화학 General Chemistry
034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302

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Electrochemistry

- The study of the interchange of **chemical** and **electrical energy.**

-Generation of an **electric current** from a **spontaneous chemical reaction**

-Use of a **current** to produce **chemical change**

oxidation-reduction (redox) reaction: involves a transfer of **electrons** from the reducing agent to the oxidizing agent.

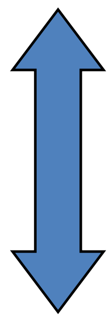
oxidation: loss of electrons

reduction: gain of electrons

In many cases, definition of oxidation and reduction is simple. However, in some other cases, it is not obvious.

Covalent bonds, Ionic bonds, and somewhere in between

- Covalent bond between two atoms:
  - Shares electrons
  - One cannot tell the number of electrons in one atom



Ionic bond between two atoms:

- Do not share electrons
- One can tell the number of atoms in anion and cation in ionic compounds

- **** Old Definitions: deal with reaction of metals**

- Oxidation: “addition of oxygen”
- Reduction: “loss of oxygen”

Ex)

- $2Na + 1/2O_2 \rightarrow Na_2O$ (Na-atom is oxidized)
- $2Fe + O_2 \rightarrow 2FeO$ (Fe-atom is oxidized)
- $2FeO \rightarrow 2Fe + O_2$ (Fe-atom is reduced)

Generalization of concepts

People already **<u>"knew"</u>** that Na wants to be in Na^+ form, and O wants to be in O^{2-}.

- $2Na + 1/2O_2 \rightarrow Na_2O = 2Na^+ + O^{2-}$
- $2Fe + O_2 \rightarrow 2FeO = 2Fe^{2+} + 2O^{2-}$
- $Pb + CO_2 \rightarrow PbO + CO = Pb^{2+} + O^{2-}$
-

Oxidation = loss of electrons!

Reduction = gain of electrons

$2Na + Cl_2 \rightarrow 2NaCl = Na^+ + Cl^-$

Na is oxidized, Cl_2 is reduced

Newer definition of oxidation and reduction

- Oxidation = gain of electrons
- Reduction = loss of electrons

$$2Na + Cl_2 \rightarrow NaCl \sim Na^+ + Cl^-$$

This definition works great for ionic compounds, but…

- For other non-ionic compounds, it is hard to tell which one lost electrons and which one gained electrons.

Pb: reduced or oxidized?

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$Pb^{?+}$ Pb^{2+}

Does the Carbon atom lost electron or gained electron?

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

However, we still want to use the concept of oxidation-reduction..

So, we invent the rule

- Regard ALL of the compound as ionic compound.
- $H_2O = 2H^{+} + O^{2-}$
- Charges in this artificial ions are called the oxidation number

The Rule

TABLE 4.2 Rules for Assigning Oxidation States

The Oxidation State of . . .	Summary	Examples
• An atom in an element is zero	Element: 0	Na(*s*), $O_2(g)$, $O_3(g)$, Hg(*l*)
• A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na^+, Cl^-
• Fluorine is −1 in its compounds	Fluorine: −1	HF, PF_3
• Oxygen is usually −2 in its compounds Exception: peroxides (containing O_2^{2-}) in which oxygen is −1	Oxygen: −2	H_2O, CO_2
• Hydrogen is +1 in its covalent compounds	Hydrogen: +1	H_2O, HCl, NH_3

Note:

- Oxidation numbers for monoatomic ionic species are actual charges.
- Pure elements have zero charges.
- All other elements follows total charge condition:

- CO_2: Net charge = 0 = 2 x (-2) + x
- X= 4+ : oxidation state of C in CO_2 is +4

Newest definition of Oxidation / Reduction

- Oxidation = increase in oxidation number
- Reduction = reduction in oxidation number

*** This definition embraces* ***all of the older definitions***

Oxidation: “addition of oxygen”
Reduction: “loss of oxygen”

Oxidation = gain of electrons
Reduction = loss of electrons

Reduction and oxidation occurs simultaneously for a given reaction= REDOX reaction

a. The oxidation state of oxygen is -2. Because CO_2 has no charge, the sum of the oxidation states must be zero.

CO_2

+4 -2 for each oxygen

$$1(+4) + 2(-2) = 0$$

b. The oxidation state of fluorine is -1.

SF_6

+6 -1 for each fluorine

$$+6 + 6(-1) = 0$$

c. NO_3^-

+5 -2 for each oxygen

$$+5 + 3(-2) = -1$$

Oxidation-Reduction Reactions

- Oxidizing agent or Oxidizer/Oxidant
  - Something that causes others to oxidize
  - Compound that is being reduced

- Reducing agent or Reducer/Reductant
  - Something that causes others to reduce
  - Compound that is being oxidized

Oxidation-Reduction Reactions

$$2Al(s) + 3I_2(s) \longrightarrow 2AlI_3(s)$$

Identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

$$PbO(s) + CO(g) \longrightarrow Pb(s) + CO_2(g)$$

Balancing Oxidation-Reduction Reaction (Redox Reaction)

$$CuS(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + NO(g)$$

H^+ H_2O

1. Number of atoms should be conserved

2. Reaction can be different for acidic and basic conditions. H_2O, OH^-, and H^+ can take parts in the chemical reaction

3. Oxidation and reduction occurs at the same time:
   -Oxidation number change should be conserved

Example 13.1.

Balance the net ionic equation for this skeletal reaction in an **acidic** aqueous solution.

$$MnO_4^- \,(aq) + H_2C_2O_4 \,(aq) \rightarrow Mn^{2+} \,(aq) + CO_2 \,(g)$$

Example 13.2.

Balance the net ionic equation for this skeletal reaction in a **basic** aqueous solution.

$$MnO_4^- \,(aq) + Br^- \,(aq) \rightarrow MnO_2 \,(s) + BrO_3^- (aq)$$

Half-Reactions/Balancing Redox Equations

- Half-reaction

  : the oxidation or reduction part of a reaction considered alone

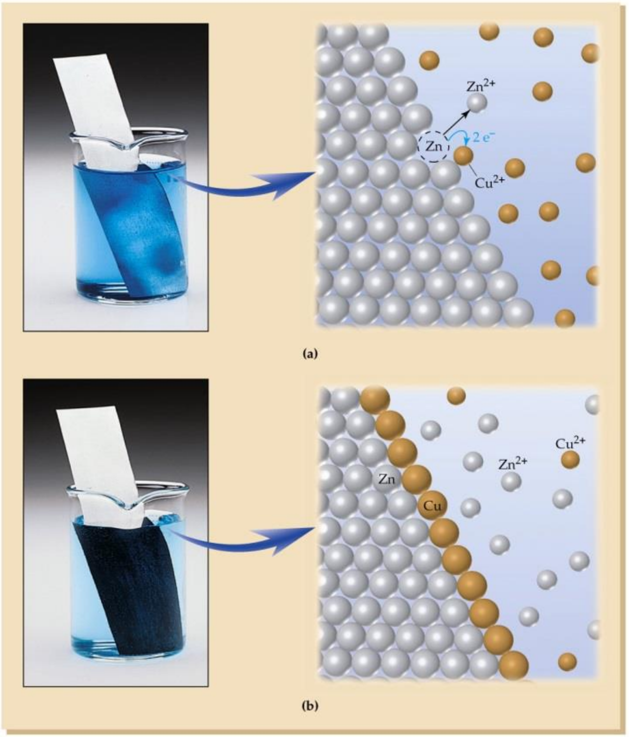
- Oxidation/Reduction

  Oxidation: loss of electrons

  Reduction: gain of electrons

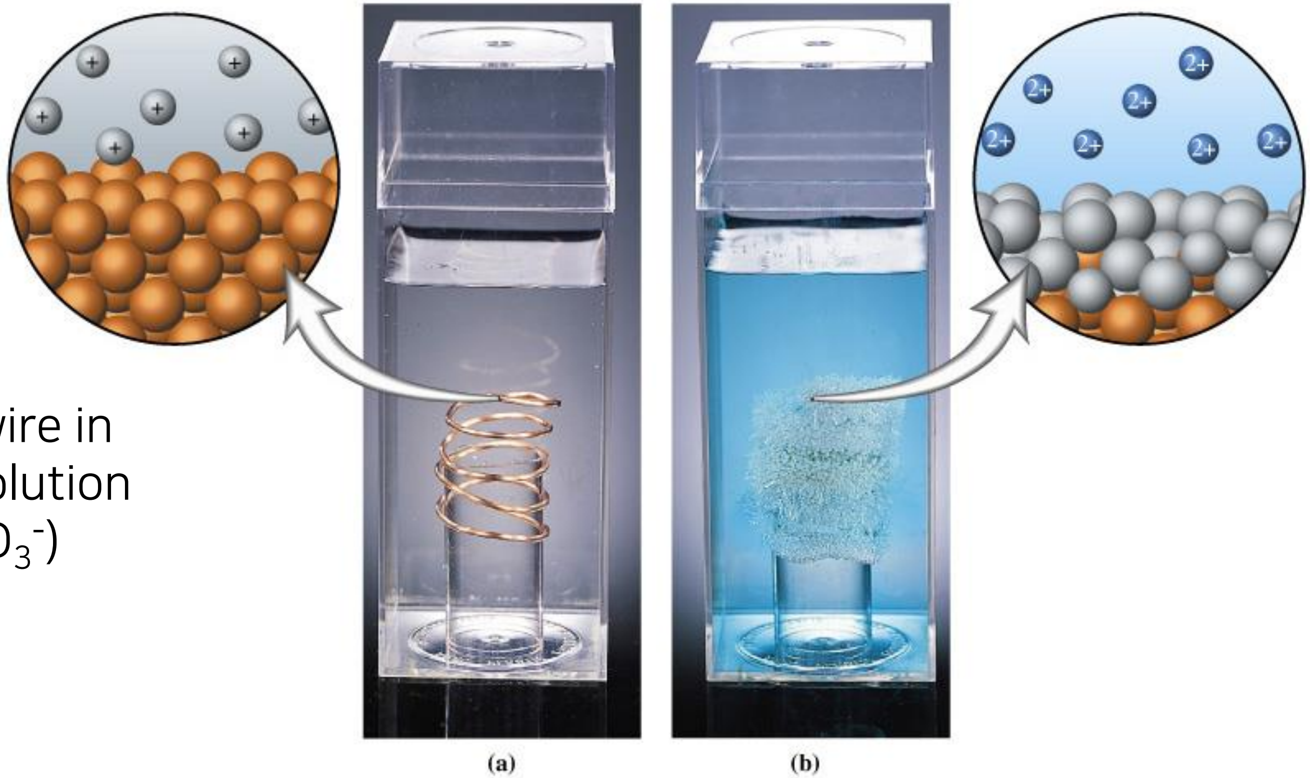
$$Zn(s) + 2\,Ag^{+}(aq) \longrightarrow Zn^{2+}(aq) + 2\,Ag(s)$$

- oxidation $Zn(s) \longrightarrow Zn^{2+}(s) + 2\,e^{-}$
- reduction $Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$



Zn^{2+}/Zn and Ag^{+}/Ag

Copper wire in
$AgNO_3$ solution
($Ag^+ + NO_3^-$)



1. Cu atoms lose electrons and dissolve into the solution:
   $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (Cu is oxidized)
2. Electrons ($2e^-$) are deposited onto the remaining Cu metal.
3. Ag^+ ions are attracted to the charged Cu metal surface.
4. Ag^+ ions obtain electrons to become Ag(s) and deposited onto the metallic Cu.
   $Ag^+(aq) + e^- \rightarrow Ag(s)$ (Ag is reduced)

