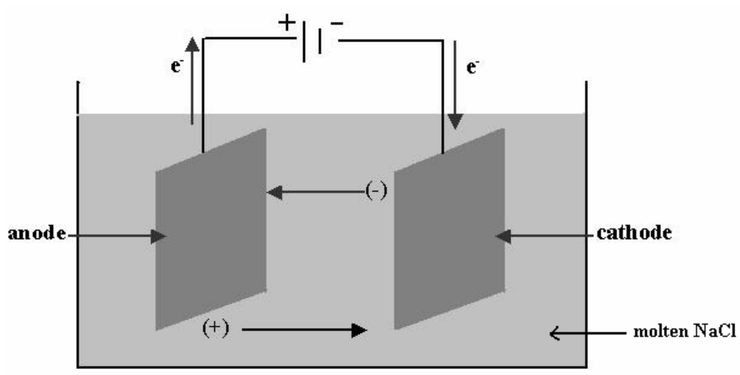
Electrolysis

Electrolysis is the process of causing the nonspontaneous reaction to occur using the external electrical source or the process of transforming the electrical energy into chemical energy. An apparatus for carrying out electrolysis is called **electrolytic cell.** The electrochemical principles underlying both galvanic cell and electrochemical cell are the same. An electrolytic cell, like galvanic cell, also consists of two electrodes in a molten salt or electrolyte solution that is connected to external battery or other voltage source. The external battery serves as the electron pump, which draws electrons in at one electrode (the positive electrode) and forcing them out at another (the negative electrode). Here I have shown a simplified electrolytic cell utilizing the molten NaCl as an electrolyte with two inert electrodes:



In molten sodium chloride (NaCl), there are two ions, namely, cation Na^+ and anion Cl^-. At the anode, the oxidation of chloride ion takes place by depositing two electrons and forming a pure chlorine gas. At the same time, the reduction of sodium ion takes place at the cathode forming a pure sodium metal. The reactions at both electrodes are given below:

Oxidation (anode):	$2Cl^- (l) \rightarrow Cl_2(g) + 2e^-$	$E^0_{ox} = -1.36$ V
Reduction (cathode):	$2Na^+(l) + 2e^- \rightarrow 2Na(l)$	$E^0_{red} = -2.71$ V
Overall:	$2Na^+(l) + 2Cl^- (l) \rightarrow 2Na(l) + Cl_2(g)$	$E^0_{cell} = -4.07$ V

It is important to note here is that pure sodium and chlorine gas are formed at cathode and anode electrodes respectively.

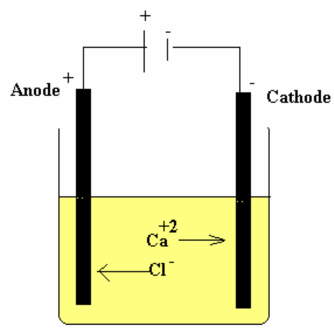
The calculated E^0_{cell} value indicates that this reaction is a nonspontaneous one and requires an external electrical energy of equal to or greater than 4.07 V to carry out reaction. Higher voltage than 4.07 may be necessary due to inefficiencies in electrolytic process.

In the above electrolytic cell, pure sodium and pure chlorine gas are produced at the electrodes. The question is, how much of these substances are formed? That all depends on various factors, like, type of electrolyte, duration of passing of electric current, and the amount of electric charge. The relation between all these aspects is known as quantitative aspects of electrolysis that is discussed below.

Example 1

Construct an electrolytic cell for the electrolysis of molten $CaCl_2$ using inert electrodes, and write half-reactions and Overall reaction.

Answer 1



Oxidation (anode) reaction: $2Cl^- \rightarrow Cl_2(g) + 2e^-$
Reduction (cathode) reaction: $Ca^{+2} + 2e^- \rightarrow Ca$

Overall: $Ca^{+2} + 2Cl^- \rightarrow Ca(l) + Cl_2(g)$

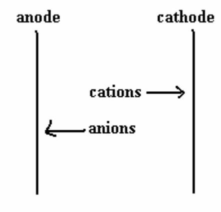
Comparison between galvanic and electrolytic cells

In galvanic cell, electrons are deposited on the anode and are removed from the cathode. As a result of this, the anode carries a slight negative (-) charge and the cathode a slight positive (+) charge. This situation is reversed in electrolytic cell. In an electrolytic cell, the oxidation at the anode must be forced to remove the electrons from the reactant at the electrode making it a positive (+), and the cathode must be negative (-) to force the reactant to accept electrons at the anode.

