, or liquid) at 25ºC is called the **standard cell potential**, $E^{\circ}_{\text{cell.}}$ Or

The standard cell potential for a redox reaction, E°_{cell}, is a measure of the tendency of the reactants in their standard states to form the products in their standard states, it is a measure of the driving force for the reaction (voltage).

E^0 can be found from:

$$\Delta G_r^0 = -zFE^o \qquad (6)$$

If the standard-state partial molar Gibbs energies μ_i^o of the species in the cell reaction are known, E^o can be determined from emf measurements on the cell by an extrapolation procedure.

For example, consider the cell, $2AgCl(s)+H_2(g)\square\ \ 2Ag+2H^++2Cl^-$

Whose cell potential is given by:

$$E = E^0 - \frac{RT}{2F}\ln\frac{(\gamma_\pm m/m^0)^4}{P(H_2)/P^0} \qquad (7)$$

Rewriting (10), we have

$$E + \frac{2RT}{F}\ln(\frac{m}{m^0}) - \frac{RT}{2F}\ln\left[P(H_2)/P^0\right] = E^0 - \frac{2RT}{F}\ln\gamma_\pm \qquad (8)$$

Standard Electrode Potential

The reference electrode chosen for work in *aqueous solutions is the hydrogen electrode* **Pt|H$_2$ (g) |H$^+$ (aq)**

The standard potential of an electrode reaction (abbreviated to standard electrode potential) at temperature **T** and pressure **P** is defined to be the standard potential E^0 for the cell at **T** and **P** that has the *hydrogen electrode on the left* of its diagram and *the electrode in question on the right*.

For example, the standard electrode potential for the Cu^{2+}|Cu electrode is E^0 for the cell

Cu'|Pt|H$_2$ (g) |H$^+$ (aq) ||Cu^{2+} (aq)| Cu is $E^o = -\frac{\Delta G_r^0}{2F}$ for the chemical reaction;

H$_2$ (g) +Cu^{2+} (aq) →2H$^+$ (aq) +Cu.

Experiment gives E^o = ***0.34 V*** for this cell at 25°C and 1 bar.

Note*: All standard electrode potentials are reduction potentials.*

We can obtain the cell potential by summing the half-cell potentials.

$E^0 = E_R^0 - E_L^0$ Where E_R^0 and E_L^0 are the standard electrode potentials of the right and left half-cells of a cell whose standard emf is E^0.

For example, the measured potential for the cell shown in Figure 3 is 1.10 V.

The cell reaction is, **Zn (s) + Cu^{2+} (aq) // Zn^{2+} (aq) +Cu(s)** which can be divided into the half reactions:

Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-, -0.76\,V$

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)\ , 0.34\,V$

Then $E^0 = E^0_{Cu^{2+} \rightarrow Cu} - E^0_{Zn \rightarrow Zn^{2+}}$

$$E^0 = 0.34\,V - (-0.76V) = \mathbf{1.10V}$$

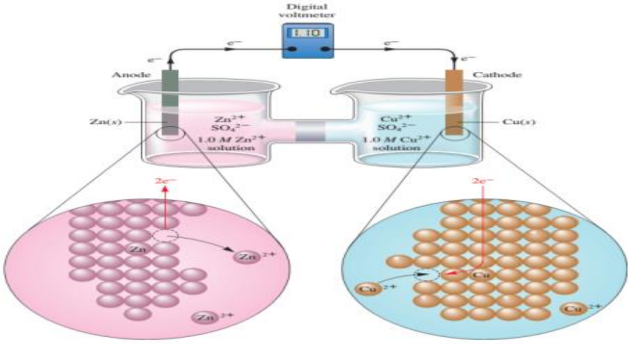


Figure 3: A galvanic cell involving the half-reactions, with $\boldsymbol{E° = 1.1V}$

***Note**: The **E°** values corresponding to reduction half-reactions with all solutes at **1 M** and all gases at **1 atm** are called standard reduction potentials.*