Overall reaction that is happening in the beaker

Half-reactions

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$ Ox

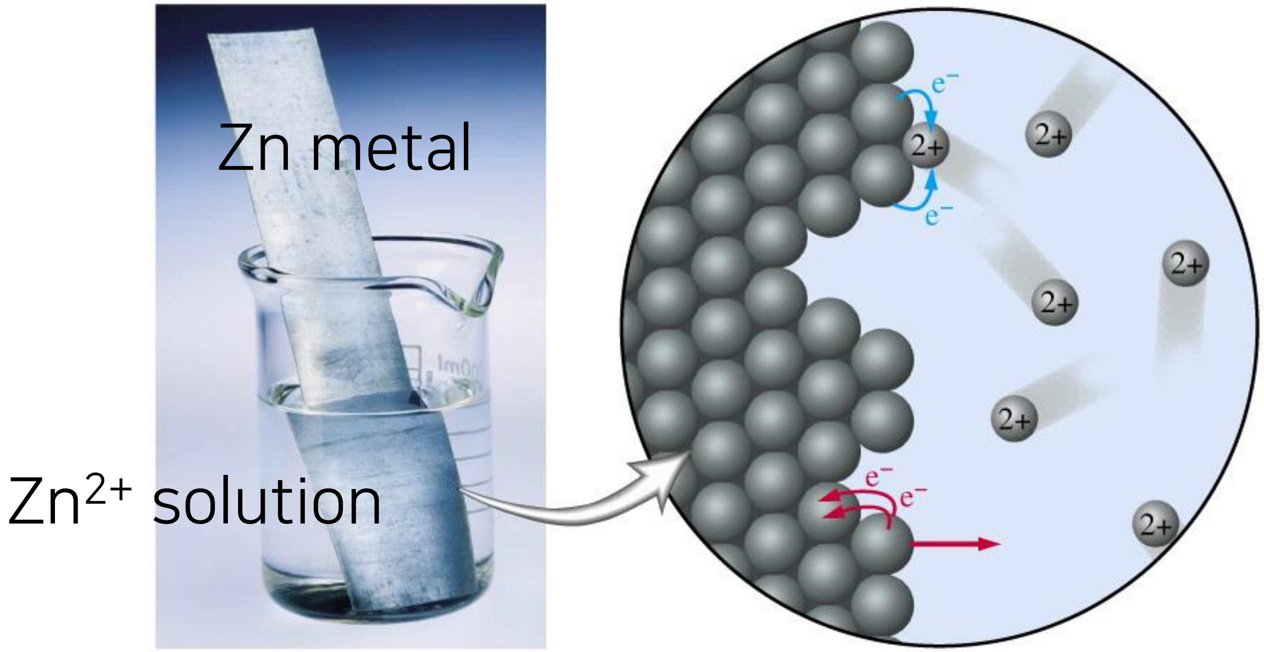
$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$ Red

$$Cu(s) + 2Ag^+(ag) \rightarrow Cu^{2+}(aq) + Ag(s)$$

Questions:

1. Why does the reverse reaction do not occur?
2. What determines the direction of the reaction?
3. How do we implement this redox reaction?

Metal Electrodes and Equilibrium



$$Zn(s) \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} Zn^{2+}(aq) + 2e^-$$

Structure of Galvanic Cells

- **Electrochemical cell**

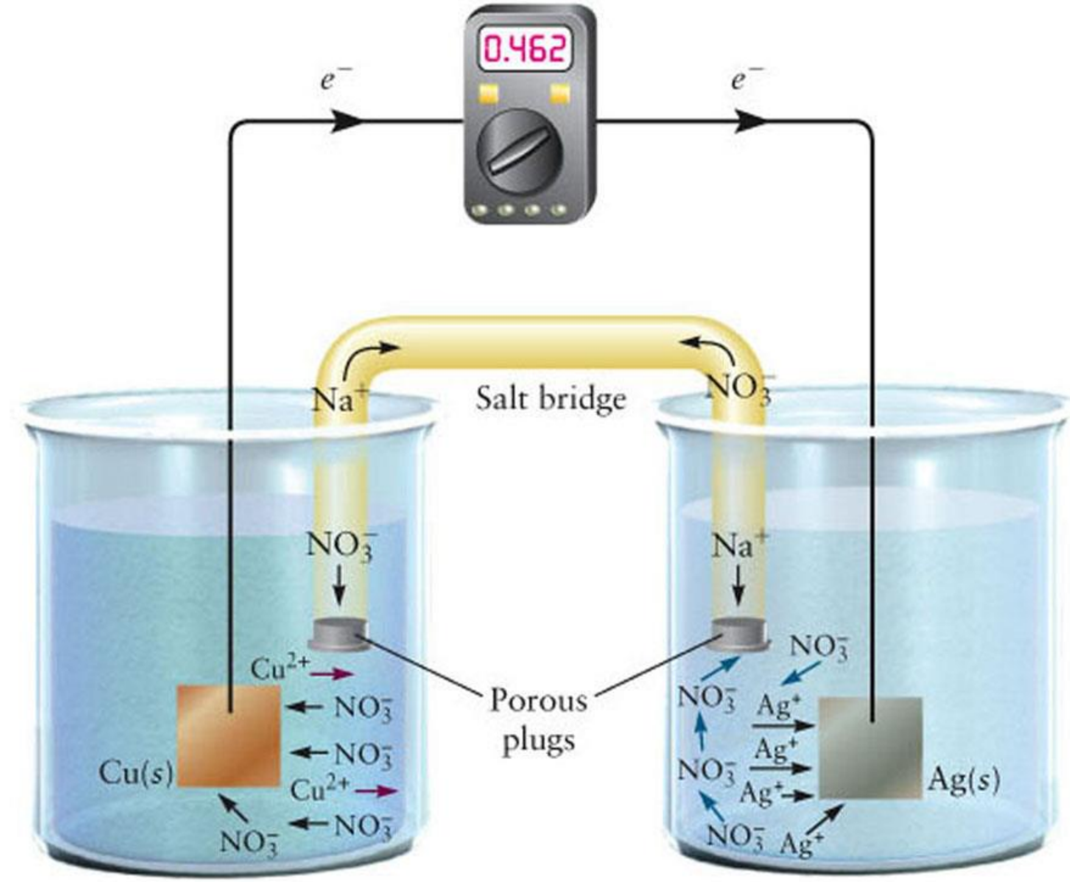
: A device in which an electric current (a flow of electrons through a circuit) is either produced by a spontaneous chemical reaction or used to bring about a nonspontaneous reaction.

-**Galvanic cell**

: An electrochemical cell in which a spontaneous chemical reaction is used to generate an electric current.

- **Battery**: a collection of galvanic cells joined in series

GALVANIC CELL



1. Metal electrodes (provide electrons)

2. Electrolyte solutions

3. Salt bridge (Current between two beakers)

OX:
$Cu(s) \rightarrow Cu^{2+} + 2e^-$
Anode

RED:
$Ag^+(aq) + e^- \rightarrow Ag(s)$
Cathode

$$Cu(s)|Cu^{2+}(aq)\ ||\ Ag^+(aq)\ |\ Ag(s)$$

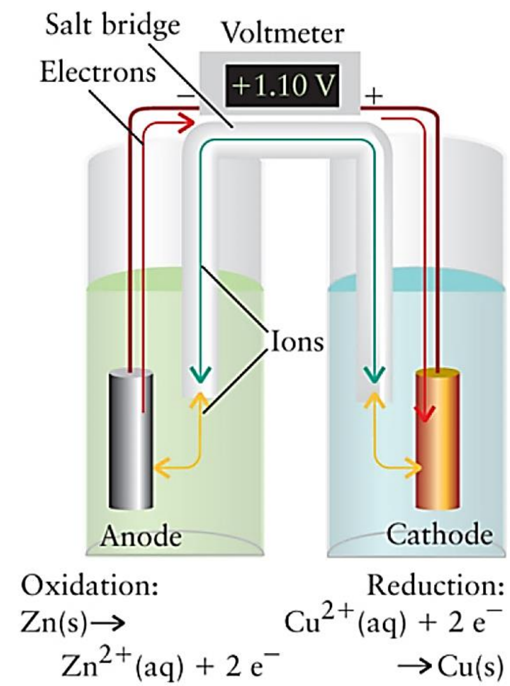
13.5. The Notation for Cells

- Cell diagram

$$Zn(s)\ |\ Zn^{2+}(aq)\ \|\ Cu^{2+}(aq)\ |\ Cu(s)$$

Phase boundary   Salt bridge

anode   cathode



electrons

$$Zn(s)\,|\,Zn^{2+}(aq)\|Cu^{2+}(aq)\,|\,Cu(s) \qquad E_{cell} = +1.10\ V$$

Anode (−)   Cathode (+)

$$Zn(s)|Zn^{2+}(aq)\|Cu^{2+}(aq)|Cu(s)$$

Left (L)	Right (R)
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
(oxidation)	(reduction)

Overall (R + L): $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad E_{cell} = +1.10\ V$

Net Reaction

$$Cu(s) \rightarrow Cu^{2+} + 2e^-$$

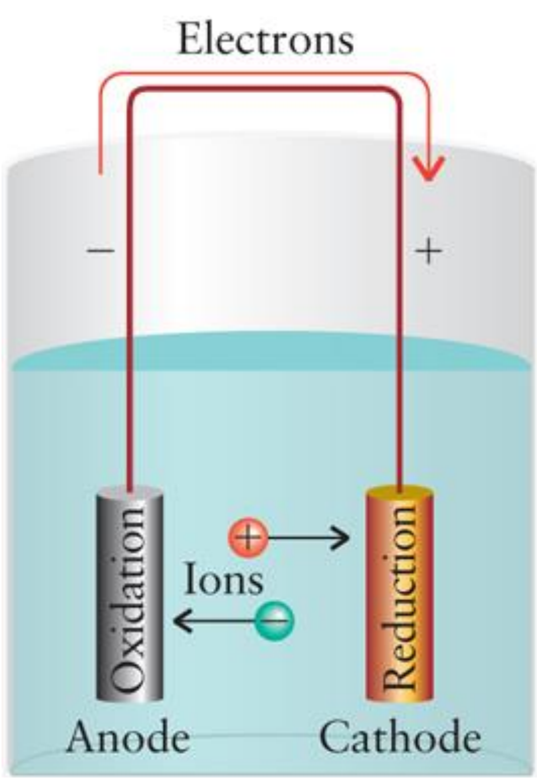
Half-reactions

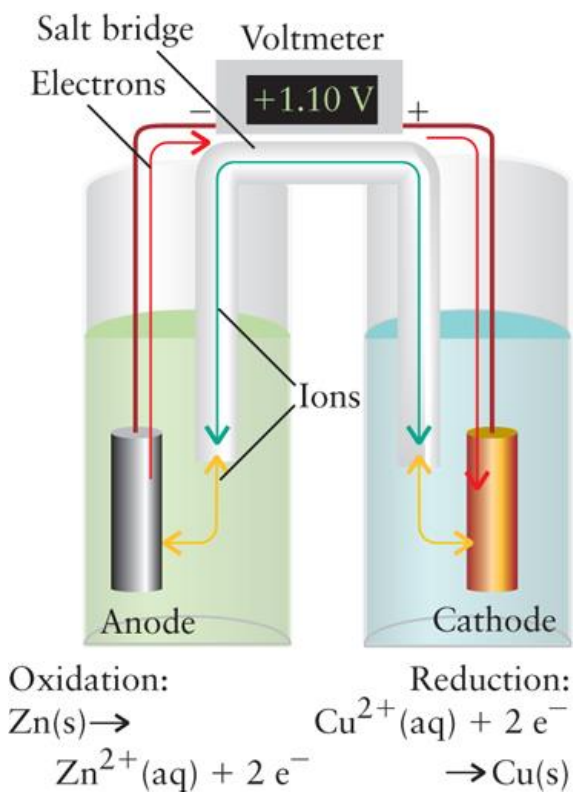
$$2Ag^+ + 2e^- \rightarrow Ag(s)$$

$$Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + Ag(s)$$

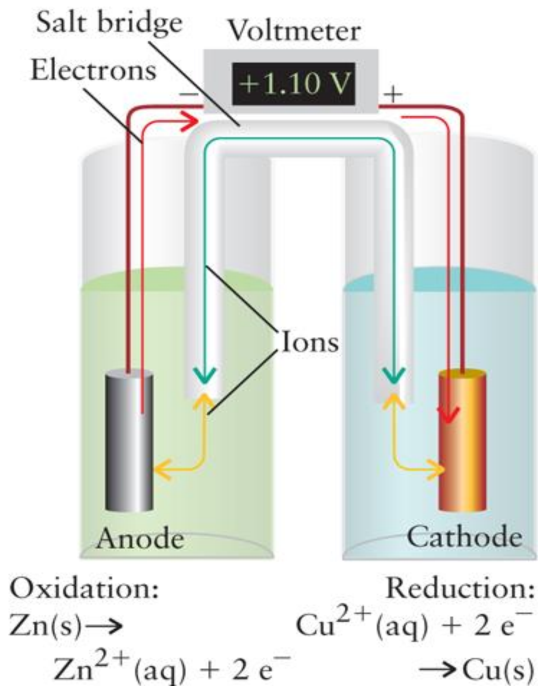
Purpose of salt bridge

- Two separate beakers without salt bridge
  → The reaction will stop after a short period of time.
- One beaker:
  → mixture of Zn^{2+} and Ag+ leads to ill-defined potential.

