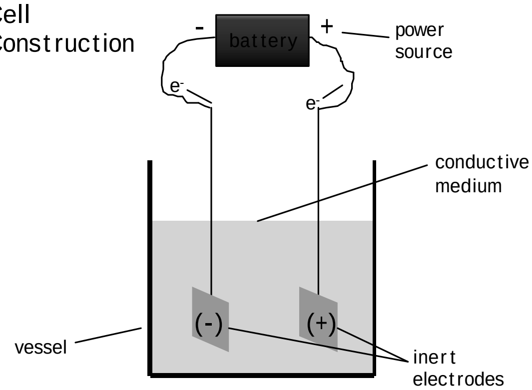
Discovering Electrochemical Cells

PGCC CHM 102 Sinex

Part I – Electrolytic Cells

Many important industrial processes

Cell Construction



Sign or polarity of electrodes

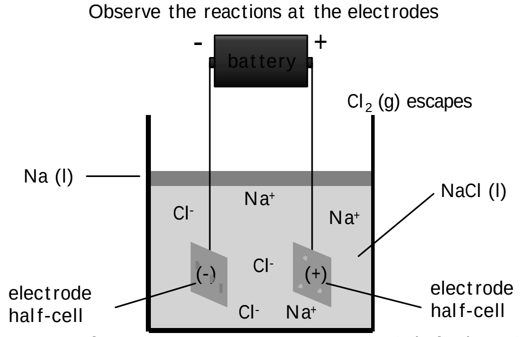
What chemical species would be present in a vessel of molten sodium chloride, NaCl (l)?

Na^+ Cl^-

Let's examine the electrolytic cell for molten NaCl.

Molten NaCl

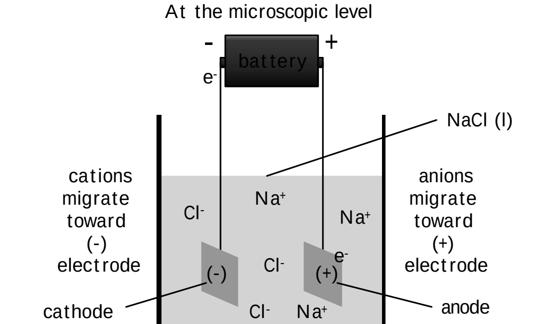
Observe the reactions at the electrodes



$Na^+ + e^- \rightarrow Na$ $2Cl^- \rightarrow Cl_2 + 2e^-$

Molten NaCl

At the microscopic level



$Na^+ + e^- \rightarrow Na$ $2Cl^- \rightarrow Cl_2 + 2e^-$

Molten NaCl Electrolytic Cell

cathode half-cell (-)
REDUCTION $Na^+ + e^- \rightarrow Na$ X 2

anode half-cell (+)
OXIDATION $2Cl^- \rightarrow Cl_2 + 2e^-$

overall cell reaction
$2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$

Non-spontaneous reaction!

Definitions:

CATHODE

REDUCTION occurs at this electrode

ANODE

OXIDATION occurs at this electrode

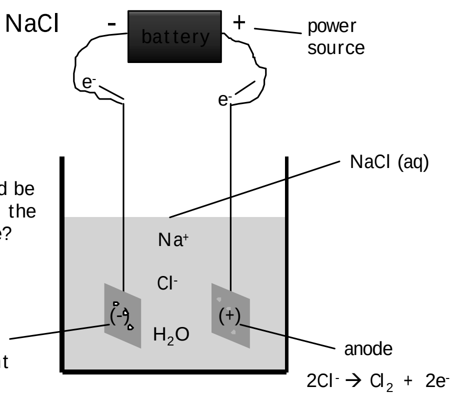
What chemical species would be present in a vessel of aqueous sodium chloride, NaCl (aq)?

Na^+ Cl^-

H_2O

Will the half-cell reactions be the same or different?

Aqueous NaCl



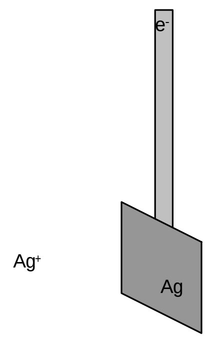
What could be reduced at the cathode?