Example:

a. Consider a galvanic cell based on the reaction:
   $Al^{+3}(aq) + Mg(s) \rightarrow Al(s) + Mg^{+2}(aq)$
   The half-reactions are

$$Al^{+3} + 3e^- \rightarrow Al\ , E° = -1.66V*$$

$$Mg^{+2} + 2e^{-} \rightarrow Mg \ , E° = -2.37V^{**}$$

Give the balanced cell reaction and calculate ***E*°** for the cell.

b. A galvanic cell is based on the reaction

$$MnO_4^{-}(aq) + H^{+}(aq) + ClO_3^{-}(aq) \rightarrow ClO_4^{-}(aq) + Mn^{+2}(aq) + H_2O(l)$$

The half reactions are:

$$MnO_4^{-} + 5e^{-} + 8H^{+} \rightarrow Mn^{+2} + 4H_2O \ , E° = 1.51V \ ^{*}$$

$$ClO_4^{-} + 2H^{+} + 2e^{-} \rightarrow ClO_3^{-} + H_2O \ , E° = 1.19V^{**}$$

Give the balanced cell reaction and calculate***E*°** for the cell.

Solution:

The half-reaction involving magnesium must be reversed and since this is the oxidation process, it is the anode:

a. $Mg \rightarrow Mg^{+2} + 2e^{-} \ , -E°_{\text{(anoode)}} = -(-2.37V) = 2.37V$

Also, since the two half-reactions involve different numbers of electrons, they must be multiplied by integers as follows:

$$2(Al^{+3} + 3e^{-} \rightarrow Al) \ , E°_{\text{(cathode)}} = -1.66V$$

$$3(Mg \rightarrow Mg^{+2} + 2e-) \ , -E°_{\text{(anode)}} = -(-2.37V) = 2.37V$$

$$2Al^{+3}(aq) + 3Mg(s) \rightarrow 2Al(s) + 3Mg^{+2}(aq)$$

$$\boldsymbol{E°_{\text{Cell}} = E°_{\text{cathode}} - E°_{\text{anode}}} = -1.66V + 2.37V = \mathbf{0.71V}$$

b. Half-reaction (**) must be reversed (it is the anode), and both half-reactions must be multiplied by integers to make the number of electrons equal:

$$2(MnO_4^{-} + 5e^{-} + 8H^{+} \rightarrow Mn^{+2} + 4H_2O) \ , E° = 1.51V$$

$$5(ClO_3^{-} + H_2O \rightarrow ClO_4^{-} + 2H^{+} + 2e^{-}), -E°_{\text{anode}} = -(1.19V) = -1.19V$$

$$2MnO_4^{-} + 5ClO3^{-} + 6H^{+}\text{ (aq)} \rightarrow 2Mn^{+2}(aq) + 3H_2O(l) + 5ClO_4^{-}(aq)$$

$$\boldsymbol{E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}}} = -1.51V - 1.19V = \mathbf{0.32V}$$

2.6. Classification of galvanic cells

If electric energy is generated in galvanic cells in consequence of chemical reactions, we speak about a ***chemical cell***. If on the other hand, it is generated in consequence of the equalization of differences in the concentrations of substances present in different parts of the cell; we speak about a ***concentration cell***.

Concentration cells are divided into two categories:

i. **Electrolyte concentration cells:** The anodic and cathodic compartments are formed by the same electrolyte of different concentrations. Both electrodes are identical. Electrolyte concentration cells are further divided into:

  a. Cells with transference,

  b. *Cells without transference*.

a. Electrolyte concentration cells with transference

The cell is formed by two identical electrodes dipped into the same but unequally concentrated solution. Both half-cells are separated in a way that allows for the transfer of ions.

Example

Consider a galvanic cell formed by two identical hydrogen electrodes dipped into HCl solutions of the activities a_1 and a_2 , with $a_1<a_2$. The solutions are separated by a frit allowing for the transfer of ions: $Pt — H_2\ (P) \mid HCl(a_1) \mid HCl(a_2) \mid Pt — H_2\ (P)$.