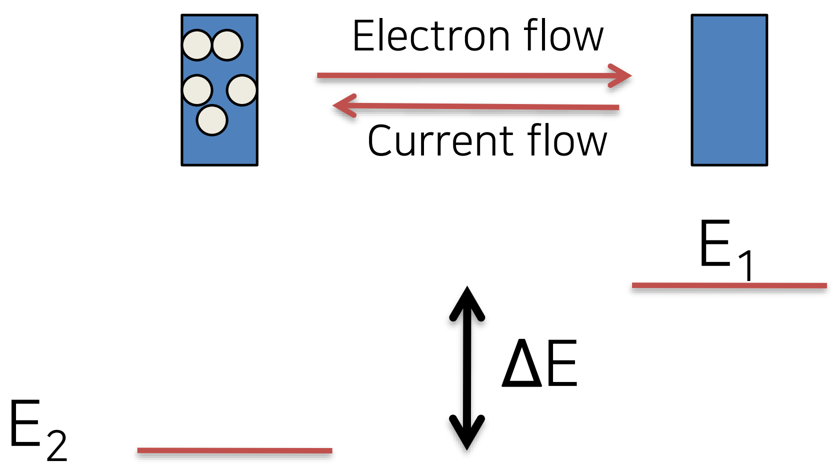




Electric potential difference, ΔE



Voltmeter measures voltage difference:



Cell Potential and Reaction Gibbs Free E

Units in electrochemisty

- Volt (V): electric potential energy/charge = N · m/C = J/C
- Coulomb (C): electric charge (*Q* or *q*) transported by a constant current of one ampere in second: A · s
- Ampere (A): electric current, one coulomb of charge going past a given point per second=C/s
- Watt (W): unit of power: J/s = V *A

Force: changes the state of motion of an object (**N**, kg · m · s^{-2}): **F= ma**

Work: the process of moving an object against an opposing force

Work = force X distance (**J**, kg · m^2 · s^{-2})

Energy: the capacity of a system to do **work**

Cell Potential and Reaction Gibbs Free E

$$\Delta \boldsymbol{G} = \boldsymbol{w_{non-expansion,\,rev}} = w_{non-expansion,\,Max} \ (\boldsymbol{at\ const.T\ and\ P})$$

- $w_{non-expansion,\,Max}$

= (Amount of charge through the circuit) x (Potential Difference)

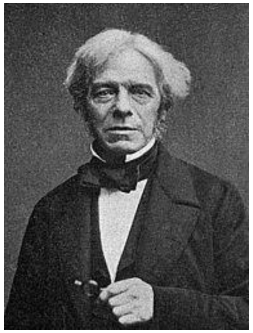
= (Total number of electrons x electron charge) $\times E$

= N x (-e) x E

= n x $N_{avogadro}$ x (-e) x E

= - n x (6 x 10^{23} x 1.6 x 10^{-19} C) x E

= - n F E



Michael Faraday
(1791-1867)

$$\therefore\ \boldsymbol{\Delta G = -nFE}$$

$$F\ (Faraday\ constant) = eN_A = (1.60 \times 10^{-19}\ C) \times (6.02 \times 10^{23}\ mol^{-1})$$

$$= \boldsymbol{9.632 \times 10^{4}\ C \cdot mol^{-1}}$$

$\Delta \boldsymbol{G} < \boldsymbol{0} \Leftrightarrow \boldsymbol{E} > \boldsymbol{0}$ (spontaneous reaction)

Cell Potential and Reaction Gibbs Free E

- For the cell at standard state, $\Delta G^{\circ} = -nFE^{\circ}$ Standard cell potential
  - Standard state: 1 atm, 1mole/liter, and usually at 298 K

: The cell potential measured when all reactants and products are in their standard states.

$\Delta G = \Delta G^{o} + RT\,lnQ$ where Q = reaction quotient

$\Delta G = -nFE$, $\Delta G_{o} = -nFE^{o}$

$-nFE = -nFE^{o} + RT\ln Q$

$$E = E^{o} - \frac{RT}{nF}\ln(Q)$$

Nernst Equation

$$E = E^{o} - \frac{0.0592}{n}\log(Q)$$

(at room temp.)

(n = number of electrons involved in the cell)

At Equilibrium,

$$G = -nFE = -nFE^{o} + RT\ln Q$$

$$\Delta G = 0, E = 0, \text{and } Q = K(\text{equilibr ium const})$$

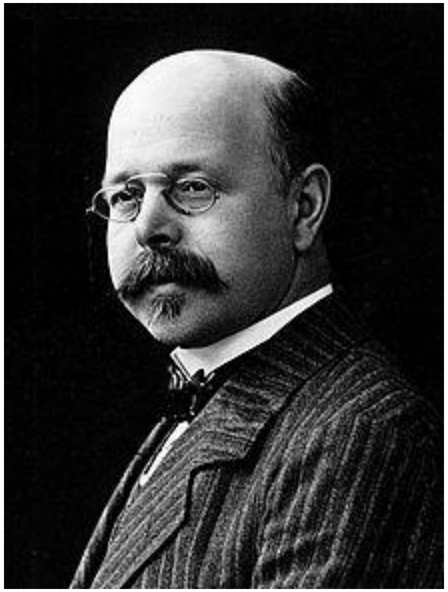
Therefore,

$$nFE^{o} = RT\ln K$$

$$E^{o} = (RT/nF)\ln K$$

$$E^{o} = \frac{0.0592}{n}\log(K)$$

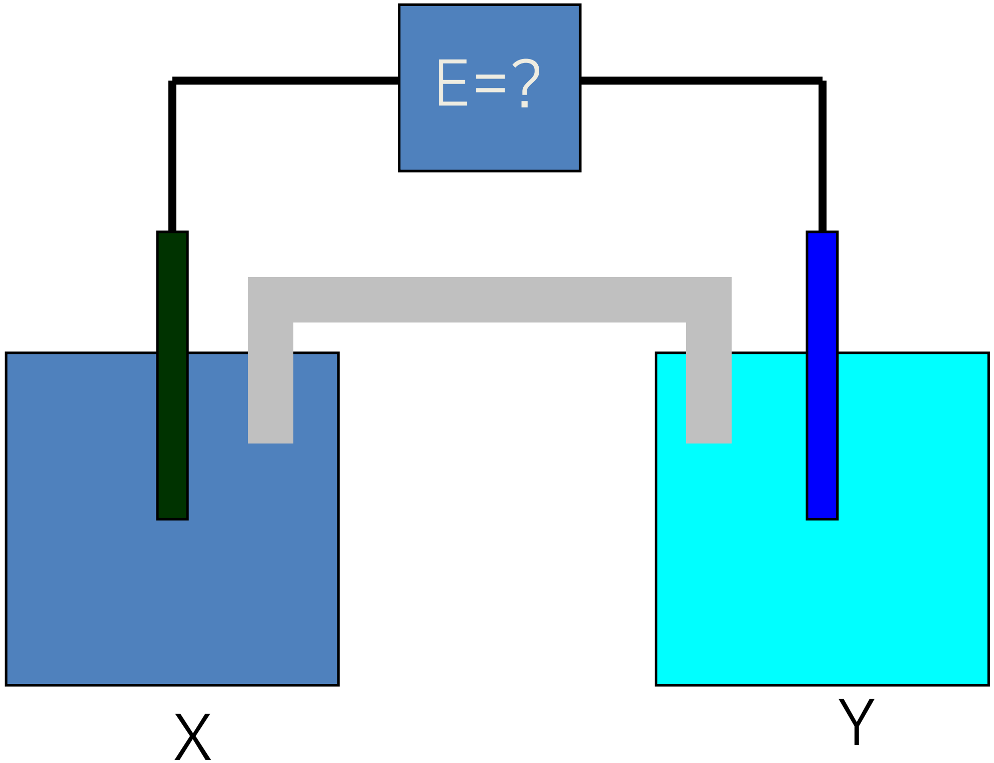
$$K = \exp\left(\frac{nE^{0}}{0.0592}\right)$$



Walther Nernst

1920 Nobel Prize in chemistry

For a combination of an anode and a cathode,
How much voltage difference (E) is generated?



$E = \mathbf{E^0}(Y) - \mathbf{E^0}(X)$ ($\mathbf{E^0}$: Standard reduction potential)

How to determine $\mathbf{E^0}(X)$ and $\mathbf{E^0}(Y)$ separately?

1. Need to define $\mathbf{E^0} = 0$ volt.
2. Need systematic ways to tabulate $\mathbf{E}(X)$.

13.6. Standard Potentials

- Standard *electrode* potential (standard reduction potential)
- Standard **cell** potential

  = difference between two standard electrode potential

$$E_{cell}{}^{o} = E_R{}^{o} - E_L{}^{o}$$

$$if \quad E_{cell}{}^{o} > 0 \Leftrightarrow \Delta G^{o} < 0 \Leftrightarrow K > 1$$

→ Spontaneous reaction at standard state (all substances)

→ Electrode on right = cathode

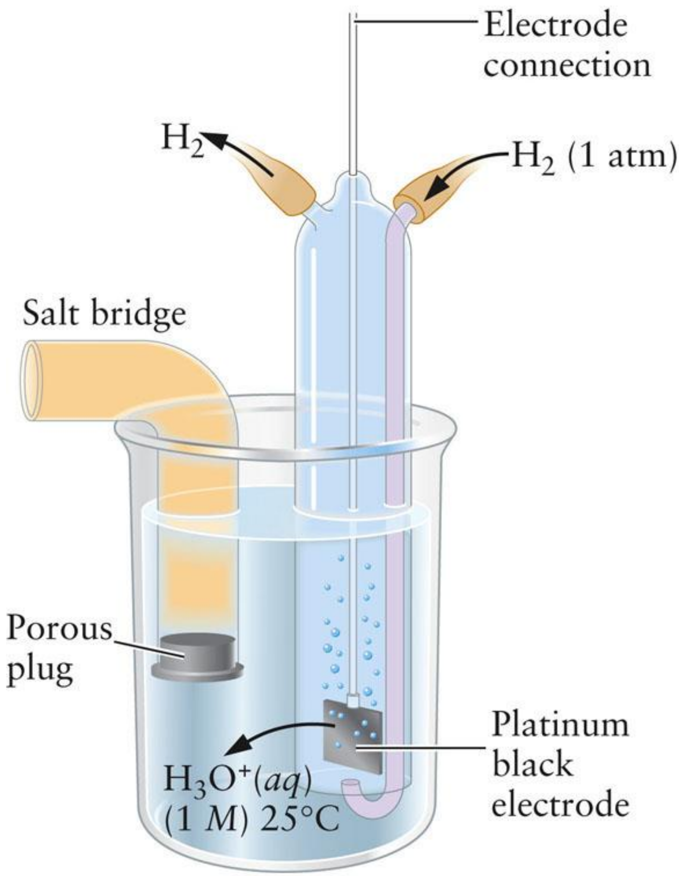
$Fe(s)\,|\,Fe^{2+}(aq)\,||\,Ag^{+}(aq)\,|\,Ag(s)$

$2\ Ag^{+}(aq) + Fe(s) \rightarrow 2\ Ag(s) + Fe^{2+}(aq)$

$E_{cell}{}^{\circ} = E^{\circ}(Ag^{+}/Ag) - E^{\circ}(Fe^{2+}/Fe)$ = +1.24 V at 25 °C

Need a Reference Electrode!!!!

