

# Electrochemistry

C020

Electrochemistry is the study of the interconversion of electrical and chemical energy

- Using chemistry to generate electricity involves using a **Voltaic Cell** or **Galvanic Cell** (battery)
- Conversely, using electricity to cause chemical changes involves using an **Electrolytic Cell**

Both Voltaic and Electrolytic Cells have the same underlying theory but they will be considered separately

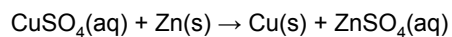
## 1.) Voltaic Cells

Consider the following reaction that can be done in the lab

Add Zn metal to a solution of CuSO<sub>4</sub>  
The following then happens simultaneously

- oThe blue color of Cu<sup>2+</sup> disappears
- oThe Zn metal slowly dissolves
- oSolid Cu metal (reddish brown) precipitates

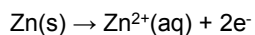
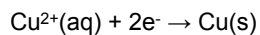
The reaction for this is:



Zn(s) is a reducing agent and is oxidized to Zn<sup>2+</sup>(aq)

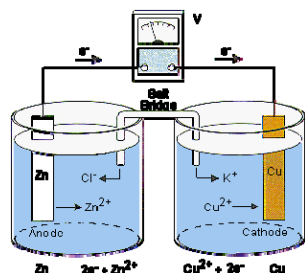
Cu<sup>2+</sup>(aq) is an oxidizing agent and is reduced to Cu(s)

The corresponding half-reactions, leaving out the spectator SO<sub>4</sub><sup>2-</sup> ion, are:



This is a redox reaction, which occurs spontaneously by itself.

If the reaction is allowed to proceed in a beaker, the liberated energy would appear as heat



However, if each half-reaction took place in separate but electrically connected beakers, the 2 e<sup>-</sup> can be made to travel along a wire and do electrical work.

The liberated energy would then appear as light (passing through a light bulb) or as shown in the picture, a signal on a volt meter

## Definitions

Oxidation occurs at the anode (an ox)

Reduction occurs at the cathode (red cat)

Thus, cations (positively charged species) travel to the cathode;  
anions (negatively charged species) travel to the anode

The e<sup>s</sup> travel through the wire because there is an unbalanced electrical force known as the electromotive force (*EMF*) which pushes electrons generated from the oxidation half-reaction towards the electrode where reduction occurs

*EMF* is measured in Volts, V (potential difference).

The greater the difference in potential energy between the two electrodes the greater the *EMF*

To generate the largest *EMF* one requires a metal that really wants to be oxidized and ion that really wants to be reduced

A potential difference of 1 Volt causes a charge of 1 Coulomb to acquire an energy of 1 Joule

$$\therefore 1 \text{ V} = 1 \text{ J C}^{-1}$$

One mole of electron corresponds to 96480 C

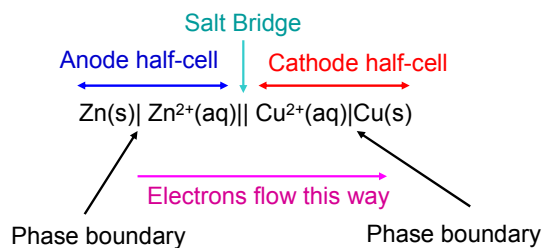
*EMF* is measured using a voltmeter.

The potential energy difference is commonly called the cell potential,  $E_{\text{cell}}$

In the diagram before there is a salt bridge. Why?