Solution

The following partial reactions occur in the cell:

$1/2H_2(g) \ = \ H + (a_1) \ + e^-$ oxidation at the anode
$t_+H^+(a_1) \ = \ t_+H^+(a_2)$transfer across the frit,
$t_+Cl^-(a_2) = t_-Cl^-(a_1)$ transfer across the frit,
$H^+(a_1) + e^- = 1/2H_2(g)$ reduction at the cathode

The Nernst equation: $E = 2t^{-}\frac{RT}{F}ln\frac{m_2\gamma_{\pm,2}}{m_1\gamma_{\pm,1}}$

Note: Since both electrodes are identical, the standard cell potential $\boldsymbol{E}^{\circ}$ is zero and does not appear in the Nernst equation. This fact is characteristic of all concentration cells.

b. Electrolyte concentration cells without transference

The cell is formed by two identical electrodes dipped into the solutions of the same electrolyte, but of different concentrations. Both half-cells are separated in a way that enables ion transfer.

Example

Consider the following galvanic cell:

$Pt - H_2(P)|HCl(a_1)|AgCl(s)|Ag - Ag|AgCl(s)|HCl(a_2)|Pt - H_2(P)$
$where\ a_2 > a_1.$

Solution

Its difference from a cell with transference is that instead of a frit it has a silver chloride electrode.

It acts as a cathode with respect to the hydrogen electrode on the left of the cell record and as an anode with respect to the hydrogen electrode on the right. The following partial reactions proceed in the cell:

$1/2H_2(g) = H^{+}(a_1) + e^{-}$ Oxidation at the hydrogen anode,
$AgCl(s) + e^{-} = Ag(s) + Cl^{-}(a_1)$ Reduction at the silver chloride electrode,
$Ag(s) + Cl^{-}(a_2) = AgCl(s) + e^{-}$ Oxidation at the silver chloride electrode,
$H^{+}(a_2) + e^{-} = 1/2H_2(g)$Reduction at the hydrogen cathode.

The Nernst equation: $E = 2\frac{RT}{F}ln\frac{m_2\gamma_{\pm',2}}{m_1\gamma_{\pm',1}}$

ii. **Electrode concentration cells:** The concentration differences occur at the (otherwise identical) electrodes. These are dipped into a shared electrolyte. Electrode concentration cells are further divided into

a. ***Gas concentration cells*** *comprised of two identical gas electrodes with different partial pressures of the gas.* The electrodes are dipped into a shared electrolyte.

Example

Let us consider a cell formed by two hydrogen electrodes with the partial pressures of hydrogen p_1 and p_2, with $p_1 > p_2$, dipped into a shared electrolyte.

$$Pt—H_2(p_1) \mid HCl(a) \mid Pt—H_2(p_2)$$

Solution

The following reactions proceed in the cell:

$1/2H_2(p_1) = H^+(a) + e^-$ Oxidation,

$H^+(a) + e^- = 1/2H_2(p_2)$ Reduction

Nernst equation: $E = \frac{RT}{2F} ln \frac{p_1 f_1}{p_2 f_2}$, where f_1 and f_2 are the fugacity coefficients of hydrogen.

b. ***Amalgam concentration cells:*** *comprised of two mercury electrodes containing a dissolved metal of different concentrations.* The electrodes are dipped into a shared electrolyte in which there are cations of the given metal.

Example

Let us consider a cell formed by two cadmium amalgam electrodes dipped into a shared electrolyte.

$Cd(Hg)(a_1) \mid CdSO_4(a) \mid Cd(Hg)(a_2)$, where $a_1 > a_2$. The following reactions proceed in the cell:

$Cd(a_1) = Cd^{2+}(a) + 2e^-$ Oxidation,

$Cd^{2+}(a) + 2e^- = Cd(a_2)$ Reduction.

