Electrochemistry

Reduction Potential

- How easily an element is reduced
  - Gains electrons
  - Oxidizing agent
  - Li is the least easily reduced (weakest oxidizing agent)
  - F_2 is most easily reduced (strongest oxidizing agent)

- Reduction potentials are given in a table
- Listed by half-reactions
  - Recall that both oxidization and reduction occur in any given reaction
  - The reduction half is given in the table
  - The oxidation half would be the reduction reaction in reverse

Example

- F_2 reacts with Cu
- Reduction half:
  - $F_2 + 2e^- \rightarrow 2F^-$
- Oxidation half:
  - $Cu \rightarrow 2e^- + Cu^{2+}$
- Net Reaction:
  - $F_2 + 2e^- + Cu \rightarrow 2F^- + 2e^- + Cu^{2+}$
  - $F_2 + Cu \rightarrow 2F^- + Cu^{2+}$

Spontaneous Reactions

- We can use standard reduction potentials to determine if a reaction can occur spontaneously or not

Example

- A zinc metal strip is placed into a 1.0 mol/L solution of copper(II) nitrate
- The species available for reaction are:
  - Zn, Cu^{2+}, NO_3^-
  - Zn: $Zn \rightarrow 2e^- + Zn^{2+}$ (+0.76)
  - Cu^{2+}: $Cu^{2+} + 2e^- \rightarrow Cu$ (+0.34)
  - NO_3^- will only react in an acid solution
- So, Zn will be oxidized and Cu will be reduced

- Net Reaction:
  - $Zn + Cu^{2+} + 2e^- \rightarrow 2e^- + Zn^{2+} + Cu$
  - $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
  - This reaction is spontaneous

Electrochemical (Voltaic) Cells

- Electrochemical cells used to convert chemical energy into electrical energy
- The first such cell was produced by Alessandro Volta
- Sometimes called galvanic cells after Luigi Galvani who first discovered the phenomenon (although he didn't recognize it correctly)

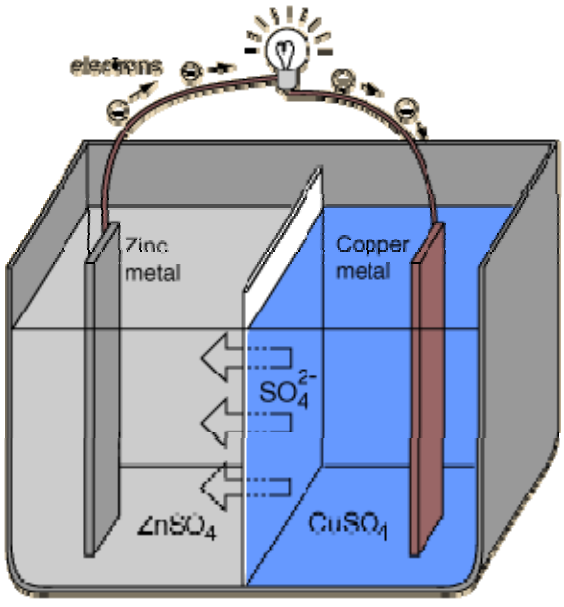
Alessandro Volta's Original "Pile", exhibited in the Volta Temple, Como, Italy.

How does a voltaic cell work?

- The voltaic cell uses a spontaneous redox reaction to produce electrical energy
- According to the law of conservation of energy, energy cannot be created nor destroyed, it is simply converted from one form to another
- The chemical energy of the redox reaction is converted into electrical energy