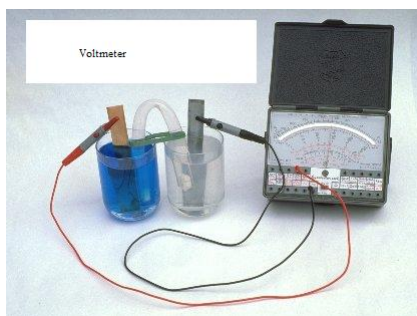
- The salt bridge, which connects the two beakers, is typically some inert solution that does not take place in the redox reaction (sodium sulfate, potassium nitrate, etc)
- As the reaction occurs, there is a build up of cation concentration at the Zn anode, and a decrease in cation concentration at the Cu electrode
- Therefore, anions migrate through the salt bridge from the Cu side to the Zn side, and cations pass in the opposite direction, to preserve charge balance

The cell can be written using the following notation:



- By convention, oxidation is on the left, and the reduction is on the right
- Phase boundary refers to the solid metal dipped into aqueous solution

When a voltmeter is used to measure the *EMF*, the red (positive) wire is connected to the right or reduction electrode (cathode) where electrons are received



If a cell is connected in this manner, a positive voltage indicates that the reaction is proceeding forwards

Experimentally, it is found that the voltage and direction of current flow depends on the electrode materials, temperature and concentration of ions involved. It is useful therefore to define *standard conditions*.

➤ Concentration of ions = 1M (for example, 1 M ZnSO<sub>4</sub>)

➤ Temperature = 25°C      Pressure = 1 atm

In C020 we will not examine the concentration effect. For those who are interested, read about the Nernst equation M&H p. 486 - 489

Cell potentials measured under standard conditions are referred to as standard cell potentials  $E^{\circ}_{\text{cell}}$  (sometimes  $E^{\circ}$ )

## 2. Standard Electrode Potentials

Any redox process can be split into two half-reactions.

Thus,  $E^{\circ}_{\text{cell}}$  is a sum of the voltages generated by the oxidation half-reaction (at the anode) and the reduction half-reaction (at the cathode).

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}$$

Electrons move through the wire from one side to the other because the two sides differ in potential energy (voltage)

Where do we get the potentials for the  $E^{\circ}_{\text{ox}}$  and  $E^{\circ}_{\text{red}}$  half-reactions?

They can't be measured individually because the e<sup>-</sup>s have nowhere to go or to come from

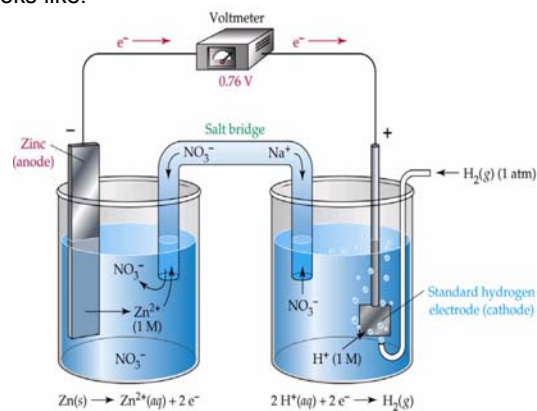
Thus, the half-cell potentials are experimentally determined using the standard hydrogen electrode (SHE) as a reference.

Since we're dealing with a gas, we use an inert electrode (like platinum)

By definition the standard potential of SHE is ZERO  
 $2\text{H}^+$  (one molar) +  $2\text{e}^- \rightarrow \text{H}_2(\text{g})$  (1 atm)  $E^{\circ}_{\text{red}} = 0.000 \text{ V}$

$E^{\circ}_{\text{red}}$  and  $E^{\circ}_{\text{ox}}$  for the species are related as  $E^{\circ}_{\text{red}} = -E^{\circ}_{\text{ox}}$   
 $\text{H}_2(\text{g})$  (1 atm)  $\rightarrow 2\text{H}^+$ (one molar) +  $2\text{e}^-$   $E^{\circ}_{\text{ox}} = 0.000 \text{ V}$

So, to determine the value of a standard potential for zinc, we need to construct a cell that looks like:



The value of  $E^\circ_{\text{cell}}$  is +0.762 V when the voltmeter is connected properly (positive side to the cathode).