Nernst equation: $E = \frac{RT}{2F} ln \frac{a_1}{a_2}$

2.7. Liquid junction potential (E_j)

- ✓ Liquid **junction potential** occurs when two solutions of different concentrations are in contact with each other.
- ✓ The more concentrated solution will have a tendency to diffuse into the comparatively less concentrated one. The rate of diffusion of each ion will be roughly proportional to its speed in an electric field.
- ✓ If the anions diffuse more rapidly than the cations, they will diffuse ahead into the dilute solution, leaving the latter negatively charged and the concentrated solution positively charged.
- ✓ This will result in an electrical double layer of positive and negative charges at the junction of the two solutions. Thus at the point of junction, a potential difference will develop because of the ionic transfer.
- ✓ This potential is called liquid junction potential or diffusion potential which is non-equilibrium potential. The magnitude of the potential depends on the relative speeds of the ions' movement.
- ✓ The emf of the cell will be equal to:

$Emf = E_{cell} + E_j$ Where E_{cell} - potential of the cell and E_j is junction potential

Then $E_j = Emf - (E_R^o - E_O^o)$ or $\boxed{Emf = E_j + E_{cell}^o}$

E_j is correction potential of the cell

2.8. Measurement of pH by Cell potential methods

The pH or the hydrogen ion concentration of a solution can be determined by measuring the emf of a cell in which one of the electrodes is reversible with respect to hydrogen ions.

We shall discuss the principle of this method using electrode reversible with respect to hydrogen ions.

The hydrogen electrode

A cell may be constructed as follows,

$Pt|H_2\,(g)(1bar)\,|H^+(a_{H^+})||Cl^-|Hg_2Cl_2(s)|Hg(l)$

which is a combination of a hydrogen electrode dipped in the solution whose pH is to be determined and a calomel electrode connected by a KCl salt bridge to keep the liquid junction potential at a low value. The emf of the cell is given by:

$$E = E_R - E_L = E_{Calomel} - E_H \qquad (11)$$

Where the electrode potentials are reduction potentials of calomel and hydrogen electrodes.

Since the potential of normal calomel electrode at 25ºC is +0.2802V,

$$E = 0.2802 - E_H = 0.2802 - (E_H^0 + \frac{RT}{F}\ln a_{H^+}) \qquad (12)$$

$$E = 0.2802 - (E_H^0 + \frac{RT}{F}\ln a_{H^+}) \qquad (13)$$

Since $E_H^0 = 0$ and $a_{H_2} = 1$ since the gas is at 1 bar.

$$E = 0.2802 - 0.0591 \log a_{H^+} \qquad (14)$$

$$E = 0.2802 + 0.0591\ P^H \qquad (15)$$

as pH = – log a_{H^+}. For ordinary purposes activity is replaced by concentration and

$$P^H = -\log C_{H^+}$$

$$P^H = (E - 0.2802)/0.0591 \qquad (16)$$

Thus from the experimentally determined value of E, the pH of the solution can be obtained.

Example: If the emf of the cell Pt/H_2 (g, 1atm)/H^+ (*x*molar)//KCl (0.1M)/Hg_2Cl_2/Hg is 0.45V at 25°C, calculate the pH of the acid solution. (Electrode potential of the calomel electrode is 0.281V at 25°C).

Solution: $E = E_{calomel} - E_H$

$$E_H = E_{calomel} - E = -0.0591\ pH \text{ (from Nernst`s eqn)}$$

$$pH = (E - E_{calomel})/0.0591$$

$$= (0.45-0.281)/0.0591 = \mathbf{2.86}$$

2.9. Membrane Potential

In cells of all types, there is an **electrical potential difference** between the inside of the cell and the surrounding extracellular fluid. This is termed the **membrane potential** of the cell. The **membrane potential** is the voltage difference between the inner and outer parts of the membrane patch (depending on other channel activities present in cells, such as potassium channels, and on specific cellular properties).

Membrane potential is a potential gradient that forces ions to passively move in one direction: positive ions are attracted by the 'negative' side of the membrane and negative ions by the 'positive' one.

Consider two KCl solutions (α and β) separated by a membrane permeable to K^+ but impermeable to Cl^- and to the solvent(s) (Fig. 4). Let solution α be more concentrated than β. The K^+ ions will tend to diffuse through the membrane from α to β. This produces a net positive charge on the β side of the membrane and a net negative charge on the α side. The negative charge on solution α slows the diffusion of K^+ from α to β and speeds up diffusion of K^+ from β to α. Eventually equilibrium is reached in which the K^+ diffusion rates are equal. At equilibrium, solution β is at a higher electric potential than α, as a result of transfer of a chemically undetectable amount of K^+.