Example

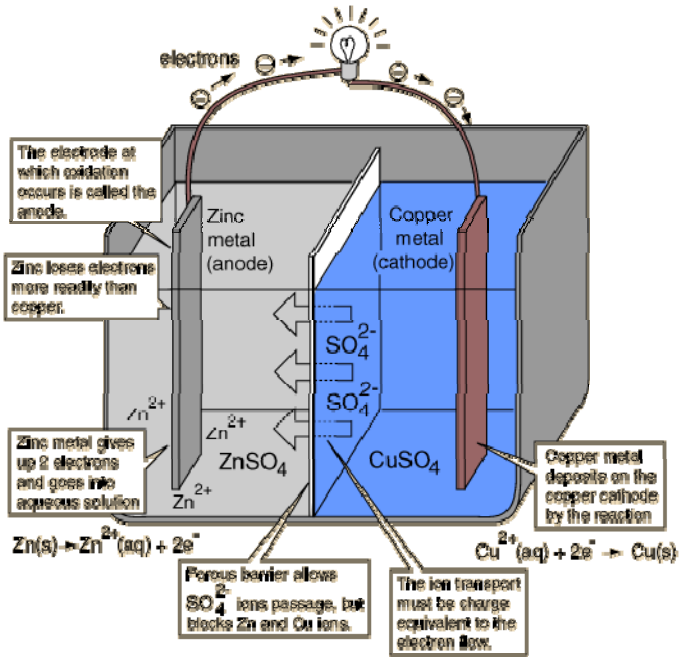
- Zinc more readily loses electrons than copper, so placing zinc and copper metal in solutions of $ZnSO_4$ and $CuSO_4$ can cause electrons to flow through an external wire which leads from the zinc to the copper.

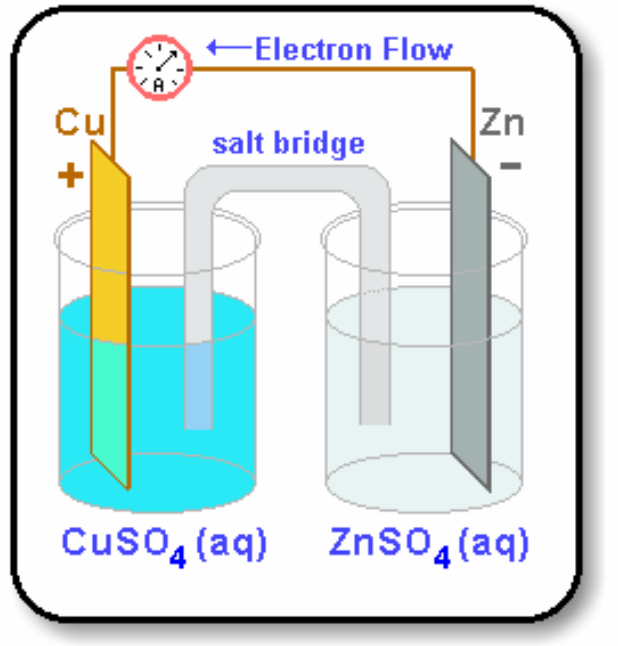


- As a zinc atom provides the electrons, it becomes a positive ion and goes into aqueous solution, decreasing the mass of the zinc electrode.
- On the copper side, the two electrons received allow it to convert a copper ion from solution into an uncharged copper atom which deposits on the copper electrode, increasing its mass.
- The two half-reactions are:
  - $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)
  - $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)

- The terminal where oxidation occurs (Zn) is called the anode
  - This corresponds to the negative terminal of a battery
- The terminal where reduction occurs (Cu) is called the cathode
  - This corresponds to the positive terminal of a battery

- For the voltaic cell to continue to produce an external electric current, there must be a movement of the sulfate ions in solution from the right to the left to balance the electron flow in the external circuit.
- The metal ions themselves must be prevented from moving between the electrodes, so some mechanism must provide for the selective movement of the negative ions in the electrolyte from the right to the left.





- A short hand notation is often used to represent the voltaic cell diagram

Oxidation half-cell

Reduction half-cell

Reactant

Product

Reactant

Product

$Zn(s) \mid Zn^{2+}$ (1 mol/L) || Cu^{2+} (1 mol/L) $\mid Cu(s)$

Phase boundary

Separation Mechanism

(Salt Bridge)