Galvanic cell	**Electrolytic cell**
Anode is negative (oxidation)	Anode is positive (oxidation)
Cathode is positive (reduction)	Cathode is negative (reduction)

Thus you can see that there is a great amount of confusion of labeling positive and negative electrodes in galvanic and electrolytic cells. Due to this, the new trend is that not to label the electrodes positive or negative, but just label them as anode or cathode as the definitions of these do not change from galvanic cell to electrolytic cell.

In spite of the above difference, the ions in solution always move in the same direction; cations (positive ions) towards cathode and anions (negative ions) move towards anode.



Remember: Cations to cathode and Anions to anode.

Quantities Aspects of Electrolysis

Michael Faraday, an English chemist and physicist (or natural philosopher, in the terminology of that time) made significant contributions to the fields of electromagnetism and electrochemistry. He was the first one to develop the quantitative treatment of electrolysis.

(Photograph by John Watkins, British Library [1])

In 1832 and 1833, he put forward the following two fundamental laws of electrolysis:

1. *The mass of a substance produced by anode or cathode reaction in electrolysis is directly proportional to the quantity of electricity passed through the cell.*

2. *The masses of different substances produced by the same quantity of electricity are proportional to their equivalent weights.*

These laws are the results of the fact that electricity is composed of individual tiny particles known as electrons. The quantity of electricity can be then expressed as the number of electrons that in turn is related to the amount of substance produced at an electrode. Hence, the amount of substance produced is proportional to the quantity of electricity passed through an electrolyte.

Quantity of electricity ↔ Number of electrons ↔ Amount of substance

The magnitude of the charge of one mole (Avogadro's number, 6.02×10^{23}) of electrons is 96,490 C (C=Coulomb). This is called one *faraday*. Therefore,

1 Mole electrons =1 Faraday = 1 F = 96,490 C ≈ 96,500 C

The amount of substance produced can be related to the quantity of electricity through coulomb of charges. Thus, the coulomb is the gateway between amount and current or time:

$$\boxed{\textbf{Amount of substance}} \underset{\textbf{mole } e^-}{\rightleftarrows} \boxed{\textbf{Coulomb}} \underset{\textbf{C = A x s}}{\rightleftarrows} \boxed{\textbf{Current, time}}$$

In the electrolysis of molten NaCl discussed above, the reduction of one mole of Na^+ at cathode requires one mole (1 Faraday) of electrons, i.e., 96,500 C:

$Na^+(l) + e^- \rightarrow Na(l)$

On the other hand, the oxidation of two moles of Cl^- at anode results in the formation of one mole Cl_2 by transferring two moles (2 Faraday) of electrons or 2 x 96,500 C to anode:

$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Similarly, 2 moles(2 Faraday) of electrons are required to reduce one mole of Ba^{+2} to form one mole of Ba or 3 moles (3 Faraday) of electrons to reduce one mole of Al^{+3} to one mole Al.

$Ba^{+2} + 2\,e^- \rightarrow Ba$
$Al^{+3} + 3\,e^- \rightarrow Al$

In an electrolysis experiment, the current in amperes (A) (amount of electric charge per second or coulombs per second (C/s)) is measured that passes through an electrolytic cell in a given period of time. The relation between ampere, time and charge is

Charge (Coulombs) = Current(Ampere) x Time (Second)

or

1 C = 1 A x 1 s

Note that the time is expressed in seconds(s). Therefore, *one Coulomb of charge is equal to passing one ampere of current for one second*. The above relation involve three quantities, knowing any two of them the third one can be calculated. Once the charge is calculated, it is further related to number of moles of electrons to determine the amount of substance formed. Let us consider the following examples.

Calculation of Charge

Suppose a current of 1.50 A is passed through an electrolytic solution for 2.5 hr, what is total amount of charge passed through?

Answer

Charge is measured in coulombs, and hence

$$C = 1.50 \text{ A x } 2.5 \text{ hr x } (3600 \text{ s/hr}) = 1.50 \text{ C/s x } 2.5 \text{ hr x } (3600 \text{ s /hr}) = 13{,}500 \text{ C}$$

Calculation of Current

Suppose a coulomb of charge of 5000 is passed through an electrolytic solution for 5 minutes, what is the current in amperes?

