

## In an electrolytic cell, a non-spontaneous redox reaction is driven by an external source of a potential difference, i.e. a battery

A voltaic cell is a battery, and an electrolytic cell needs one to function. You need a reverse "pump" to make the non-spontaneous reaction occur.

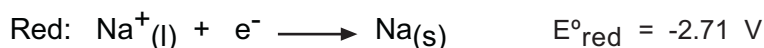
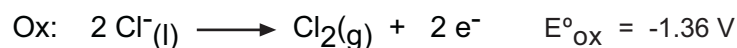
Typically, the voltage source supplies a potential difference that is much higher than that needed based on adding up the reduction half reactions. What this means is that the species in solution in significant concentration with the least negative oxidation potential will get oxidized and the species in solution in significant concentration with the least negative reduction potential will get reduced. You need to get that idea. As you'll see below, an electrolytic cell is a single container, I mean it's okay to mix the reactants because they will not spontaneously react, right?. There will also be other molecules in solution, such as water and you need to take all the molecules into account when determining which species gets reduced and which one gets oxidized. Here is an example of a system that at first has not water present and then is done in aqueous solution. Make sure you understand why the overall redox reaction is not the same for each cell.

### The Downs Cell

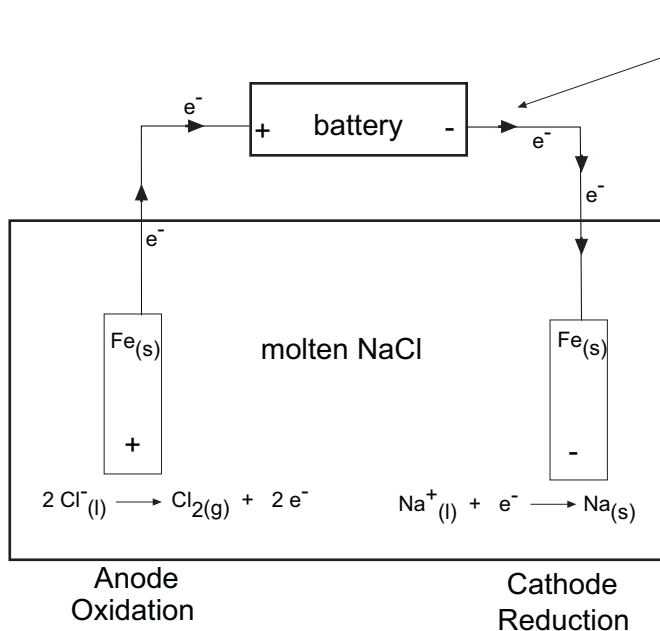
In the Downs Cell, solid sodium and chlorine gas are produced from molten sodium chloride. (no water present)



You should know from your general understanding of the chemistry of elements and the octet rule that neither of these ions wants to spontaneously undergo this process. Quite the opposite in fact.



$E^\circ_{\text{cell}} = -4.07 \text{ V} < 0$  so its not spontaneous A battery supplying a voltage greater than the reaction potential can drive this reaction.



Chlorine gas is produced at the iron anode  
Solid sodium is deposited on the iron cathode

electrons flow from the positive end of a battery to the negative end (from higher to lower potential. This switches the signs of the anode and cathode from a voltaic cell. In an electrolytic cell, the anode is positive and the cathode is negative. (note: electrons are negative and current is defined as the flow of positive charge. That means that current flows in the opposite direction of electrons and from negative to positive in a battery.)

The question is, it takes a lot of heat energy to melt NaCl, why not just dissolve salt in water and hook up a battery? Do we still get the same products of the redox reaction?

## The Electrolysis of Aqueous Sodium Chloride

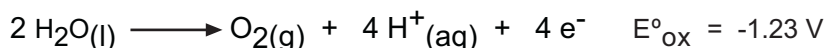
So, you are the bright engineer that said, "why are we wasting all this money melting salt? We can get it into the liquid phase and thus in the electrolysis cell just by dissolving it in water. Well Boss, where is my raise? And, you Boss, an experienced engineer may politely say, not so fast zippy, I think we need to refresh your understanding of electrolysis.

You have to look at each molecule in solution and pick the first one that will get oxidized and the first one that will get reduced. In aqueous NaCl, we have H<sub>2</sub>O, Na<sup>+</sup>, and Cl<sup>-</sup>. We need to look at the oxidation and reduction possibilities for each of these species.