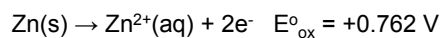
In this case the cathode is the hydrogen side which means that  $\text{H}^+$  is being reduced to  $\text{H}_2$

Likewise Zn is being oxidized at the anode side

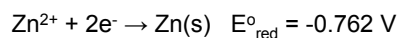
$$\text{Thus, } E^\circ_{\text{cell}} = +0.762 \text{ V} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$$

$$\text{By definition, } E^\circ_{\text{red}} \text{ of the SHE} = 0 \text{ V so } E^\circ_{\text{ox}} = +0.762 \text{ V}$$

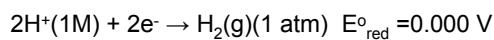
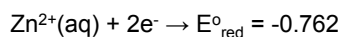
However it must be remembered that  $E^\circ_{\text{ox}}$  corresponds to the oxidation of Zn(s)



Since  $E^\circ_{\text{red}} = -E^\circ_{\text{ox}}$  we can write the following: essentially flip the reaction to get the reduction potential



Thus, if electrons were present in the reference cell comprised of zinc and SHE they have a choice. Will they go to  $\text{H}^+$  or will they go to  $\text{Zn}^{2+}$ ?



When written as reduction half-reactions, the reaction that will occur is the one with the most positive potential

In this case,  $H^+$  is preferentially reduced over  $Zn^{2+}$ .  
 Corollary:  $H^+$  is a stronger oxidizing agent than  $Zn^{2+}$ .  
 In other words,  $H^+$  is capable of oxidizing  $Zn(s)$

This is observed experimentally in the  $Zn/SHE$  system

A table of standard electrode potentials, shown as reduction half-reactions, is provided in the tutorial manual.  
 When comparing any two half-reactions, the one that will proceed as written will have the highest potential  $E^{\circ}_{red}$ .  
 The other half-reaction will need to be reversed to obtain  $E^{\circ}_{ox}$ .

Some common  $E^{\circ}_{red}$  values and reactions are shown here. Remember, the higher the value, the more likely the reduction will occur.

**TABLE 18.1** Standard Reduction Potentials at 25°C

	Reduction Half-Reaction	$E^{\circ}$ (V)	
Stronger oxidizing agent ↑	$F_2(g) + 2 e^-$	$\rightarrow 2 F^-(aq)$	2.87
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\rightarrow 2 H_2O(l)$	1.78
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^-$	$\rightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51
	$Cl_2(g) + 2 e^-$	$\rightarrow 2 Cl^-(aq)$	1.36
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^-$	$\rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33
	$O_2(g) + 4 H^+(aq) + 4 e^-$	$\rightarrow 2 H_2O(l)$	1.23
	$Br_2(l) + 2 e^-$	$\rightarrow 2 Br^-(aq)$	1.09
	$Ag^+(aq) + e^-$	$\rightarrow Ag(s)$	0.80
	$Fe^{3+}(aq) + e^-$	$\rightarrow Fe^{2+}(aq)$	0.77
	$O_2(g) + 2 H^+(aq) + 2 e^-$	$\rightarrow H_2O_2(aq)$	0.70
	$I_2(s) + 2 e^-$	$\rightarrow 2 I^-(aq)$	0.54
	$O_2(g) + 2 H_2O(l) + 4 e^-$	$\rightarrow 4 OH^-(aq)$	0.40
	$Cu^{2+}(aq) + 2 e^-$	$\rightarrow Cu(s)$	0.34
	$Sn^{4+}(aq) + 2 e^-$	$\rightarrow Sn^{2+}(aq)$	0.15
		<b><math>2 H^+(aq) + 2 e^-</math></b>	<b><math>\rightarrow H_2(g)</math></b>
	$Pb^{2+}(aq) + 2 e^-$	$\rightarrow Pb(s)$	-0.13
	$Ni^{2+}(aq) + 2 e^-$	$\rightarrow Ni(s)$	-0.26
	$Cd^{2+}(aq) + 2 e^-$	$\rightarrow Cd(s)$	-0.40
	$Fe^{2+}(aq) + 2 e^-$	$\rightarrow Fe(s)$	-0.45
	$Zn^{2+}(aq) + 2 e^-$	$\rightarrow Zn(s)$	-0.76
	$2 H_2O(l) + 2 e^-$	$\rightarrow H_2(g) + 2 OH^-(aq)$	-0.83
	$Al^{3+}(aq) + 3 e^-$	$\rightarrow Al(s)$	-1.66
	$Mg^{2+}(aq) + 2 e^-$	$\rightarrow Mg(s)$	-2.37
	$Na^+(aq) + e^-$	$\rightarrow Na(s)$	-2.71
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\rightarrow Li(s)$	-3.04