Answer

$$A = C / s = 5000 \text{ C} / (5 \text{ min x } 60 \text{ s/min}) = 16.67 \text{ C/s} = 16.67 \text{ A}$$

Calculation of Time

How much time is required to produce 6,500 C of charges using a current of 15 A?

Answer

$$s = C / A = 6500 \text{ C} / 15 \text{ A} = 6500 \text{ C} / (15 \text{ C/s}) = 433.33 \text{ s or } 7.22 \text{ min}$$

Example 2

A current of 10 A is passed through the molten sodium chloride for 2.5 hours. What is the amount of metallic sodium at the cathode? How much chlorine gas is produced at the anode?

Answer

First calculate the coulombs using given current and time

$$C = 10 \text{ A x } 2.5 \text{ hr} = 10 \text{ (C/s) x } 2.5 \text{ hr } (3600 \text{ s /hr}) = 90{,}000 \text{ C}$$

Convert 90,000C to mole of electrons using the relation, 1 mole electrons = 96,500 C. Thus

Moles of electrons = 90,000 C / (96,500 C/mol) = 0.93 mol of electrons

The sodium metal is produced at the cathode according to the reaction

$Na^+ + 1\ e^- = Na$

This means that one mole of electrons are required to produce one mole (23 g) of Na. Therefore, calculate the amount of sodium produced for 0.93 moles of electrons.

Amount of Na = 0.93 mol of electrons x (23 g / 1 mol of electrons) = 21.45 g

The chlorine gas is produced at the anode according to the reaction

$2Cl^- (l) \rightarrow Cl_2(g) + 2e^-$

To produce one mole chlorine gas (70.90 g) two mole of electrons are required. The amount of Cl_2 produced can be calculated as

Amount of Cl_2 = 0.93 mol of electrons x (70.90 g/ 2 mol of electrons) = 32.97 g

Example 3

How many faradays of electrons and coulombs of charge are needed to deposit 20 g of Mg from molten magnesium chloride ($MgCl_2$)?

Answer

Magnesium carries +2 charges and reduces to Mg according to the following equation.

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

One mole Mg^{+2} ions requires 2 moles or 2 Faraday of electrons to form 1 mole of Mg or 24.31 g of Mg. That is,

2 mole of e^- = 2 Faraday of electrons = 24.32 g Mg

Now you calculate the number of faraday of electrons needed to deposit 20g of Mg:

Faraday = 20 g Mg x (2 Faraday / 24.32 g Mg) = 1.64 F

By definition, 1F = 96,500 C, Therefore

C = 1.64 F x 96,500 C/ F = 1.58×10^5 C

Example 4

How many minutes are needed to deposit 25g of copper from a Cu^{+2} solution, using 4.5 A of current?

Answer

The time is calculated known coulomb of charges (C) and current (A) through the following equation:

$$s = C /A = C/ 4.5 A$$

Now we calculate the coulombs. One mole of Cu^{+2} requires 2 moles of electrons to deposit one mole of Cu (63.55 g), that is,

$$2 \text{ mole } e^- = 63.55 \text{ g Cu}$$

One mole of electrons equal to 1 Faraday or 96,500 C, that is, 1 F = 1 mol e^- = 96,500 C . Hence,

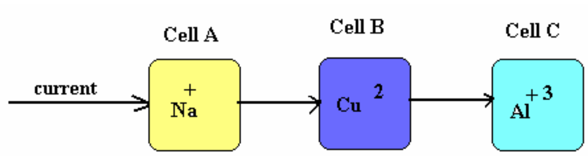
$$C = 25 \text{ g Cu} \times (2 \text{ mole } e^- / 63.55 \text{ g Cu}) \times (96{,}500 \text{ C} / 1 \text{ mole } e^-) = 7.59 \times 10^4 \text{ C}.$$

Therefore the time required in seconds is

$$s = 7.59 \times 10^4 \text{ C} / 4.5 \text{ A} = 16{,}872.10 \text{ s 0r } 281.20 \text{ min or } 4.69 \text{ hrs.}$$

Example 5

Three cells are setup in series, and a current of 1.5 A is passed through them for 30 minutes. The cell A contains an molten salt of sodium chloride, cell B contains molten copper (I) chloride, and cell C contains molten aluminum chloride as shown below:



What is the amount in grams of sodium, copper, and aluminum produced in cell A, cell B, and cell C respectively?