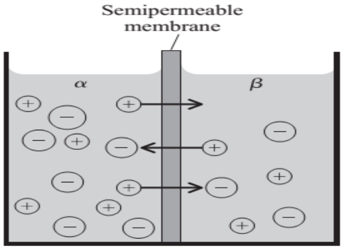


Figure 4: Two KCl (aq) solutions separated by a membrane permeable to only K^+. Diffusion of K^+ through the membrane produces a transmembrane potential.

To derive an expression for the potential difference across the membrane, consider two electrolyte solutions α and β that are separated by a membrane permeable to ion K^+ and possibly to some (but not all) of the other ions present; the membrane is impermeable to the solvent(s).

At equilibrium,

$$\tilde{\mu}_K^{\alpha} = \tilde{\mu}_K^{\beta} \tag{17}$$

$$\tilde{\mu}_K^{\alpha} = \mu_K^{\alpha} + z_K F \phi^{\alpha} = \mu_K^{0,\alpha} + RT \ln a_K^{\alpha} + z_K F \phi^{\alpha} \tag{18}$$

$$\mu_k^{o,\alpha} + RT \ln a_k^{\alpha} + z_k F \phi^{\alpha} = \mu_k^{0,\beta} + RT \ln a_k^{\beta} + z_k F \phi^{\beta} \tag{19}$$

$$\Delta\phi = \phi^{\beta} - \phi^{\alpha} = -\frac{\mu_k^{0,\beta} - \mu_k^{0,\alpha}}{z_{kF}} - \frac{RT}{z_k F} \ln \frac{a_k^{\beta}}{a_k^{\alpha}} \tag{20}$$

$\Delta\phi$ is the **membrane (or transmembrane) potential**. Note the resemblance of (eqn. 20) to the Nernst equation.

If the solvents in solutions α and β are the same, then $\mu_K^{0.\alpha} = \mu_K^{0,\beta}$ and (eqn. 20) becomes

$$\phi^{\beta} - \phi^{\alpha} = -\frac{RT}{z_k F} \ln \frac{a_k^{\beta}}{a_k^{\alpha}} = \frac{RT}{z_k F} \ln \frac{\gamma_k^{\alpha} m_k^{\alpha}}{\gamma_k^{\beta} m_k^{\beta}} \tag{21}$$

If the membrane is permeable to several ions, the equilibrium activities and the equilibrium value of $\Delta\phi$ must be such that (eqn. 21) is satisfied for each ion that can pass through the membrane.

The preceding situation where the membrane is impermeable to the solvent is called **non-osmotic membrane equilibrium**. More commonly, the membrane is permeable to the solvent, as well as to one or more of the ions. The requirements of equal electrochemical potentials in the two phases for the solvent and for the permeating ions lead to a pressure difference between the two solutions at equilibrium.

2.10. Commercial Galvanic Cells

Galvanic cells can be self-contained and portable and can be used as batteries and fuel cells. A **battery** (storage cell) is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. A **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants in order to generate electricity.

Batteries

Two basic kinds of batteries

(i) Disposable, or primary, batteries in which the electrode reactions are effectively irreversible and which cannot be recharged.

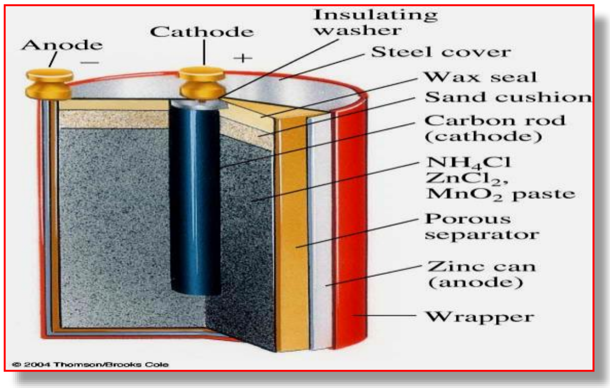
(ii) Rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes; can be recharged by applying an electrical potential in the reverse direction, which temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Major difference between batteries and galvanic cells is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass.