Aqueous NaCl Electrolytic Cell

possible cathode half-cells (-)
REDUCTION ~~$Na^+ + e^- \rightarrow Na$~~
$2H_20 + 2e^- \rightarrow H_2 + 2OH^-$

possible anode half-cells (+)
OXIDATION $2Cl^- \rightarrow Cl_2 + 2e^-$
~~$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$~~

overall cell reaction
$2Cl^- + 2H_20 \rightarrow H_2 + Cl_2 + 2OH^-$



For every electron, an atom of silver is plated on the electrode.
$Ag^+ + e^- \rightarrow Ag$

Electrical current is expressed in terms of the ampere, which is defined as that strength of current which, when passed thru a solution of $AgNO_3$ (aq) under standard conditions, will deposit silver at the rate of 0.001118 g Ag/sec

1 amp = 0.001118 g Ag/sec

Faraday's Law

The mass deposited or eroded from an electrode depends on the quantity of electricity.

Quantity of electricity – coulomb (Q)

Q is the product of current in amps times time in seconds

coulomb → $Q = I\,t$ ← time in seconds

↑ current in amperes (amp)

1 coulomb = 1 amp-sec = 0.001118 g Ag

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

1.00 mole e^{-} = 1.00 mole Ag = 107.87 g Ag

$$\frac{107.87 \text{ g Ag/mole } e^{-}}{0.001118 \text{ g Ag/coul}} = 96{,}485 \text{ coul/mole } e^{-}$$

↖ 1 Faraday (***F***)

mole e^{-} = Q/***F***

mass = $mole_{metal}$ x MM

$mole_{metal}$ depends on the half-cell reaction

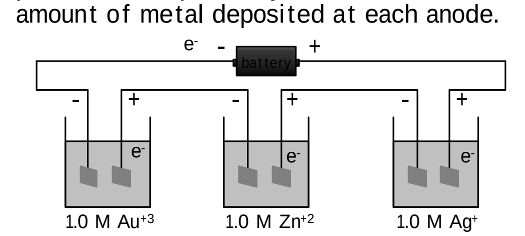
Examples using Faraday's Law

- How many grams of Cu will be deposited in 3.00 hours by a current of 4.00 amps?

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

- The charge on a single electron is 1.6021 x 10^{-19} coulomb. Calculate Avogadro's number from the fact that 1 ***F*** = 96,487 coulombs/mole e^{-}.

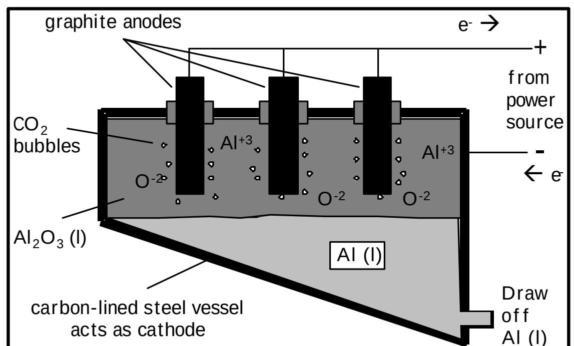
- A series of solutions have 50,000 coulombs passed thru them, if the solutions were Au^{+3}, Zn^{+2}, and Ag^{+}, and Au, Zn, and Ag were plated out respectively, calculate the amount of metal deposited at each anode.



$Au^{+3} + 3e^{-} \rightarrow Au$ $Zn^{+2} + 2e^{-} \rightarrow Zn$ $Ag^{+} + e^{-} \rightarrow Ag$

The Hall Process for Aluminum

- Electrolysis of molten Al_2O_3 mixed with cryolite – lowers melting point
- Cell operates at high temperature – 1000ºC
- Aluminum was a precious metal in 1886.
- A block of aluminum is at the tip of the Washington Monument!



Cathode: $Al^{+3} + 3e^{-} \rightarrow Al\ (l)$

Anode: $2\,O^{-2} + C\ (s) \rightarrow CO_2\ (g) + 4e^{-}$

The Hall Process

Cathode: Al^{+3} + $3e^-$ → Al (l)   x 4

Anode: 2 O^{-2} + C (s) → CO_2 (g) + $4e^-$ x 3

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4 Al^{+3} + 6 O^{-2} + 3 C (s) → 4 Al (l) + 3 CO_2 (g)

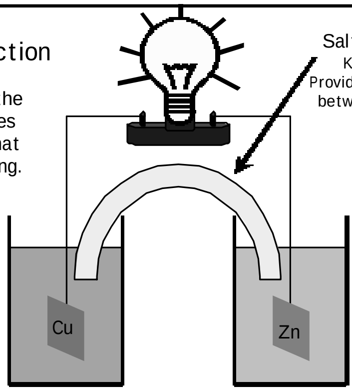
The graphite anode is consumed in the process.