(standard hydrogen electrode, SHE)



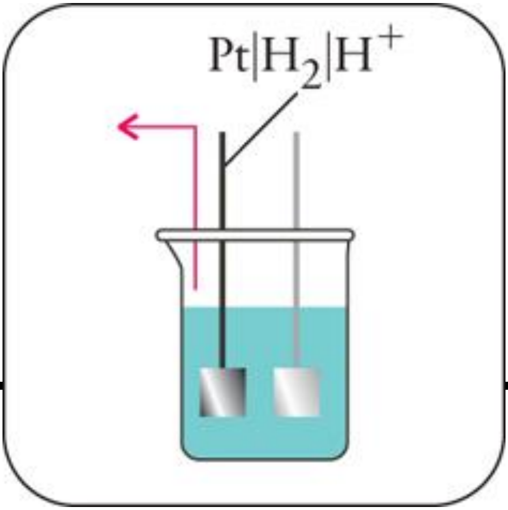
$$2H^+ (aq) + 2e^- (aq) \rightarrow H_2 (g)$$

where $[H^+] = 1$ M

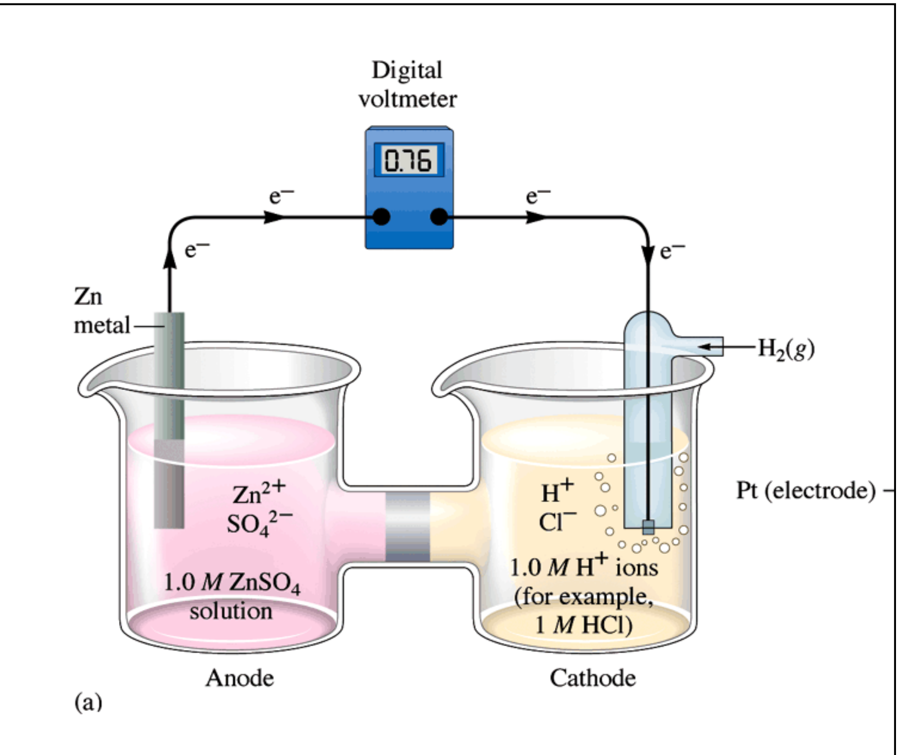
and $p_{H2} = 1$ atm

DEFINE:

E^o (S.H.E.) = 0 volt



Standard Reduction Potentials:



$$E_{cell}{}^{o} = E_R{}^{o} - E_L{}^{o}$$

$$E^\circ_{cell} = E^\circ_{H+\rightarrow H2} - E^\circ_{Zn2+\rightarrow Zn}$$
$$= 0 - E^0_{Zn\ 2+\rightarrow Zn} = 0.76\ V$$

$$\boxed{E^0_{Zn2+\rightarrow Zn} = -0.76\ V}$$

$Zn(s)|Zn^{2+}(aq)\ ||\ H^+(aq)\ |\ H_2\ (g)$

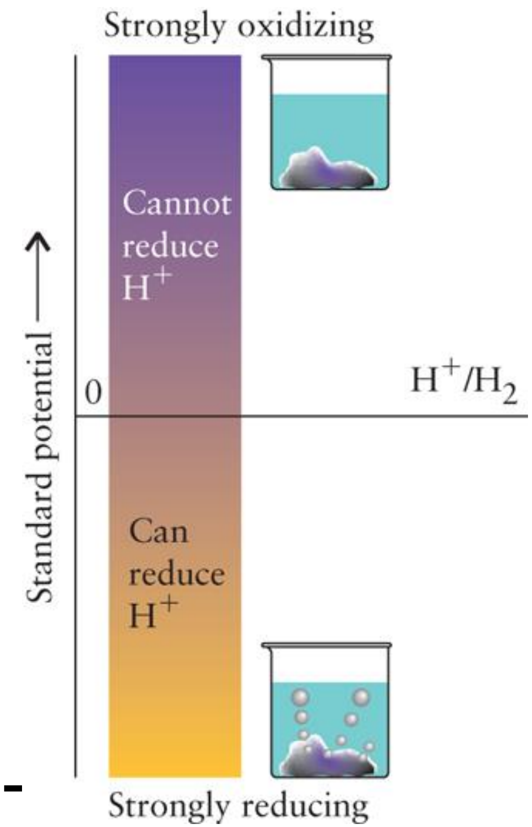
Standard Reduction Potential

Electric Potential of half-cell *reduction reaction*
in standard state:

$X^{n+} + ne^- \rightarrow X$, where $[X^{n+}] = [X] = 1$ M

$$E^{0}_{Zn2+ \rightarrow Zn} = -0.76\ \text{V}$$

* Standard reduction potentials
are measured with SHE.



$E^0(X/X^+) > 0$ :: Favors **reduction** : $X^+ + e^- -$

$E^0(X/X^+) < 0$ :: Favors **oxidation** : $X^+ + e^- \leftarrow X$

$$E^o = \frac{0.0592}{n}\log(K)$$

Standard Reduction Potentials:

Species	Reduction half-reaction	$E°$ (V)
Oxidized form is strongly oxidizing		
F_2/F^-	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.87
Au^+/Au	$Au^+(aq) + e^- \longrightarrow Au(s)$	+1.69
Ce^{4+}/Ce^{3+}	$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-,H^+/Mn^{2+},H_2O$	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
Cl_2/Cl^-	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.36
$Cr_2O_7^{2-},H^+/Cr^{3+},H_2O$	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$O_2,H^+/H_2O$	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.23; +0.82 at pH = 7
Br_2/Br^-	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.09
$NO_3^-,H^+/NO,H_2O$	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$	+0.96
Ag^+/Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Fe^{3+}/Fe^{2+}	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
I_2/I^-	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.54
$O_2,H_2O/OH^-$	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$	+0.40; +0.82 at pH = 7
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.34
$AgCl/Ag,Cl^-$	$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
H^+/H_2	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0, by definition
Fe^{3+}/Fe	$Fe^{3+}(aq) + 3\,e^- \longrightarrow Fe(s)$	−0.04
$O_2,H_2O/HO_2^-,OH^-$	$O_2(g) + H_2O(l) + 2\,e^- \longrightarrow HO_2^-(aq) + OH^-(aq)$	−0.08
Pb^{2+}/Pb	$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.13
Sn^{2+}/Sn	$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.14
Fe^{2+}/Fe	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.44
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.76
$H_2O/H_2,OH^-$	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83; −0.42 at pH = 7
Al^{3+}/Al	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.66
Mg^{2+}/Mg	$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.36
Na^+/Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
K^+/K	$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
Li^+/Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05
Reduced form is strongly reducing		

*For a more extensive table, see Appendix 2B.

For a Gavanic Cell of the type:

$X|X+||Y+|Y$,

If $E^0(Y/Y^+) > E^0(X/X^+)$,

Y^+ will be reduced

$X + Y^+ \rightarrow X^+ + Y$

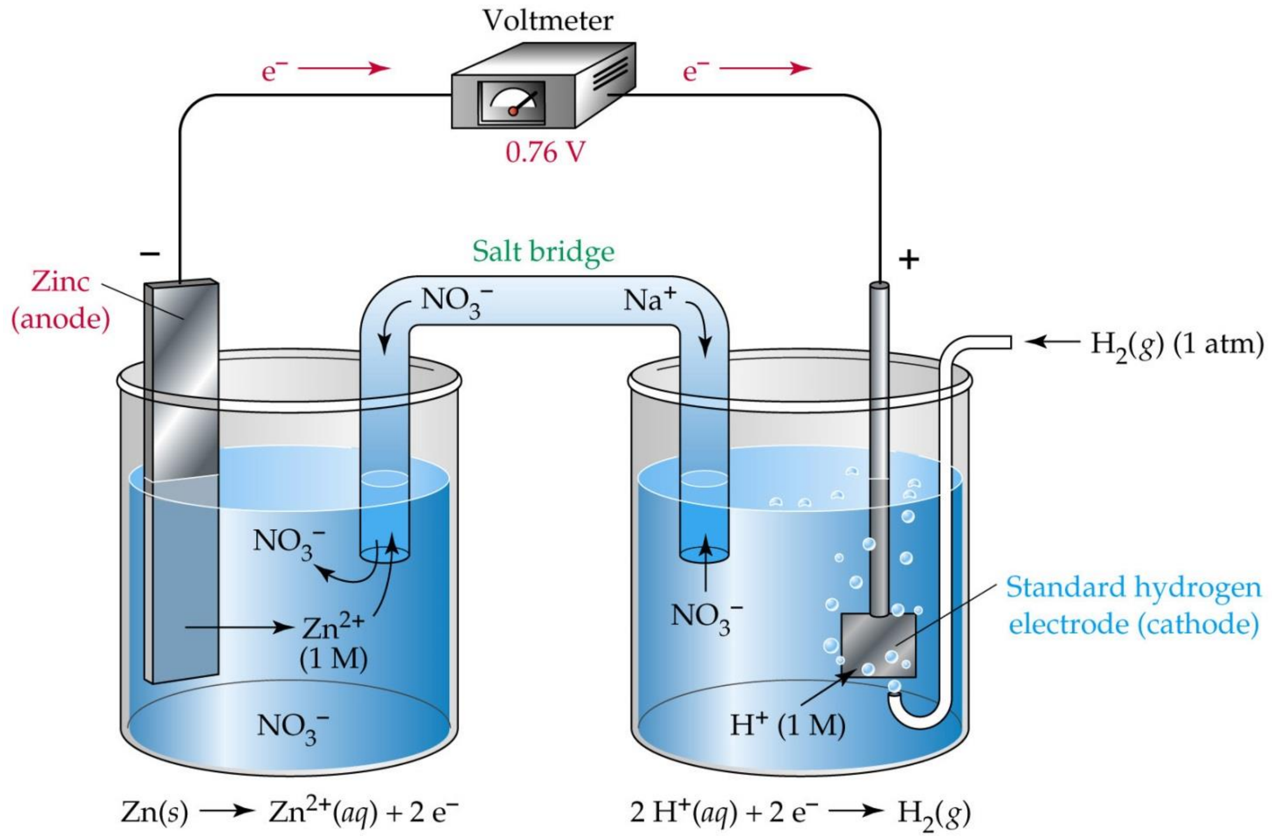
If $E^0(Y/Y^+) < E^0(X/X^+)$,

X^+ will be reduced

$Y + X^+ \rightarrow Y^+ + X$

Cell voltage

$= E^0(Y/Y^+) - E^0(X/X^+)$



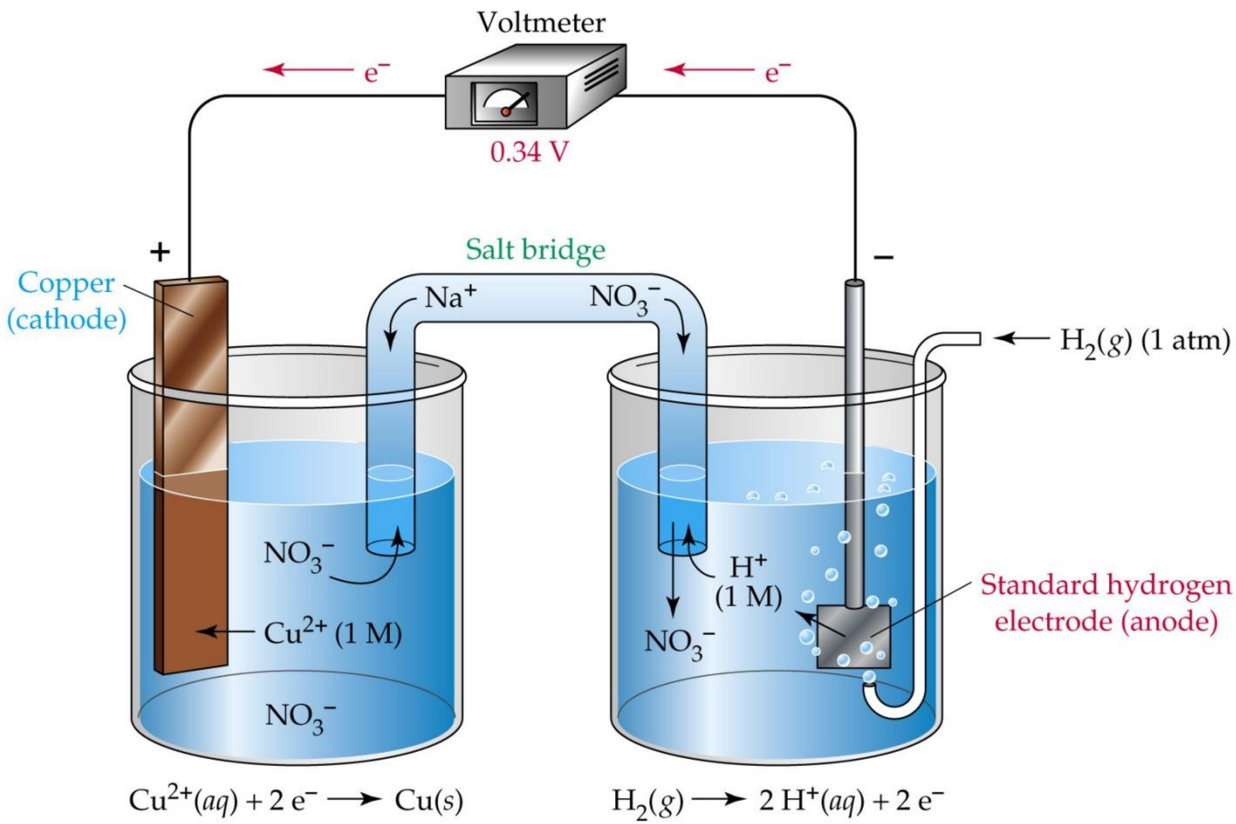
$$E^o = \frac{0.0592}{n}\log(K)$$

$Pt(s)\,|\,H_2(g)\,|\,H^+(aq)\,\|\,Zn^{2+}(aq)\,|\,Zn(s)$

$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s) \qquad E°(Zn^{2+}/Zn) = -0.76\ V$

the reverse of the cell reaction,

$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) \qquad$ **K > 1**



$$Pt(s)\,|\,H_2(g)\,|\,H^+(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$$