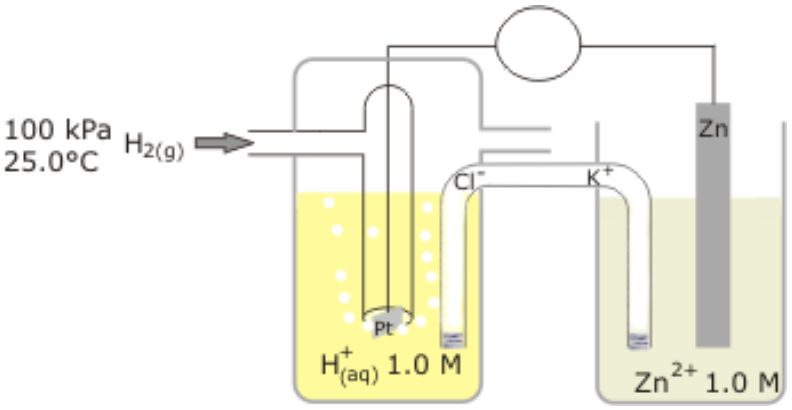
Phase boundary

- By convention, the anode is written first

Standard Electrode Potential

- Electrode potentials are measured against a standard electrode, Hydrogen
- Under standard conditions of 1 atm for hydrogen gas and 1 mol/L HCl, the potential for reduction (electrode potential) of H^+ at 25°C is considered to be exactly zero
  - $2H^+ + 2e^- \rightarrow H_2$ $\quad E^0 = 0$ V

Example: Measuring Electrode Potential for Zinc



- During the reaction, the zinc electrode loses mass indicating that the half-cell reaction must be
  - $Zn \rightarrow Zn^{2+} + 2e^-$
- That is, it is oxidizing and therefore the anode
- The reduction half-cell reaction would be
  - $2H^+ + 2e^- \rightarrow H_2$
- Giving a net reaction of
  - $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

- The short hand notation for the cell would be:
  - $Zn(s) \mid Zn^{2+}$ (1 mol/L) $\parallel H^+$ (1 mol/L) $\mid H_2(g)$
- The electrode potential (also called emf) of the cell, E^0_{cell} , is the difference between the potentials of the oxidation and reduction half-reactions

$$E^0_{cell} = E^0_{reduction} - E^0_{oxidation}$$

- In our example, the zinc reaction is the oxidation half and the hydrogen reaction is the reduction half

$$E^0_{cell} = E^0_{H_2} - E^0_{Zn}$$

  - When we measure the voltage across the cell we get 0.76 V and the potential for hydrogen is 0, so

$$0.76 = 0 - E^0_{Zn}$$

- This gives a potential of -0.76 V for Zinc
- In a similar way, all electrode potentials were determined and placed together with their half-cell reactions

- We can use these standard potentials to determine spontaneity and electric potential of any given cell
- A positive cell value indicates a spontaneous reaction
- A negative cell value indicates a non-spontaneous reaction

Example

- Calculate the cell potential for a copper-zinc cell
- The half-reactions are:
  - $Cu^{2+} + 2e^- \rightarrow Cu(s)$ +0.34 V
  - $Zn^{2+} + 2e^- \rightarrow Zn(s)$ −0.76 V
- Since Cu^{2+} ions are more easily reduced than Zn^{2+} ions, $Cu^{2+} + 2e^- \rightarrow Cu$, is the reduction half reaction and $Zn^{2+} + 2e^- \rightarrow Zn$ needs to be reversed to become the oxidation half-reaction

- The cell potential is then calculated as follows:

$$E^0_{cell} = E^0_{reduction} - E^0_{oxidation}$$
$$E^0_{cell} = (0.34) - (-0.76)$$
$$E^0_{cell} = 1.10\,V$$