↓ Stronger reducing agent

➤ We showed how the  $\text{Zn}^{2+}|\text{Zn}$  half-potential was determined.

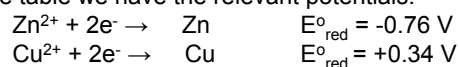
All half-potentials of all the other species in the table above were determined in the same way: by comparing against the SHE

➤ To construct a cell using any two of the reduction half-potentials, one must be reversed to correspond to an oxidation.

Returning to the Cu/Zn cell, it is clearer now why the reaction was written as:  
(Zn oxidized;  $\text{Cu}^{2+}$  reduced)

Cell notation:  $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$

From the table we have the relevant potentials:



The most positive reduction potential is the one that occurs, which is the one with Cu involved.

This is because  $\text{Cu}^{2+}$  is more likely to be reduced than  $\text{Zn}^{2+}$  or  $\text{Cu}^{2+}$  is a stronger oxidizing agent.

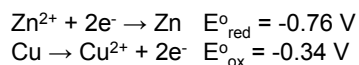
Since  $\text{Cu}^{2+}$  is the species being reduced, we must flip the zinc reduction half-reaction to convert it to an oxidation.



Therefore,  $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} = +0.34 + 0.76 = +1.10 \text{ V}$

Because  $E_{\text{cell}}^{\circ}$  is positive, the reaction will go as written; that is, the reaction will be spontaneous

How about the cell?:  $\text{Cu}|\text{Cu}^{2+}||\text{Zn}^{2+}|\text{Zn}$



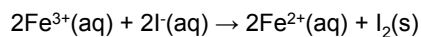
This cell potential would be  $-1.10 \text{ V}$ , which means the reaction would not proceed as written spontaneously.

In fact the reverse would occur.

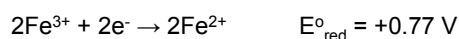


**Example:**

Calculate  $E^\circ_{\text{cell}}$  for the voltaic cell:  $\text{I} | \text{I}_2 || \text{Fe}^{3+} | \text{Fe}^{2+}$



From the table we find:



**Note: NEVER multiply the voltage by the coefficients of the balanced equation!!!**

This is because the voltage is related to the energy of a mole of electrons transferred

The more positive reaction will go as written.

The other reaction must be reversed to be an oxidation;

that is,  $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$   $E^\circ_{\text{ox}} = -0.53\text{V}$

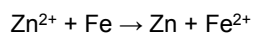
Therefore  $E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} = +0.77 + (-0.53) = +0.24 \text{ V}$

The reaction will proceed spontaneously, as written

Note: a voltaic cell based on the reverse reaction will **not** work as there the cell potential would be  $-0.24 \text{ V}$

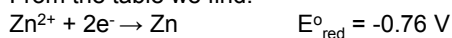
**Example:**

Determine if the following reaction is spontaneous



This can be written as:  $\text{Fe} | \text{Fe}^{2+} || \text{Zn}^{2+} | \text{Zn}$

From the table we find:



The reaction shows Fe being oxidized so turn it around:



Therefore,  $E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} = -0.76 + 0.45 = -0.31 \text{ V}$

Since  $E^\circ_{\text{cell}} < 0$ , the reaction will NOT spontaneously occur as written.