$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \qquad E°(Cu^{2+}/Cu) = +0.34\ V$$

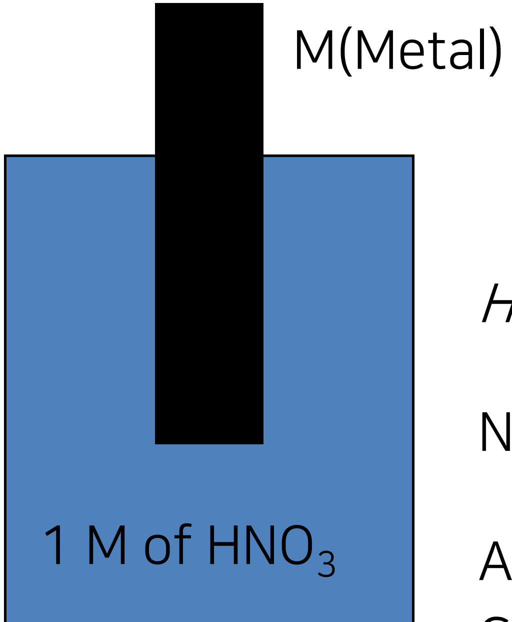
$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2\,H^+(aq)$$

K > 1

TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

Dissolution (or corrosion) of metals in acid solution



Cr versus Au: which one will be corroded?

HNO_3 is an oxidizing agent:

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$, $E^0(NO_3^-) = 0.96$ V

$Au^{3+} + 3e^- \rightarrow Au$, $E^0\,(Au^{3+}) = 1.5$ V

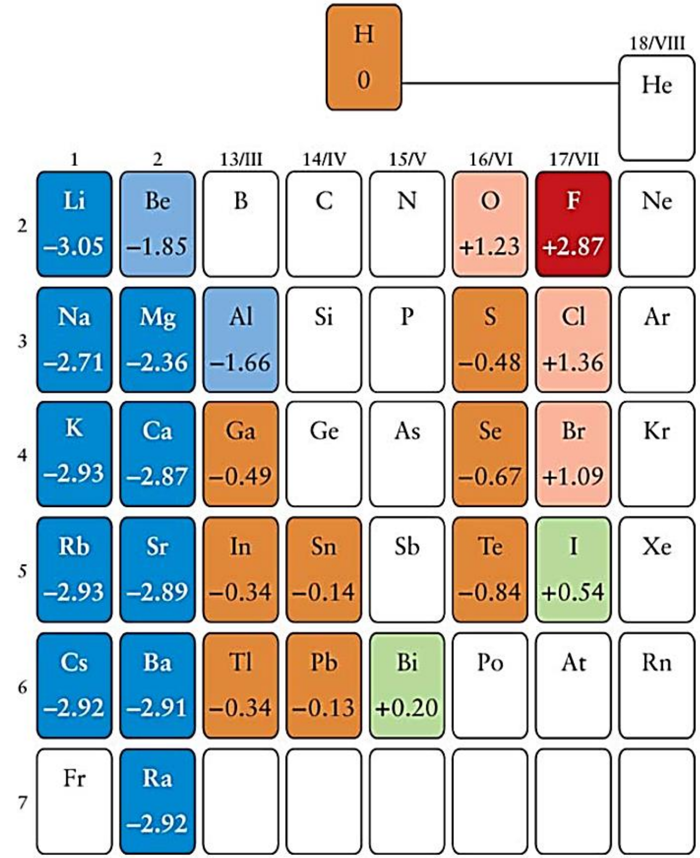
$Cr^{3+} + 3e^- \rightarrow Cr$, $E^0\,(Cr^{3+}) = -0.73$ V

$E^0(Au^{3+}) > E^0(NO^{3-})$:
Therefore, Au^{3+} wants to be reduced. Au is not oxidized by HNO_3.

$E^0(Cr^{3+}) < E^0(NO^{3-})$:
Therefore, Cr wants to be oxidized.

Example The standard potential of the following standard cell potential is 0.91V when Zn^{2+}/Zn standard potential is -0.76 V. What is the standard potential for Sn^{4+}/Sn^{2+}?

$Zn(s)|Zn^{2+}(aq)||Sn^{4+}(aq), Sn^{2+}(aq)|Pt(s)$



$0.91 = x - (-0.76) = x + 0.76$

Therefore, $x = 0.15$ V

Example The standard potential of $Ce^{4+}(aq) + 4e^- \rightarrow Ce(s)$?

$$Ce^{3+}(aq) + 3\,e^- \longrightarrow Ce(s) \qquad E° = -2.48\ V$$

$$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq) \qquad E° = +1.61\ V$$

Stoichiometry of electrochemical reaction:
Obtain the potential for the following redox reaction:

$$3Ag(s) + Cr^{3+}(aq) \rightarrow 3Ag^{+}(aq) + Cr(s)$$

Reduction half-reactions:

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $E^0 = 0.80$ volts
$Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$ $E^0 = -0.73$ volts

$3Ag(s) \rightarrow 3Ag^{+}(aq) + 3e^{-}$ $-3E^0 = -3\times0.80$ volts
$Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$ $E^0 = -0.73$ volts

$E^0 = -0.73-3 \times 0.80$
$= -3.13$ volt

$3Ag(s) \rightarrow 3Ag^{+}(aq) + 3e^{-}$ $-E^0 = -0.80$ volts
$Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$ $E^0 = -0.73$ volts

$E^0 = -0.73- 0.80$
$= -1.53$ volt

Ex)

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

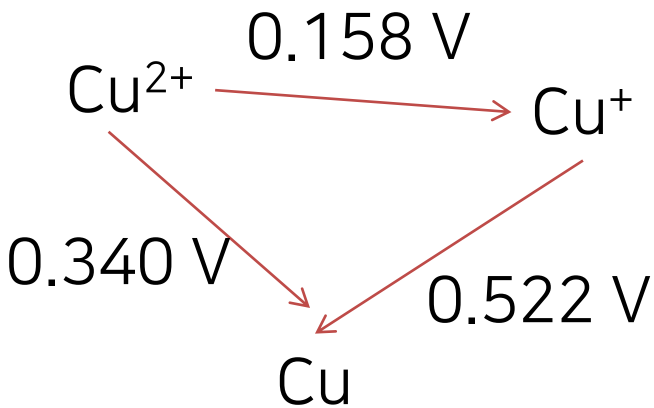
Is this reaction spontaneous at standard state?

What is the ΔG^0 of this reaction?

$Cu^{2+} + 2e^- \rightarrow Cu(s)$ $E_1^0 = 0.340\ V$

$Cu^+ + e^- \rightarrow Cu(s)$ $E_2^0 = 0.522\ V$

$Cu^{2+} + e^- \rightarrow Cu^+$ $E^0 = E_1^0 - E_2^0?$



Disproportionation rxn:
a process in which a single substance is both reduced and oxidized

$$Cu^{+} + Cu^{+} \rightarrow Cu(s) + Cu^{2+}$$

Is it a spontaneous reaction?

Standard Potentials and K

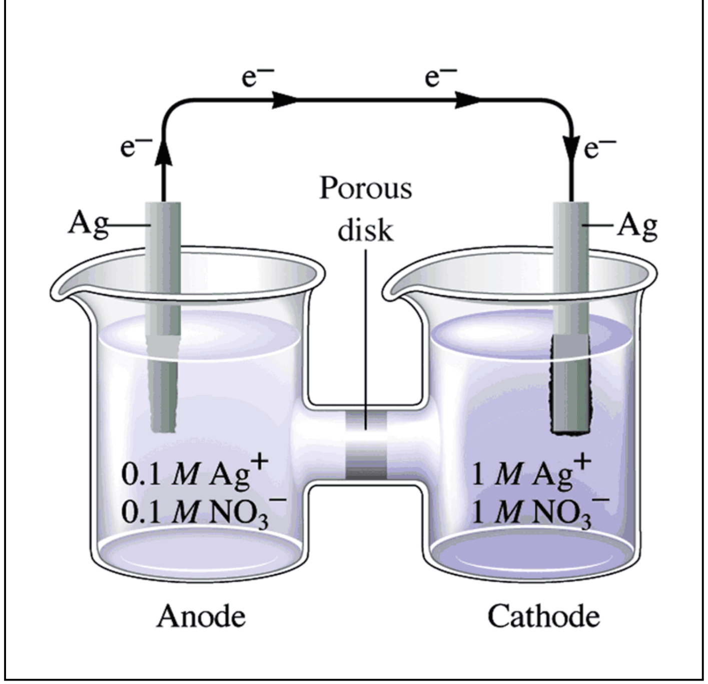
- Equilibrium constant
- $\Delta G = -nFE\ (Chapter\ 13)$
- $\Delta G\ \ = -RT\ \ ln\, K$ *(Chapter 10)*

$$\frac{-\Delta G^{o}}{RT} = \ln K = \frac{nFE^{o}}{RT}$$

Example: Calculate the equilibrium constant of $AgCl\ (s)\ \leftrightarrow\ Ag^{+}\ (aq) +$ $Cl^{-}\ (aq)$ at 298 K.

Concentration Cell

: a cell in which both compartments have the same components but at different concentrations.



Reduction Potentials of Half-Cells

$Ag^+ + e^- \rightarrow Ag(s)$

$E(Right) = E^0\ (Ag/Ag^+) - 0.0592/1 \times \log(1) = E^0\ (Ag/Ag^+)$

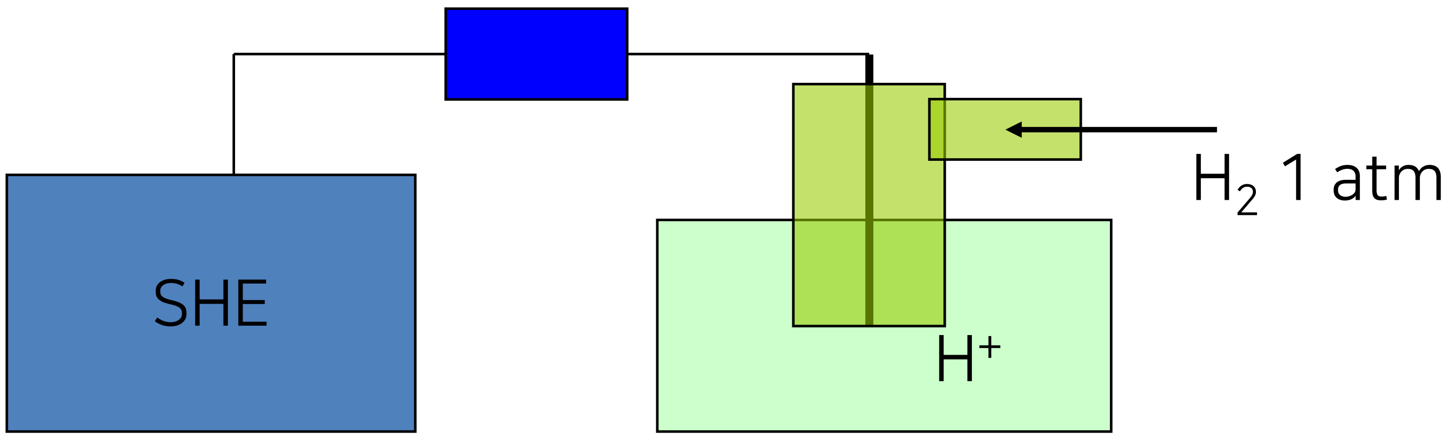
$E(Left) = E0\ (Ag/Ag+) - 0.0592/1 \times \log(1/0.1)$

Potential Difference = Right - Left

$= 0.0592/1 \times \log(1/0.1) = 0.0592$ volt >

Reduction occurs at concentrated region!