The Dry Cell

One example of a dry cell is flashlight and radio batteries.

- ✓ The cell’s container is made of zinc which acts as an electrode.
- ✓ A graphite rod is in the center of the cell which acts as the other electrode.



The space between the electrodes is filled with a mixture of:

- ✓ ammonium chloride, NH_4Cl
- ✓ manganese (IV) oxide, MnO_2
- ✓ zinc chloride, $ZnCl_2$
- ✓ and a porous inactive solid

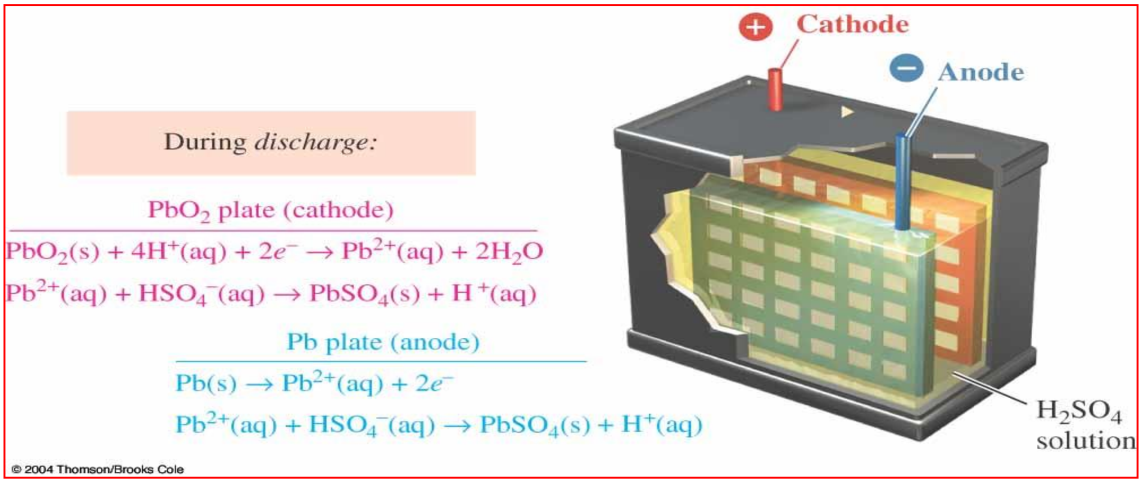
Secondary Voltaic Cells

- ✓ Secondary cells are reversible, rechargeable.
- ✓ The electrodes in a secondary cell can be regenerated by the addition of electricity.
- ✓ These cells can be switched from voltaic to electrolytic cells.
- ✓ One example of a secondary voltaic cell is the lead storage or car battery.

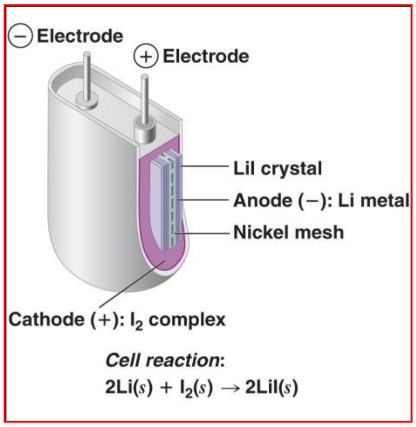
The Lead Storage Battery

- ✓ In the lead storage battery the electrodes are two sets of lead alloy grids (plates).
- ✓ Holes in one of the grids are filled with lead (IV) oxide, PbO_2.
- ✓ The other holes are filled with spongy lead.
- ✓ The electrolyte is dilute sulfuric acid.