Part II – Galvanic Cells

Batteries and corrosion

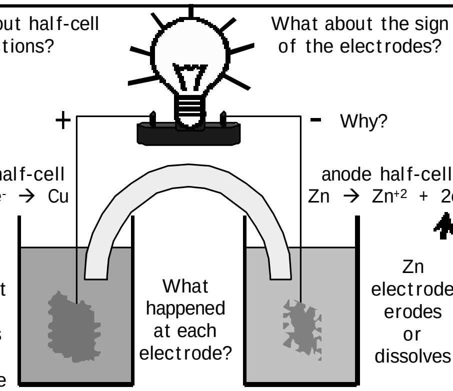
Cell Construction

Observe the electrodes to see what is occurring.



What about half-cell reactions?

What about the sign of the electrodes?



Galvanic cell

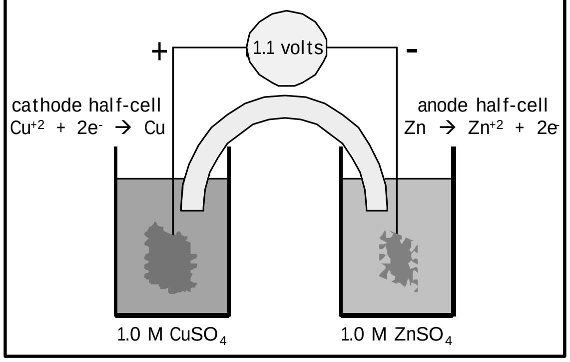
- cathode half-cell (+)
  REDUCTION Cu^{+2} + $2e^-$ → Cu
- anode half-cell (-)
  OXIDATION   Zn → Zn^{+2} + $2e^-$
- overall cell reaction
  Zn + Cu^{+2} → Zn^{+2} + Cu

Spontaneous reaction that produces electrical current!

Now for a standard cell composed of Cu/Cu^{+2} and Zn/Zn^{+2}, what is the voltage produced by the reaction at 25°C?

<u>Standard Conditions</u>
Temperature - 25°C
All solutions – 1.00 M
All gases – 1.00 atm

Now replace the light bulb with a volt meter.

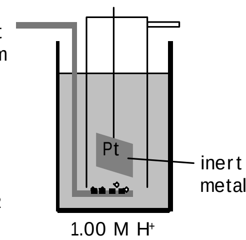


We need a standard electrode to make measurements against!

The Standard Hydrogen Electrode (SHE)

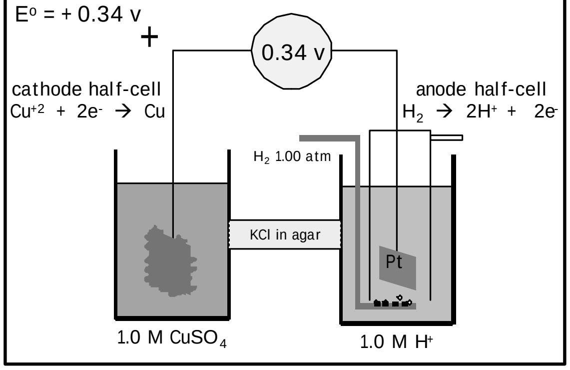
25°C
$1.00\ M\ H^+$
$1.00\ atm\ H_2$

Half-cell
$2H^+ + 2e^- \rightarrow H_2$
$E^o_{SHE} = 0.0$ volts



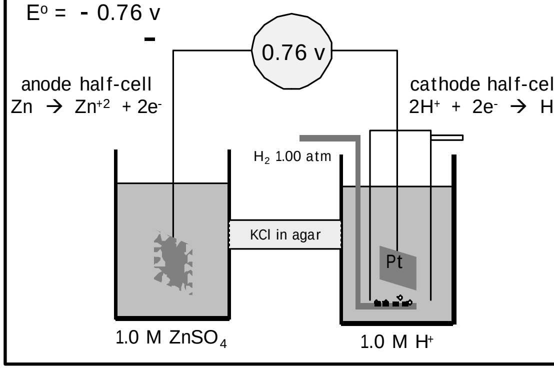
Now let's combine the copper half-cell with the SHE