An example of conc. cell: pH meter



$2H^+ + 2e^- \rightarrow H_2$

$Q = 1\ (\mathrm{atm}) / [H^+]^2$

$$E(left) = E^0(2H^+/H_2) = 0\ \mathrm{volt}$$

$$E(right) = E^0(2H^+/H_2) - \frac{0.0529}{2}\log\left(\frac{1}{[\mathrm{H}^+]^2}\right)$$

$$= 0.0529\log\left([\mathrm{H}^+]\right) = -0.0592\,pH$$

Electrolytic Cells

13.11. Electrolysis

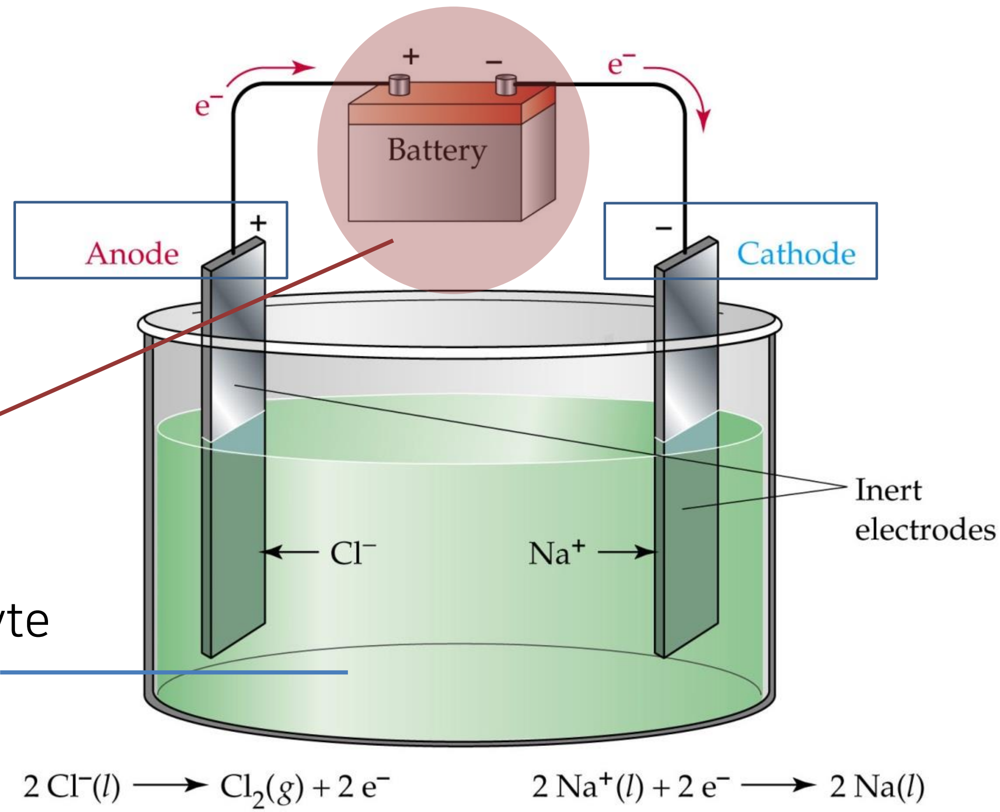
- Electrolysis (전기분해)

  : process of driving a reaction in a nonspontaneous direction by using an electric current

- Electrolytic cell (전해전지)

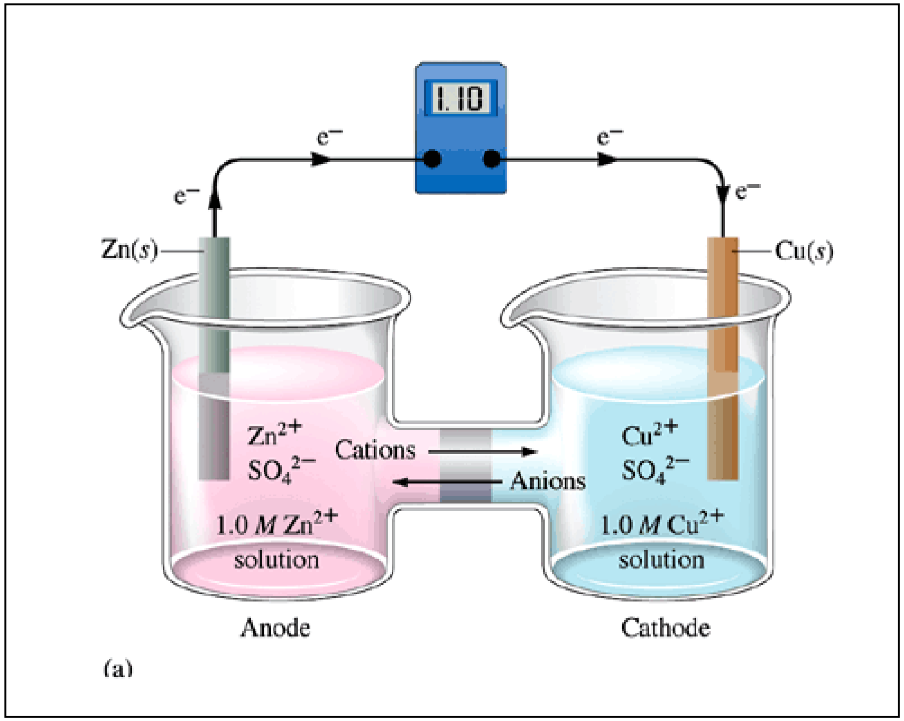
External voltage

Common electrolyte
(molten NaCl)



Electrolysis

:forcing a current through a cell to produce a chemical change for which the cell potential is negative.



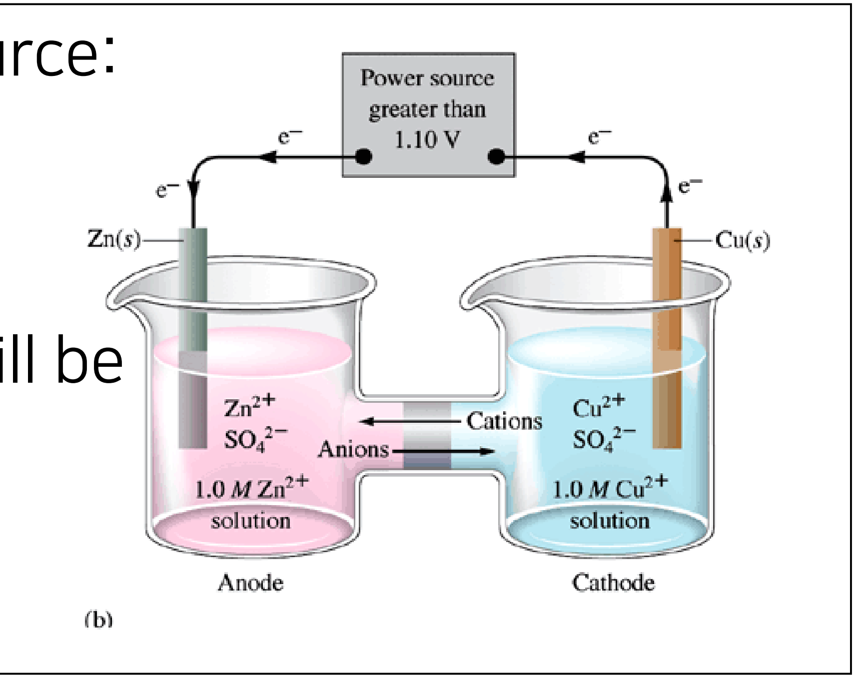
Spontaneous rxn:

Electron flows from anode to cathode because of the potential difference between the cells.

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

Disappearance of Zn $\quad$ Deposition of Cu

Now, apply external voltage source: (E_{ext})

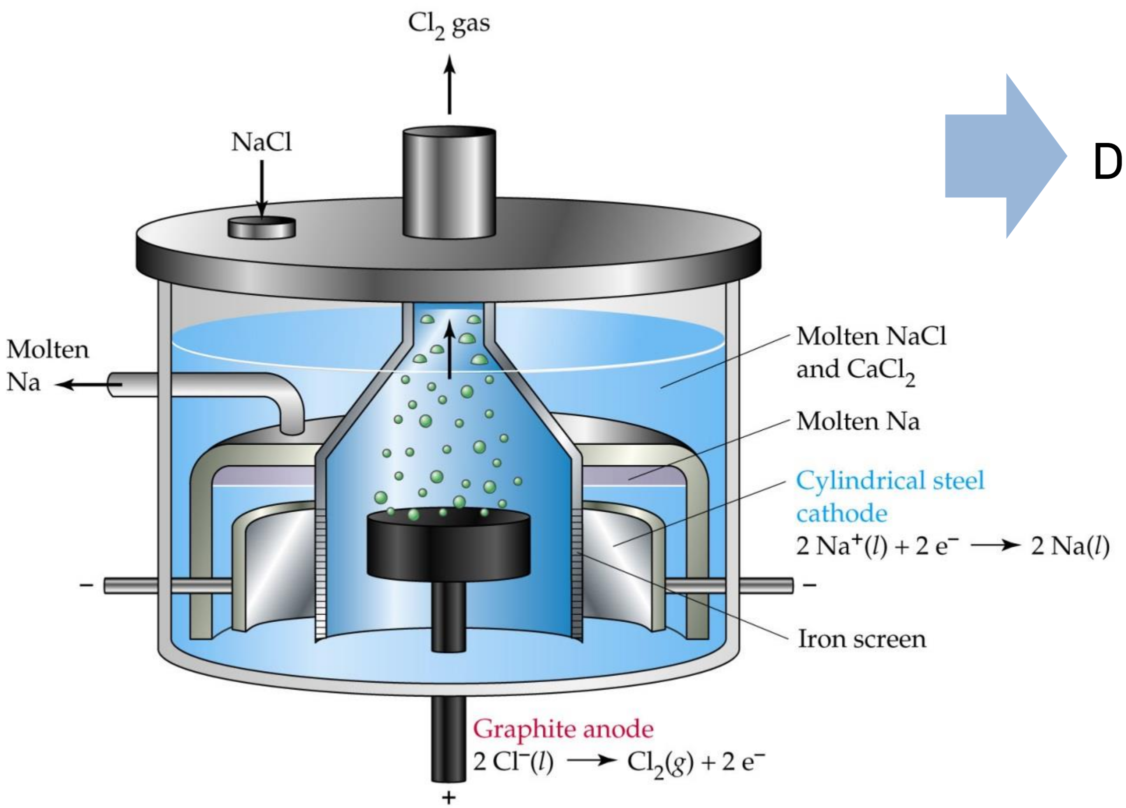


1. If $|E_{ext}| < 1.10$ volt; spontaneous electron flow will be *slowed down*

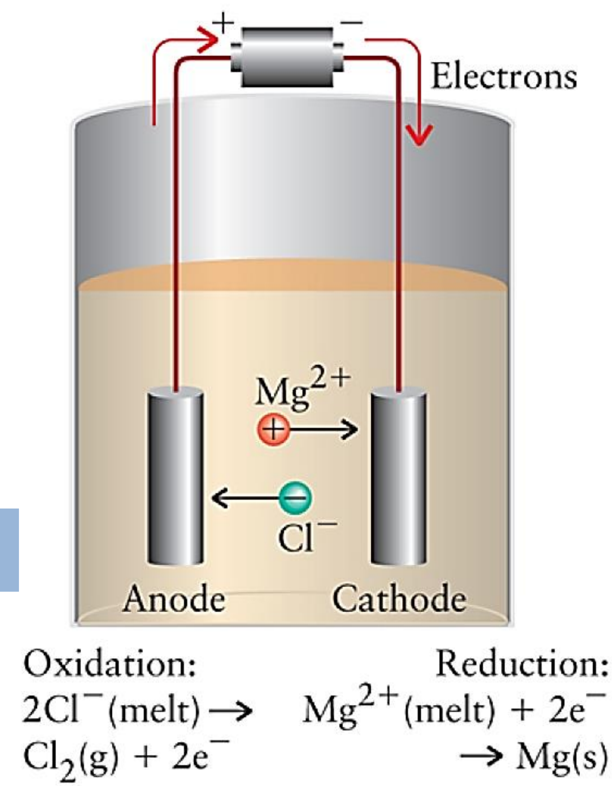
2. If $|E_{ext}| = 1.10$ volt: *electron flow stops*

3. If $|E_{ext}| > 1.10$ volt; *electrons flow in reverse direction*

We can reverse the direction of the redox reaction!!!