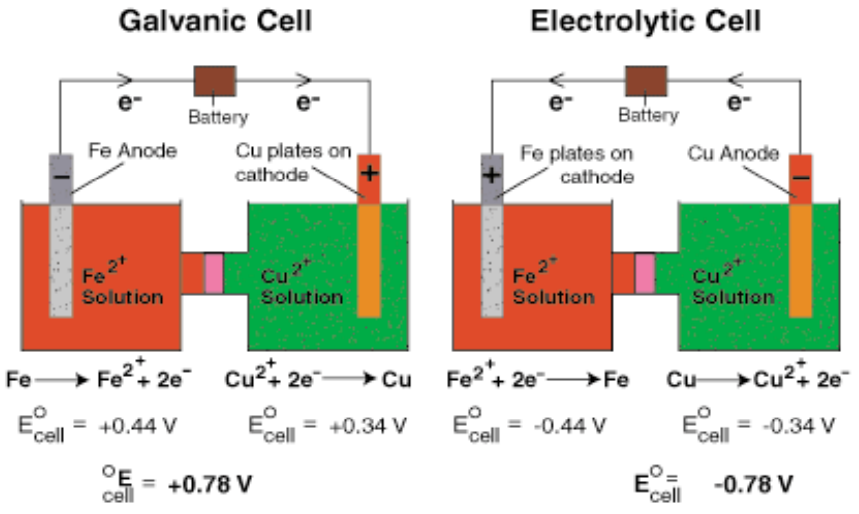
- The cell potential is +1.10 V and is spontaneous

Electrolytic Cells

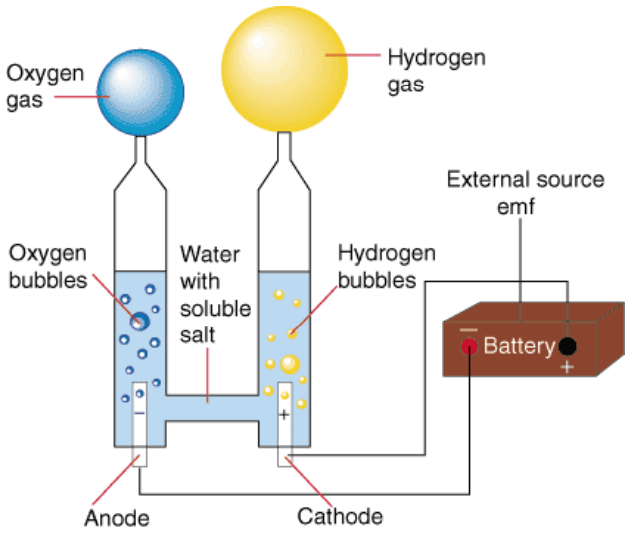
- The use of electrical energy to bring about a chemical reaction is called electrolysis
- An electrochemical cell in which electrolysis occurs is called an electrolytic cell
- For example, when we charge a battery, it is acting as an electrolytic cell

Comparing Electrochemical and Electrolytic Cells

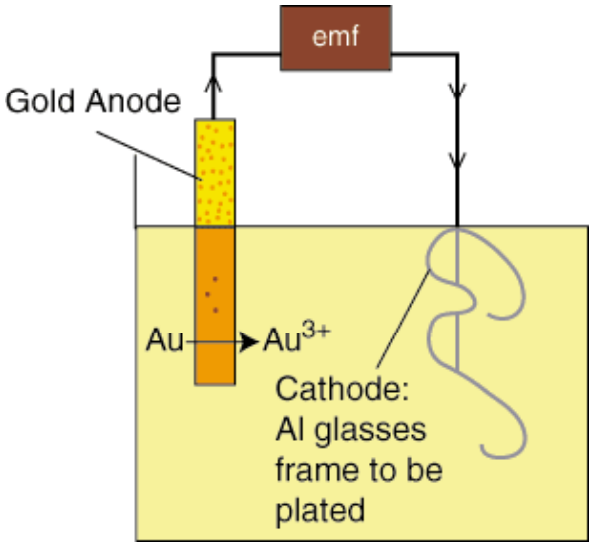
	Electrochemical Cell	Electrolytic Cell
Reaction Spontaneity	Spontaneous	Non-spontaneous
Cell Potential	Positive	Negative
Electricity	Produces	Consumes
Electrode Charge	Cathode + Anode -	Cathode – Anode +
Cathode Anode	Reduction Oxidation	Reduction Oxidation
Change in Energy	Converts chemical energy into electrical energy	Converts electrical energy into chemical energy