The backwards reaction will in fact take place

**Corollary:**

$\text{Fe}^{2+}$  is a better oxidizing agent than  $\text{Zn}^{2+}$ , so  $\text{Fe}^{2+}$  can oxidize Zn.  
Recall that the species with the most positive  $E_{\text{red}}^{\circ}$  is the strongest oxidizing agent (likes to be reduced the most).

**Example:**

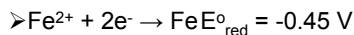
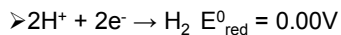
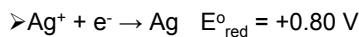
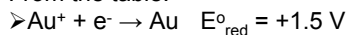
A student makes three pieces of jewelry, each from a different type of metal: Fe, Ag, and Au. The student places them in 1M acid. Which one(s) will be resistant to acid?

The items that are **not** resistant to acid will most likely dissolve; that is, the metal will oxidize to its aqueous ion

The only likely reduction is the reduction of  $\text{H}^+$

The cell equation will therefore be: metal | metal ion ||  $\text{H}^+|\text{H}_2$

From the table:



The only metal  $\text{H}^+$  can oxidize is Fe.  
Thus, the items made of Au and Ag are resistant to acid!

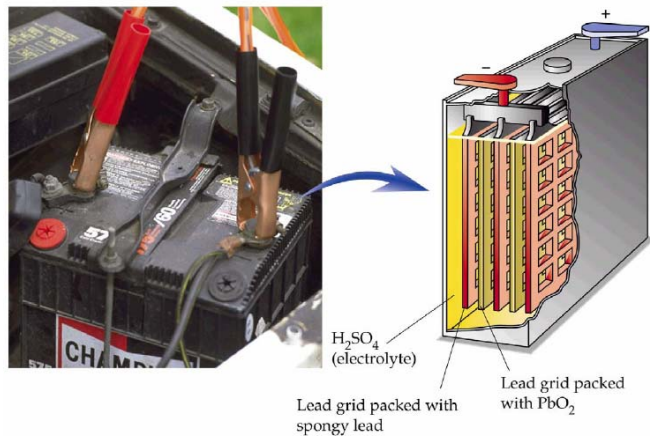
Realize that the value of  $E_{\text{cell}}^{\circ}$  only predicts if a reaction is spontaneous or not. Spontaneity is governed by equilibrium constants. It says nothing about the rate of the chemical reaction (or how many e-s can be delivered per second... related to current; units = amperes, A

### 3. Reversibility: Electrolytic Cells

In voltaic cells chemical energy was converted into electricity spontaneously; for example, using a battery

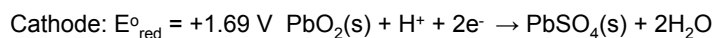
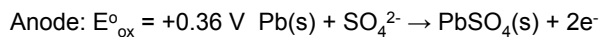
However, often we want to do the reverse:  
use electrical energy to force a non-spontaneous reaction;  
for example, recharge a battery.  
In this context where electrical energy is applied, we have an **electrolytic cell**.

Consider the lead-acid battery which can be used in both voltaic- and electrolytic modes (discharge and recharge)



There are separate Pb and PbO<sub>2</sub> plates

As a voltaic cell the following reactions are taking place:



$E^{\circ}_{\text{cell}} = \sim +2\text{V}$  and six of these are connected in series to provide a car battery of +12 V

Interesting notes:

➤ As a car battery discharges, the level of H<sub>2</sub>SO<sub>4</sub> decreases, as does the density of the electrolyte.

Some batteries have a green “eye” that lets you estimate this condition... when the electrolyte is dense the eye floats up and appears green.