Answer

First, let us calculate the amount of charge when 1.5 A current is passed for 30 minutes.

$$C = A \times s = 1.5 \text{ (C/s)} \times (30 \text{ min} \times 60 \text{ s /min}) = 2{,}700 \text{ C}$$

Then convert this coulomb into moles of electrons.

Mol of e^- = 2,700 C x (1 mol e^-/ 96,500 C) = 0.028 mol of e^-

Now we can calculate the amount of each substance deposited using 0.028 moles of electrons in each cell. First we write the reduction of ion to metal reactions as

Cell A: $Na^+ + e^- \rightarrow Na$
Cell B: $Cu^{+2} + 2e^- \rightarrow Cu$
Cell C: $Al^{+3} + 3e^- \rightarrow Al$

To produce one mole or 22.99 g of sodium, it requires one mole electrons, to produce one mole or 63.55g of copper, it requires 2 moles of electrons, and to produce one mole or 26.98g of aluminum, it requires 3 moles of electrons. Then calculate the grams of each substance produced by 0.028 moles of electrons.

g of Na = 0.028 mol e^- x (22.99 g Na/ 1 mol e^-) = 0.64 g Na
g of Cu = 0.028 mol e^- x (63.55 g Cu/ 2 mol e^-) = 0.89 g Cu
g of Al = 0.028 mol e^- x (26.98 g Al / 3 mol e^-) = 0.25 g Al

Example 6

A particular object with a surface area of 200 cm^2 is silver-plated using a solution containing $Ag(CN)^-_2$. How many minutes does it take to cover an object with silver to a thickness of 0.0050 mm by using a current of 2.5 A? The density of silver is 10.5 g/cm^3.

Answer

First we need to calculate the amount of silver required to cover surface area of 200 cm^2 to a thickness of 0.0050 mm (0.00050 cm). When we multiply the surface area by the thickness, we get the volume of the metal.

Volume of metal = 200 cm^2 x 0.00050 cm = 0.100 cm^3

Now using the density, we can calculate the amount in grams to cover this volume.

g Ag = 0.100 cm^3 x 10.5 g /cm^3 = 1.05 g Ag

When the silver is deposited from $Ag(CN)^-_2$, the following reduction reaction takes place.

$Ag^+ + e^- \rightarrow Ag$

According to this reaction, it requires one mole of electrons to deposit one mole or 107.9 g of silver. Now find out how many moles of electrons are needed to deposit 1.05 g silver.

$$\text{Mole } e^- = 1.05 \text{ g Ag x } (1 \text{ mol } e^- / 107.9 \text{ g Ag}) = 0.00973 \text{ mol } e^-$$

Convert these mol of electrons into coulomb of charges.

$$C = 0.00973 \text{ mol } e^- \text{ x } (96{,}500 \text{ C}/ 1 \text{ mol } e^-) = 939.06 \text{ C}$$

The time required is computed as

$$s = C / A = 939.06 \text{ C} / (2.5 \text{ A}) = 375.62 \text{ s or } 6.26 \text{ min}$$

Application of Electrolysis

There are two areas in which the electrolysis plays a major role, production of elements and metallurgy.

A. Electrolytic Production of Elements

Many metals can be extracted in pure forms by electrolytic methods; the alkali metals, alkaline-earth metals, magnesium, aluminum, and many other metals. Some nonmetals can also be extracted by electrolytic method; oxygen and hydrogen are produced by the electrolysis of water containing an electrolyte, chlorine gas using the molten sodium chloride. Few of them are listed below.

- The Production of Sodium (Na) and Chlorine (Cl_2)
- The production of Aluminum (Al)
- The Refinement of Metals

B. Metallurgy – The reduction of Ores

Metals are extracted from **ores,** which are minerals or other natural materials. The process of extracting a metal from an ore is known as *winning* the metal. The process of purification of a metal that has been extracted from the ore is called *refining*. Therefore, metallurgy is the science and art of winning and refining metals. Here is the small list of them.

- The metallurgy of Copper (Cu)
- The metallurgy of Silver(Ag) and Gold(Au)
- The metallurgy of Zinc(Zn), Cadmium(Cd), and Mercury(HG)
- The Metallurgy of Tin (Sn) and Lead(Pb)
- Reduction of Metal Oxides or Halides by Strong Electropositive Metals