### Possible oxidation reactions (loss of electrons)



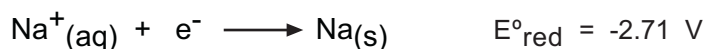
Na<sup>+</sup> is not going to lose another electron. It has an empty valence shell.



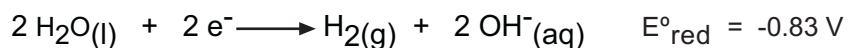
It appears that water will be oxidized before chloride ion. It has a less negative oxidation potential. **BUT THIS IS NOT THE CASE.**

The oxidation of water is an exception to using redox potentials as they are strictly calculated. It turns out that the oxygen gas produced interferes with water molecules getting to the anode. More voltage or an **OVERVOLTAGE is required to make this oxidation reaction occur at a significant rate**. Remember this, the potential needed for the oxidation of water is **more like -2.0 V than the calculated value of -1.23 V**. Because of this, chloride will be the species oxidized.

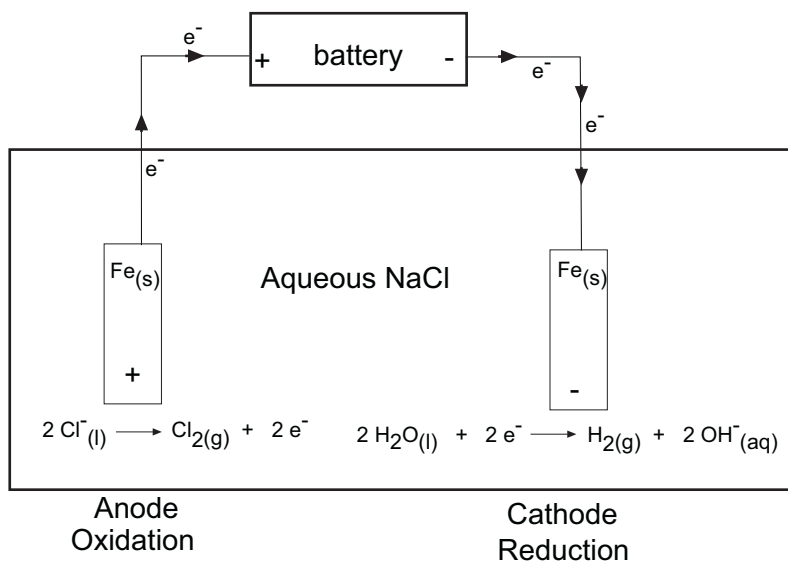
### Possible reduction reactions (gain of electrons)



Cl<sup>-</sup> is not going to gain another electron. It has full valence shell.



Here water, instead of sodium cation will get reduced. Hydrogen gas will be produced at the cathode and the solution will become more basic.



Chlorine gas is produced at the iron anode

Hydrogen gas is produced at the iron cathode

### Quantitative Electrolysis

Current is the rate at which electrons flow through a wire (and again, because electrons are defined with a -1 charge, current flows in the opposite direction of electrons). It is measured in coulombs per second or (C/s). If you know the current and the period of time over which it was passed, you can calculate all sorts of things, like the mass of a metal that is oxidized, the mass of a metal that plates out, how much gas is produced, etc. This all comes down to converting a current and time to a total charge passed, using the Faraday constant to convert that total charge to a number of moles and then using the stoichiometry of the redox reaction to convert from moles of electrons to moles of the species in question.

Here is an example:

A steady current of 1.00 ampere is passed through an electrolytic cell containing a 1 molar solution of  $\text{AgNO}_3$  for a time period of 23 minutes. How much silver is deposited?

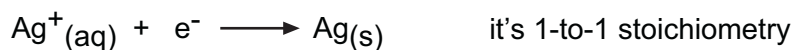
First question, where is the silver being deposited? Well silver cation to silver metal requires the gaining of an electron, so that is a reduction reaction and reduction always occurs at the cathode.

Second question, how many moles of electrons are passed during this time period?

calculate the total charge:  $(1 \text{ Ampere})(1380 \text{ seconds}) = 1380 \text{ Coulombs}$

calculate the moles electrons:  $(1380 \text{ Coulombs})/(96,485 \text{ C/mol e}^-) = .0143 \text{ moles e}^-$

What is the stoichiometry between the species reduced and electrons?



moles silver plated = .0143 moles

mass silver plated =  $(.0143 \text{ moles})(107.9 \text{ g/mol}) = 1.54 \text{ g}$