Diagram of the lead storage battery



Lithium-iodine battery



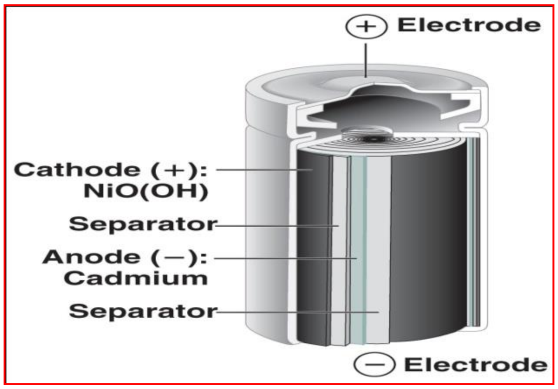
- ✓ Water-free battery
- ✓ Consists of two cells separated by a metallic nickel mesh that collects charge from the anodes
- ✓ The anode is lithium metal, and the cathode is a solid complex of I_2
- ✓ Electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode
- ✓ Highly reliable and long-lived
- ✓ Used in cardiac pacemakers, medical implants, smoke alarms, and in computers

<u>The Nickel-Cadmium (Nicad) Cell</u>

Nicad batteries are the rechargeable cells used in calculators, cameras, watches, etc. a water-based cell with a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity. Lightweight, rechargeable, and high capacity but tend to lose capacity quickly and do not store well; also presents disposal problems because of the toxicity of cadmium.

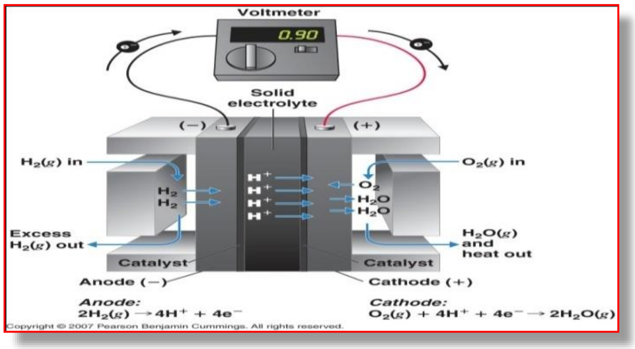
***Cell reaction*:**

$$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$$



Fuel Cells

- ✓ A galvanic cell that requires an external supply of reactants because the products of the reaction are continuously removed.
- ✓ Does not store electrical energy but allows electrical energy to be extracted directly from a chemical reaction.
- ✓ Have reliability problems and are costly.
- ✓ Used in space vehicles.
    - ✓ Hydrogen is oxidized at the anode.
    - ✓ Oxygen is reduced at the cathode.



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A brief summary of these six fuel cell types is given below.

- PEMFC, Proton Exchange Membrane Fuel Cell.
- DMFC, Direct Methanol Fuel Cell.
- PAFC, Phosphoric Acid Fuel Cell.
- AFC, Alkaline Fuel Cell.
- MCFC, Molten Carbonate Fuel Cell.
- SOFC, Solid Oxide Fuel Cell.

2.11. Applications of standard potentials

a) The determination of Activity Coefficients

Once the standard potential of an electrode in the cell is known, we can use it to determine mean activity coefficients by measuring the cell emf with the ions at the concentration of interest.

For example, the mean activity coefficients of the ions in HCl of molality m is obtained in the form of: $\ln \gamma_{\pm} = \frac{E^{o} - E}{2RT/F} - \ln m$

b) The determination of equilibrium constants

Substitution of $\Delta G^{o} = -nFE^{0}$ into $\Delta G^{0} = -RT \ln K^{0}$ gives $\ln K^{0} = \frac{nFE^{0}}{RT}$

c) The determination of thermodynamic functions

The standard emf of a cell is related to the standard reaction Gibbs energy through Equation ($\Delta G^{o} = -nFE^{0}$). Therefore, by measuring E^{o} we can obtain this important thermodynamic quantity. Its value can then be used to calculate the Gibbs energy of formation of ions.

d) The determination of pH

A cell may be constructed as follows,

Pt|H_2 (g) (1bar) |H^+ (a_{H^+}) ||Cl^-|Hg_2Cl_2(s) |Hg (l)

which is a combination of a hydrogen electrode dipped in the solution whose pH is to be determined and a calomel electrode connected by a KCl salt bridge to keep the liquid junction potential at a low value. The pH of the cell after determination of emf is given by:

$$\boxed{pH = \frac{(E - 0.2802)}{0.0591}}$$

e) Determination of solubility product

In saturated solution of sparingly soluble salt such as AgCl the equilibrium is represented by:

$$AgCl(s) \xrightarrow{H_2O} Ag^{+} + Cl^{-} \quad k = \frac{[Ag^{+}][Cl^{-}]}{[AgCl]} \Rightarrow k[AgCl] = [Ag^{+}][Cl^{-}]$$