➤ PbSO<sub>4</sub>(s) coats the cathode as the battery discharges.

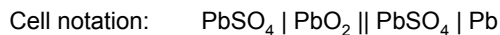
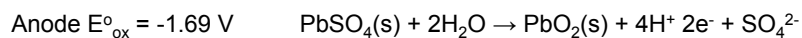
Thus the more discharged the battery is, the thicker the coating, and the less contact with the electrolyte.

If you have a dead battery and wait a few minutes, you can crank your engine again ...the electrolyte needs time to diffuse through the coating

Again, the cell potential does not tell you the rate of the chemical reaction.

Battery makers for automobiles aim for the largest number of Cold Cranking Amps, a measure of how many Coulombs per second can be produced

➤ To recharge the battery, the products of the discharge needs to be converted back to starting materials (electrolytic cell)



➤ Note that in recharge mode (electrolytic cell) the anode and cathode have switched places!

Nonetheless, the anode is always the electrode where oxidation occurs

➤  $E_{\text{cell}}^{\circ} = -2\text{V}$ , which indicates the reaction is not spontaneous (expected).

Therefore to recharge we must apply an external voltage of at least 2 V to force this undesirable reaction to occur.

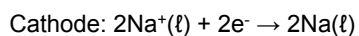
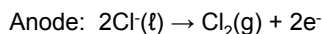
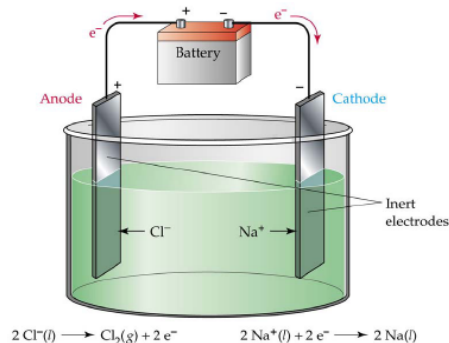
When a redox reaction is driven by electricity, it is called **electrolysis**

➤ Recharging batteries is just one example of electrolysis but the principle is the same

### Example:

Industrial electrolysis of molten (not aqueous) NaCl to generate Na(s) + Cl<sub>2</sub>(g)

A battery or power source drives the reaction. A small amount of CaCl<sub>2</sub> is also added to lower the melting point



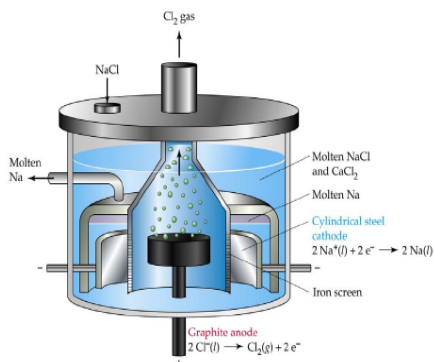
**Challenge for you:**

Calculate the minimum external voltage needed for this electrolysis

**Industrial problem:**

How do you keep  $\text{Cl}_2(\text{g})$  from reacting with the  $\text{Na}(\text{s})$  product?

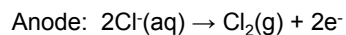
The solution is a cell design that incorporates an inverted funnel to isolate the chlorine gas product ( $\equiv$  Downs electrolysis cell)



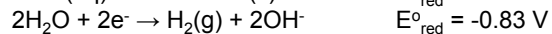
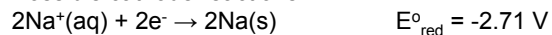
**Another question:**

Why use molten  $\text{NaCl}$ ? Why not simply use  $\text{NaCl}$  dissolved in water?