Downs cell for Na production



i.e.) **Dow process**: commercial production of Mg from molten $MgCl_2$

Anode reaction: $2Cl^-(\text{melt}) \rightarrow Cl_2(g) + 2e^-$

Cathode reaction: $Mg^{2+}(\text{melt}) + 2e^- \rightarrow Mg(l)$

- Overpotential (additional voltage)

: For electrolysis to occur, an external potential at least as great as that of the spontaneous cell reaction must be applied to an electrolytic cell.

$$2\,H_2\,(g) + \;O_2\,(g)\;\rightarrow 2\,H_2O\,(l) \qquad E_{cell}{}^{o} = 1.23\,V$$

$$2\,H_2O\,(l) \rightarrow\; 2\,H_2\,(g) + \;O_2\,(g) \qquad E_{cell}{}^{o} = -1.23\,V$$

- In practice, the high overpotential may produce byproducts.

$$O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \;\rightarrow\; 2H_2O\,(l) \qquad E = \;+0.82\,V\;at\;pH = 7$$

$$Cl_2\,(g) + 2\,e^- \;\rightarrow 2\,Cl^-\,(aq) \qquad E^o = \;+1.36\,V$$

The Products of Electrolysis

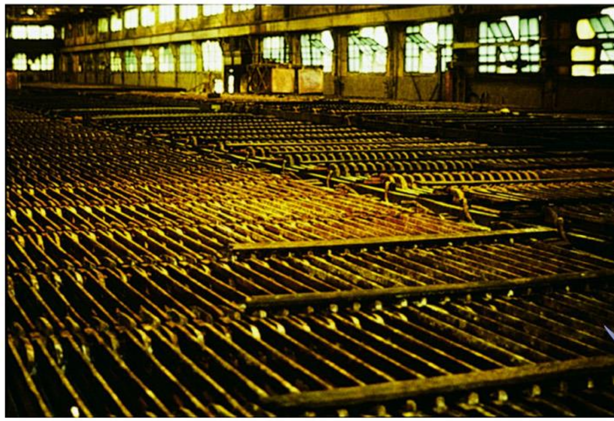
- Faraday's law of electrolysis

  : The number of moles of product formed is stoichiometrically equivalent to the number of moles of electrons supplied.

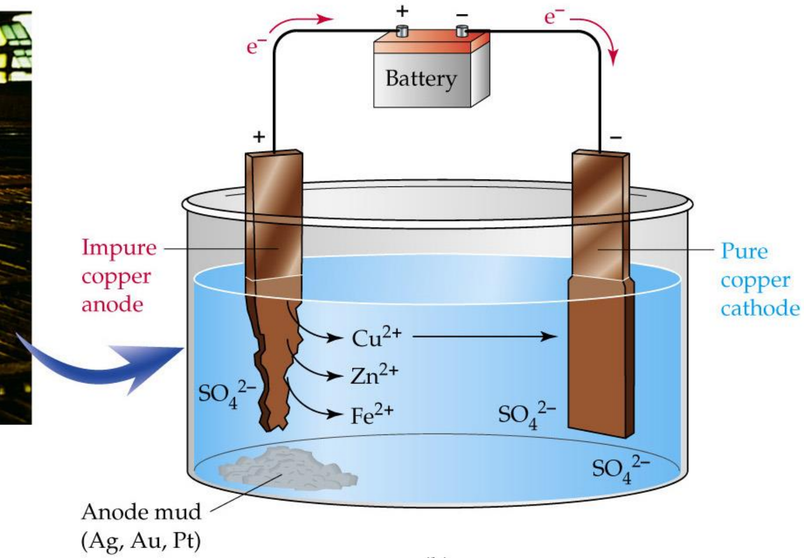
Example Calculate the mass of **Al** produced from the electrolysis of Na_3AlF_6 operating at 1.00 * 10^5 A in one day.

The Impact on Materials

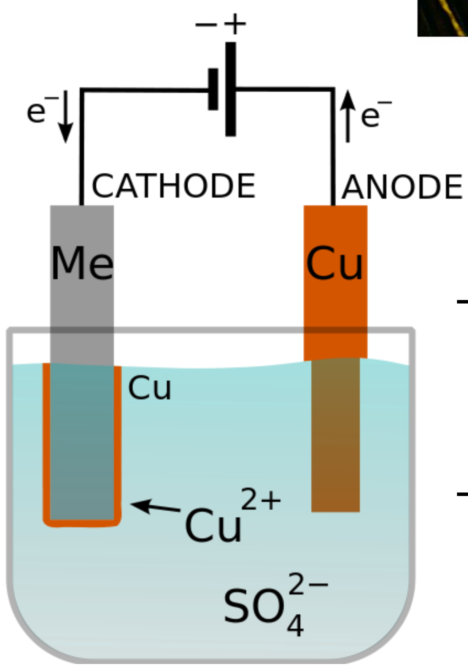
13.13. Applications of Electrolysis



(a)



(b)



- Production or purification of metal with electrolysis.

- Electroplating (전기 도금)

13.14. Corrosion

- **Corrosion**: unwanted oxidation of metal

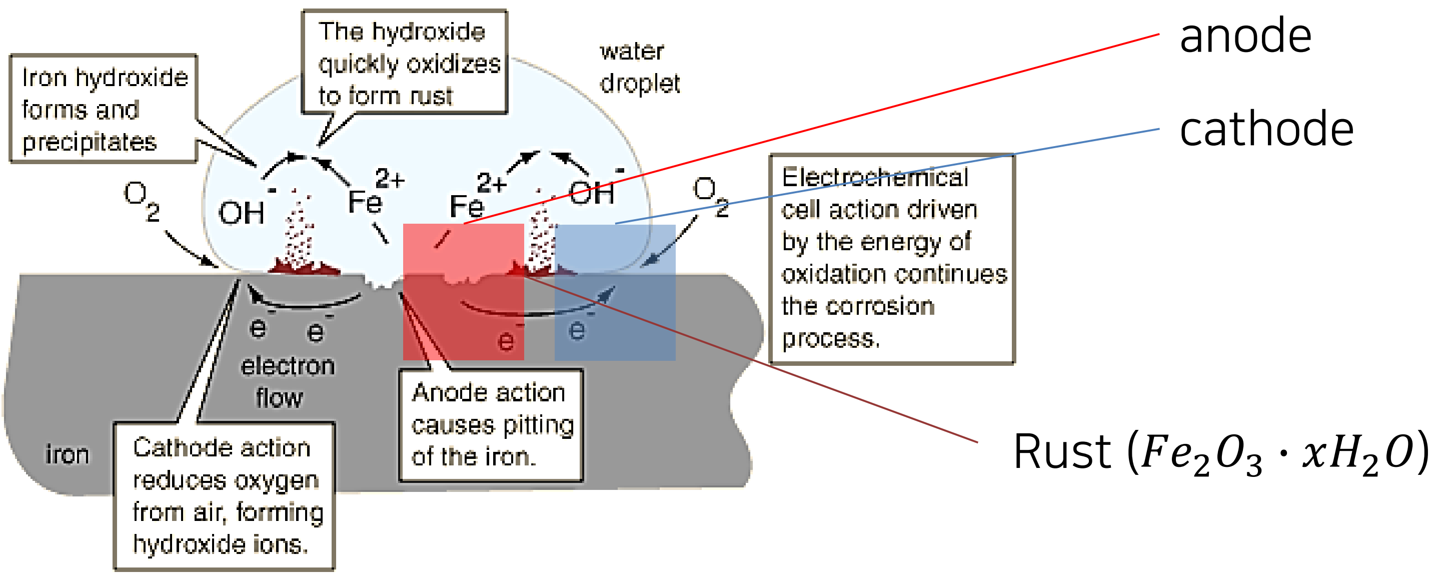
$$2\,H_2O\,(l) + 2\,e^- \rightarrow H_2\,(g) + 2\,OH^-\,(aq) \quad E = -0.42\,V\ at\ pH = 7$$

$$Fe^{2+}\,(aq) + 2\,e^- \rightarrow Fe\,(s) \qquad E^o = -0.44\,V$$

→ Fe slightly reduces water in an oxygen-free condition.

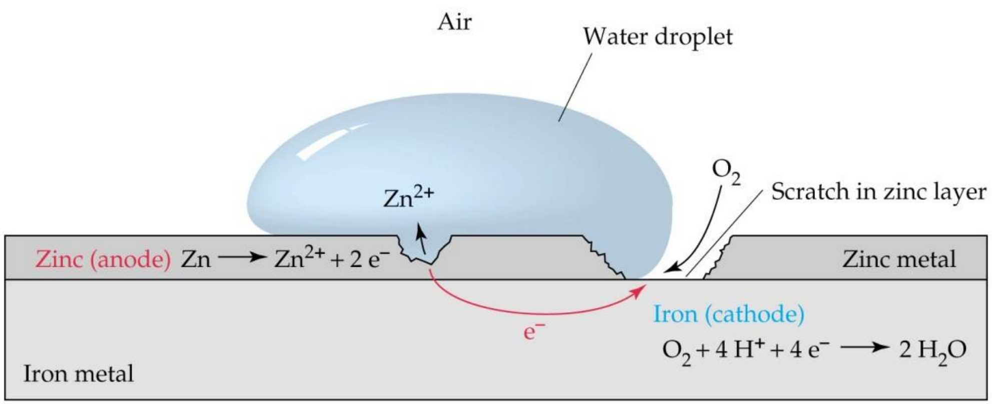
$$O_2\,(g) + 2\,H_2O\,(l) + 4\,e^- \rightarrow 4\,OH^-\,(aq) \quad E = +0.82\,V\ at\ pH = 7$$

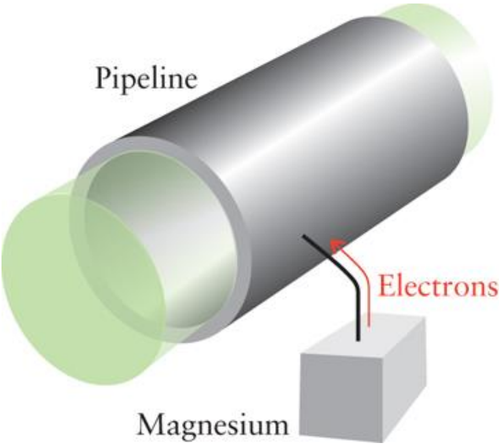
→ Water containing oxygen oxidize Fe.

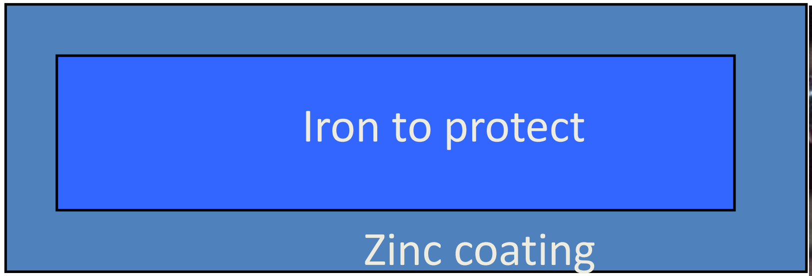


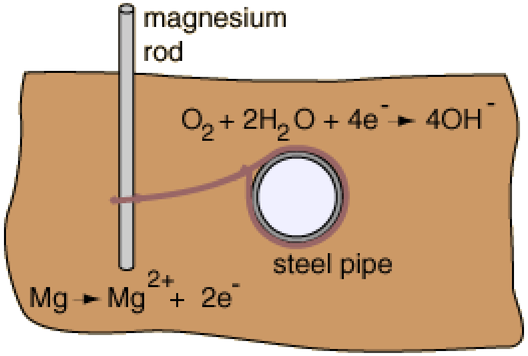
- Corrosion prevention

1. Coating the metal with paint
2. Galvanization (coating the iron with the layer of zinc)
3. Passivation (protective oxide)
4. Cathodic protection (sacrificial anode)



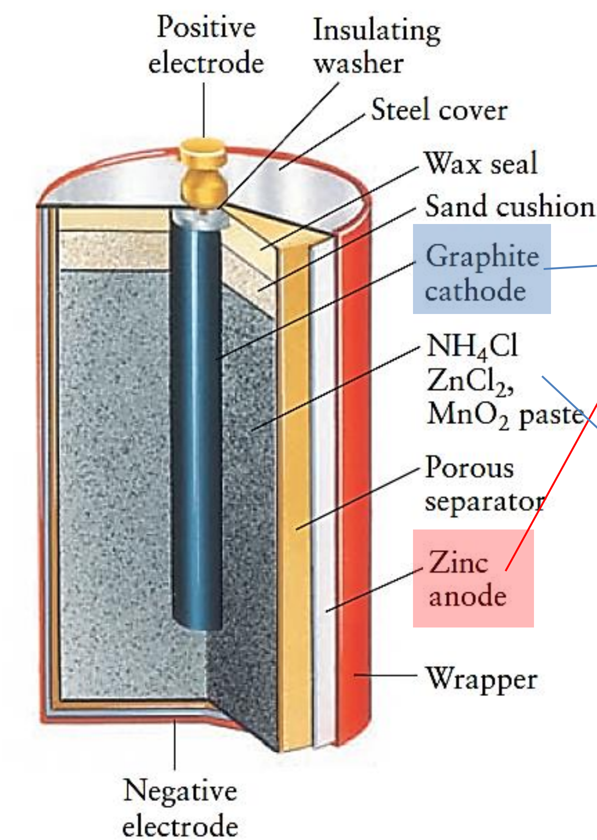






13.15. Practice Cells

- Conventional battery



$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \quad \text{(anode)}$$

$$2\,NH_4^+(aq) + 2\,e^- \longrightarrow H_2(g) + 2\,NH_3(aq)$$

$$H_2(g) + 2\,MnO_2(s) \longrightarrow Mn_2O_3(s) + H_2O(\ell)$$

(cathode)