Electrolysis of Water



Electroplating

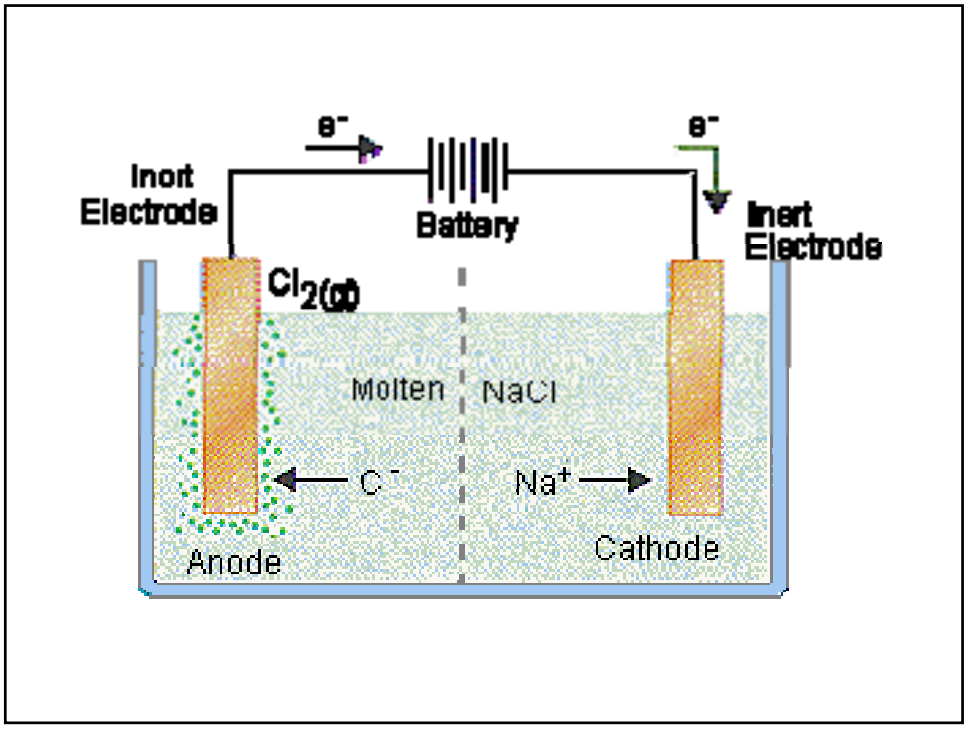


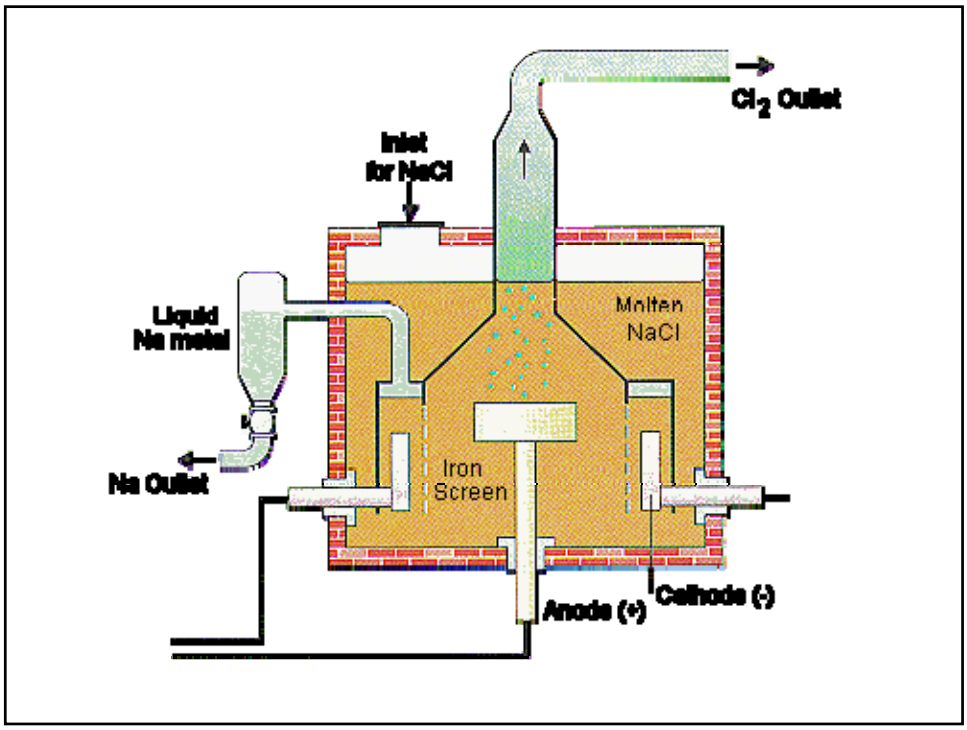
Electrolysis of Molten Solutions

- Molten solutions are melted forms of the pure substance
- Obviously, the cell container would be made of material that would withstand the high temperatures required to maintain the solution in the molten state
- The negative side of the battery is connected to the cathode
- The cations move towards the cathode and the anions to the anode

Example (NaCl)

- Anode (oxidation)
  - $2Cl^- \rightarrow Cl_2 + 2e^-$
- Cathode (reduction)
  - $2Na^+ + 2e^- \rightarrow 2Na$
- Net Reaction
  - $2Cl^- + 2Na^+ \rightarrow Cl_2 + 2Na$
- This process is used to produce pure supplies of sodium and chlorine gas


e⁻
e⁻
Inert Electrode
Battery
Inert Electrode
$Cl_{2(g)}$
Molten NaCl
Cl^-
Na^+
Anode
Cathode


Cl_2 Outlet
Inlet for NaCl
Liquid Na metal
Molten NaCl
Na Outlet
Iron Screen
Anode (+)
Cathode (-)

Electrolysis of an Aqueous Solution

- We can also create an electrolytic cell using an aqueous solution
- In this case, we have more possibilities for the reduction and oxidation half-reactions

Example: Electrolysis of Brine (a saturated NaCl solution)

- Anode (Oxidation)
  - * – $2Cl^- \rightarrow Cl_2 + 2e^-$ (-1.36V)
  - – $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (-1.23V)

- H_2O should be oxidized (higher potential), but due to complex reasons regarding the voltage required, it doesn't and Cl^- is actually what is oxidized

- Cathode (Reduction)
  - $2H+ + 2e^- \rightarrow H_2$ (0V)
  * – $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (-0.83V)