Then k [AgCl] = k_{sp} , $k_{sp} = [Ag^{+}][Cl^{-}]$

At any temperature, $E^o_{cell} = \frac{RT}{nF} \ln k_{sp}$

From this, $\boxed{\ln k_{sp} = \frac{nF}{RT} (E^o_{cell})}$

2.12. Applications of Electrochemical system

A) Electroplating

Electroplating is the process of coating an electrically conductive object with a thin layer of metal using an electrical current. Electroplating occurs when an electrically conductive object is coated with a layer of metal using electrical current. Sometimes, electroplating is used to give a metal particular properties or for aesthetic reasons:

- ✓ corrosion protection
- ✓ abrasion and wear resistance
- ✓ the production of jewellery

B) Electrorefining of Metals

Purification of metals is another important application of electrolysis. For example, impure copper from the chemical reduction of copper ore is cast into large slabs that serve as the anodes for electrolytic cells. Aqueous copper sulfate is the electrolyte, and thin sheets of ultra-pure copper function as the cathodes.

The main reaction at the anode is: $Cu \rightarrow Cu^{+2} + 2e^-$

Other metals such as iron and zinc are also oxidized from the impure anode:

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

$$Fe \rightarrow Fe^{+2} + 2e^-$$

The Cu^{+2} ions from the solution are deposited onto the cathode: $Cu^{+2} + 2e^- \rightarrow Cu$ producing copper that is 99.95% pure.

C) The chloralkali industry

The chlorine-alkali (chloralkali) industry is an important part of the chemical industry, which produces **chlorine** and **sodium hydroxide** through the electrolysis of the raw material **brine**. Brine is a saturated solution of sodium chloride (NaCl) that is obtained from natural salt deposits.

D) Electrolysis of Water

Hydrogen and oxygen combine spontaneously to form water and that the accompanying decrease in free energy can be used to run a fuel cell to produce electricity. **Electrolysis of water** is the decomposition of **water** (H_2O) into oxygen (O_2) and hydrogen gas (H_2) due to an electric current being passed through the **water.**

$$\text{Anode Reaction: } 2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad -E^o = -1.23V$$

$$\text{Cathode Reaction: } 4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^- \quad E^o = -0.83\ V$$

$$\text{Net Reaction: } 6H_2O \longrightarrow 2H_2 + O_2 + 4(H^+ + OH^-) \quad E^o = -2.06\ V$$

E) Electrolysis of Mixtures of Ions

Suppose a solution in an electrolytic cell contains the ions Cu^{+2}, Ag^+, and Zn^{+2}. If the voltage is initially very low and is gradually turned up, in which order will the metals be plated out onto the cathode? This question can be answered by looking at the standard reduction potentials of these ions:

$$Ag^+ + e^- \rightarrow Ag, E^\circ = 0.80V$$

$$Cu^{+2} + 2e^- \rightarrow Cu, E^\circ = 0.34V$$

$$Zn^{+2} + 2e^- \rightarrow Zn, E^\circ = -0.76V$$

Remember that the more positive the ***E°*** value, the more the reaction has a tendency to proceed in the direction indicated. Of the three reactions listed, the reduction of Ag^+ occurs most easily, and the order of oxidizing ability is $Ag^+ > Cu^{+2} > Zn^{+2}$. This means that silver will plate out first as the potential is increased, followed by copper, and finally zinc.

Generally, there are various extremely important electrochemical processes in both nature and industry like:

- ✓ The coating of objects with metals
- ✓ Detection of alcohol in drunken drivers through the redox reaction of ethanol
- ✓ The generation of chemical energy through photosynthesis
- ✓ Production of metals like aluminum and titanium from their ores
- ✓ Assessment of food/package interactions
- ✓ Analysis of milk composition
- ✓ Characterization and the determination of the freezing end-point of ice-cream mixes
- ✓ Determination of free acidity in olive oil.