$E^o = +0.34$ v



Now let's combine the zinc half-cell with the SHE

$E^o = -0.76$ v



Assigning the E°

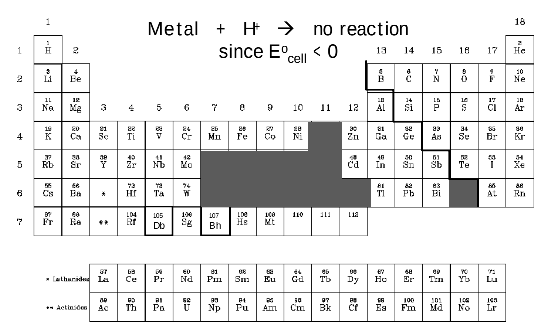
Write a reduction half-cell, assign the voltage measured, and the sign of the electrode to the voltage.

$Al^{+3} + 3e^- \rightarrow Al$	$E^o = -1.66$ v
$Zn^{+2} + 2e^- \rightarrow Zn$	$E^o = -0.76$ v
$2H^+ + 2e^- \rightarrow H_2$	$E^o = 0.00$ v
$Cu^{+2} + 2e^- \rightarrow Cu$	$E^o = +0.34$
$Ag^+ + e^- \rightarrow Ag$	$E^o = +0.80$ v

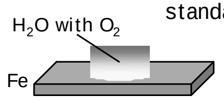
Increasing activity ↑

The Non-active Metals

Metal + $H^+ \rightarrow$ no reaction
since $E^o_{cell} < 0$



Calculating the cell potential, E^o_{cell}, at standard conditions



Consider a drop of oxygenated water on an iron object

Fe^{+2} + $2e^-$ → Fe $E^o = -0.44$ v reverse

2x Fe → Fe^{+2} + $2e^-$ $-E^o = +0.44$ v

O_2 (g) + $2H_2O$ + $4e^-$ → 4 OH^- $E^o = +0.40$ v

2Fe + O_2 (g) + $2H_2O$ → $2Fe(OH)_2$ (s) $E^o_{cell} = +0.84$ v

This is corrosion or the oxidation of a metal.

Is iron an active metal?

Fe + $2H^+$ → Fe^{+2} + H_2 (g) $E^o_{cell} = +0.44$ V

What would happen if iron is exposed to hydrogen ion?

2x Fe → Fe^{+2} + $2e^-$ $-E^o = +0.44$ v

O_2 (g) + $4H^+$ + $4e^-$ → $2H_20$ $E^o = +1.23$ v

2Fe + O_2 (g) + $4H^+$ → $2Fe^{+2}$ + $2H_2O$ $E^o_{cell} = +1.67$ v

How does acid rain influence the corrosion of iron?

Enhances the corrosion process

What happens to the electrode potential if conditions are not at standard conditions?

The Nernst equation adjusts for non-standard conditions

For a reduction potential: ox + ne → red

$$\text{at } 25^oC: \quad E = E^o - \frac{0.0591}{n} \log \frac{(red)}{(ox)}$$

Calculate the E for the hydrogen electrode where 0.50 M H^+ and 0.95 atm H_2.

Free Energy and the Cell Potential

Cu → Cu^{+2} + $2e^-$ $-E^o = -0.34$

2x Ag^+ + e^- → Ag $E^o = +0.80$ v

Cu + $2Ag^+$ → Cu^{+2} + 2Ag $E^o_{cell} = +0.46$ v

$$\Delta G^o = -n\mathbf{F}E^o_{cell}$$

where n is the number of electrons for the balanced reaction

What is the free energy for the cell?

1**F** = 96,500 J/v

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from thermodynamics:
$\Delta G^o = -2.303RT \log K$

and the previous relationship:
$\Delta G^o = -n\mathbf{F}E^o_{cell}$

$-n\mathbf{F}E^o_{cell} = -2.303RT \log K$

$$\text{at } 25^oC: \quad E^o_{cell} = \frac{0.0591}{n} \log K$$

where n is the number of electrons for the balanced reaction

Comparison of Electrochemical Cells