  - $Na^+ + e^- \rightarrow Na$ (-2.71V)

- H^+ should be reduced, however, in a neutral salt solution, the concentration of H^+ is $1x10^{-7}$ mol/L which is too low to even consider
- Therefore, H_2O will be reduced

- This gives a net reaction of
  - $2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^-$

Practical Uses of Electrolytic Cells

- Electrolysis of brine for the purification of water
- Electrolysis of molten sodium chloride to obtain sodium and chlorine gas
- Electrolysis of aluminum oxide to obtain aluminum
- Extraction of metals like lithium, beryllium, magnesium, calcium, and radium by electrolysis of their molten chlorides

- Refining metals like copper or nickel by removing impurities electrolytically
- Electroplating with metals such as gold, silver, or copper
- Galvanizing (iron electroplated with zinc)
- Preventing rust by electroplating a substance with a more reactive metal
  - Ship hulls, oil and gas pipe lines, boat motors, underground iron pipes, gasoline storage tanks

Faraday's Law of Electrolysis

- The amount of a substance consumed or produced at one of the electrodes in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell

$$mol\ e^- = \frac{It}{96\,500}$$

Example

- If 9.0 A flows for 10.0 minutes through a molten silver fluoride solution, what mass of silver metal would be deposited at the cathode?

Cathode (Reduction): $Ag^+ + e^- \rightarrow Ag$

$$mol\ e^- = \frac{It}{96\,500} = \frac{(9.0A)(10 \times 60)}{96\,500} = 0.0560\ mol\ e^-$$

$$0.0560\ mol\ \mathrm{Ag} \times 107.9\ {}^{g}\!/_{mol} = 6.04\ g$$