Electrolysis of  $\text{NaCl}$  in water results in the same oxidation of  $\text{Cl}^-$  to  $\text{Cl}_2$ , but  $\text{H}_2\text{O}$  is reduced much more readily than  $\text{Na}^+$

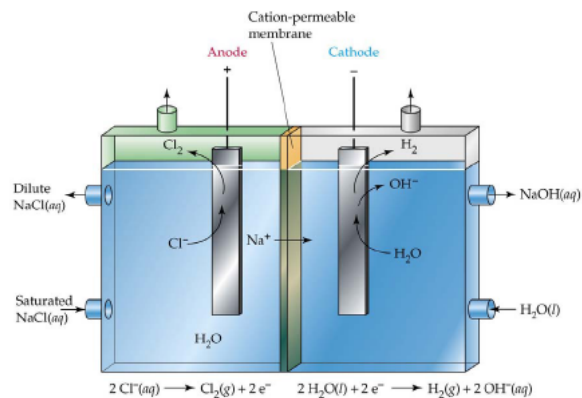


Possible cathode reactions:



- • reduction of water is much more favorable
- • No  $\text{Na}(\text{s})$  is formed but that is not so bad because  $\text{Cl}_2$ ,  $\text{H}_2$ , and  $\text{NaOH}$  are industrially important. Therefore, the electrolysis of salt water is important

Electrolysis cell for this purpose:



#### 4. Quantitative Analysis

In redox reactions, electrons are formed or consumed in stoichiometric ratios. The amount of electrons can be measured by moles or by charge (Coulombs)

$$1 \text{ mole } \text{e}^- = 96480 \text{ Coulombs } (\equiv \text{Faraday's constant})$$

However, physicists, electricians, and engineers usually measure electric current instead of electrons

$$1 \text{ ampere (A)} = 1 \text{ Coulomb per second}$$

Thus, it is possible to express A in terms of electrons:

$$1 \text{ mole } \text{e}^- = 96480 \text{ V}$$

$$1.036 \times 10^{-5} \text{ mol } \text{e}^- = 1 \text{ C}$$

$$6.240 \times 10^{18} \text{ e}^- = 1 \text{ C (using Avogadro number)}$$

that is;  $1 \text{ A} = 6.240 \times 10^{18} \text{ e}^- \text{ per second}$

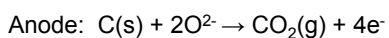
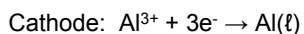
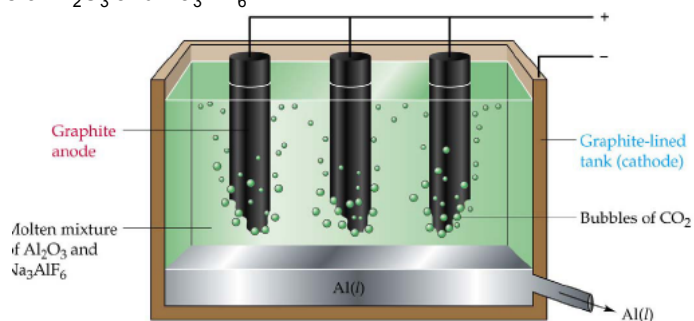
**Take home exercise:**

Calculate how many electrons go through your toaster if it draws 10 A of electricity for 4 minutes.

Since redox reactions are stoichiometric it should be possible to calculate how much electric current and what length of time is necessary for a particular reaction

**Example:**

Aluminium smelters in Canada electrolytically produce Al metal using a molten mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Na}_3\text{AlF}_6$ .



The production of 1 mole Al requires 3 mole  $\text{e}^-$ , so it is possible to calculate the Coulombs needed and  $\text{CO}_2$  emissions (knowing the voltage):

Current:  $1 \text{ A} = 1 \text{ C s}^{-1}$       Voltage:  $1 \text{ V} = 1 \text{ J C}^{-1}$

Power:  $1 \text{ W (Watt)} = 1 \text{ J s}^{-1}$       Energy:  $1 \text{ J} = \text{power} \times \text{time} = \text{V} \times \text{C}$

Process is energy intensive and environmentally unfriendly.