Electrolyte

(overall)

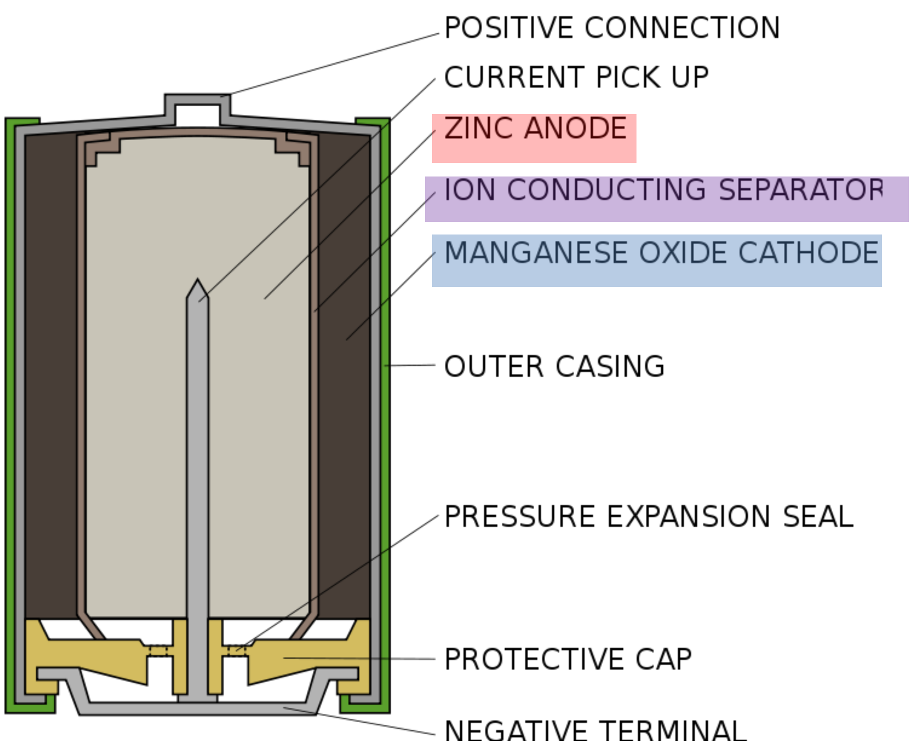
$$Zn(s) + 2\,MnO_2(s) + 2\,NH_4^+(aq) \longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(\ell)$$

- Alkaline battery

$$Zn\,(s) + 2\,OH^-\,(aq) \rightarrow ZnO\,(s) + H_2O\,(l) + 2\,e^- \qquad (anode)$$

$$2\,MnO_2\,(s) + H_2O\,(l) + 2\,e^- \rightarrow Mn_2O_3\,(s) + 2\,OH^- \qquad (cathode)$$

$$Zn\,(s) + 2\,MnO_2\,(s) \rightarrow ZnO\,(s) + Mn_2O_3\,(s) \qquad (overall)$$



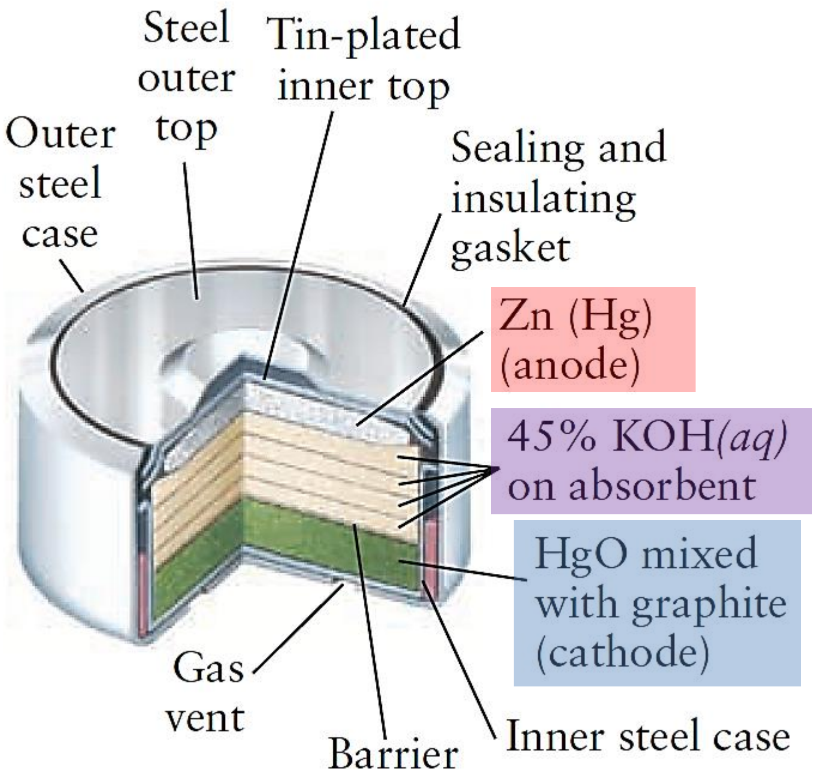
alkali electrolyte

- Zn-Hg alkaline cell

$$Zn\,(s) + 2\,OH^-\,(aq) \rightarrow ZnO\,(s) + H_2O\,(l) + 2\,e^- \quad (anode)$$

$$HgO\,(s) + H_2O\,(l) + 2\,e^- \rightarrow Hg\,(l) + 2\,OH^- \quad (cathode)$$

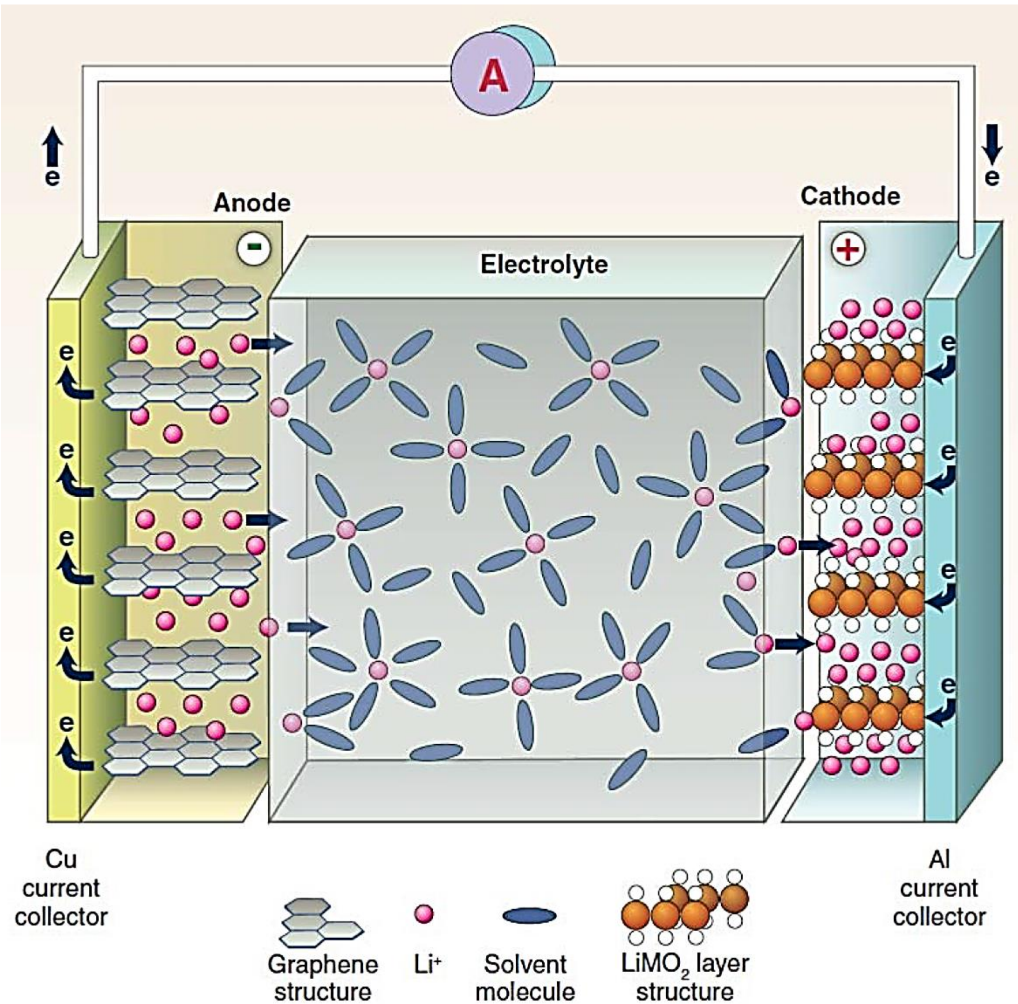
$$Zn\,(s) + HgO\,(s) \rightarrow ZnO\,(s) + Hg\,(l) \quad (overall)$$



- Lithium battery

$$Li_nC \rightarrow n\,Li^+ + n\,e^- + C \qquad (anode)$$

$$Li_{1-n}CoO_2 + n\,Li^+ + n\,e^- \rightarrow LiCoO_2 \qquad (cathode)$$

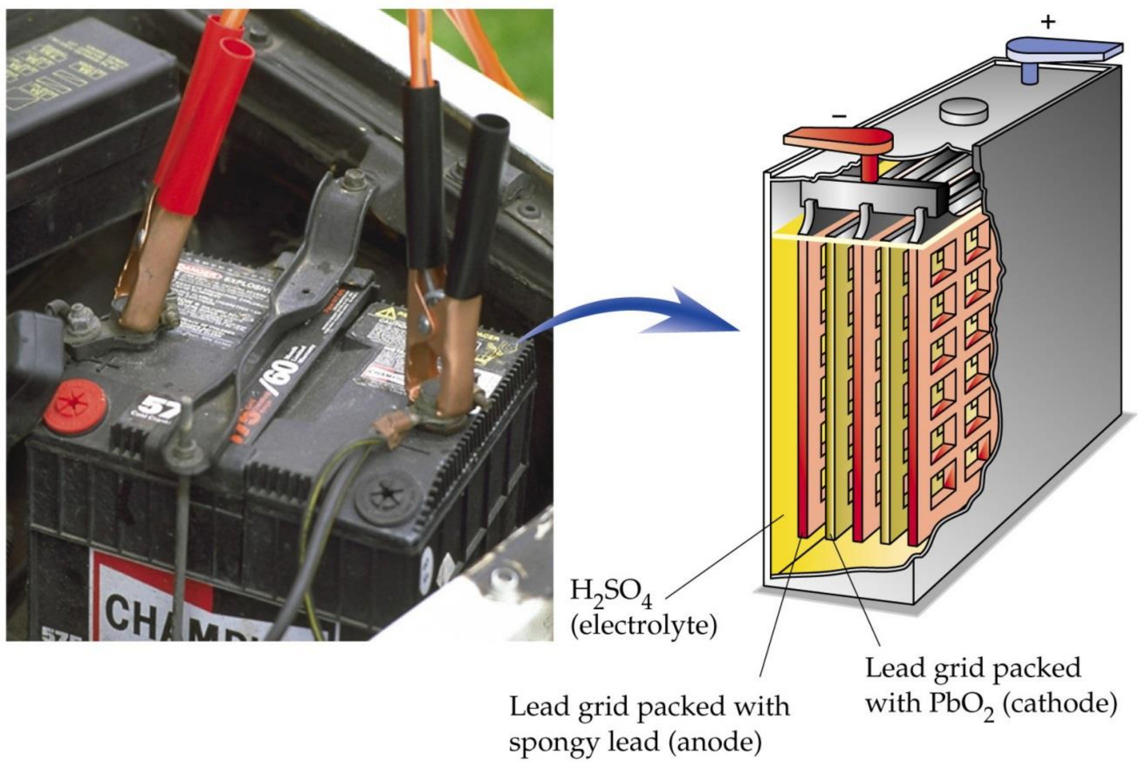


- Lead-acid battery

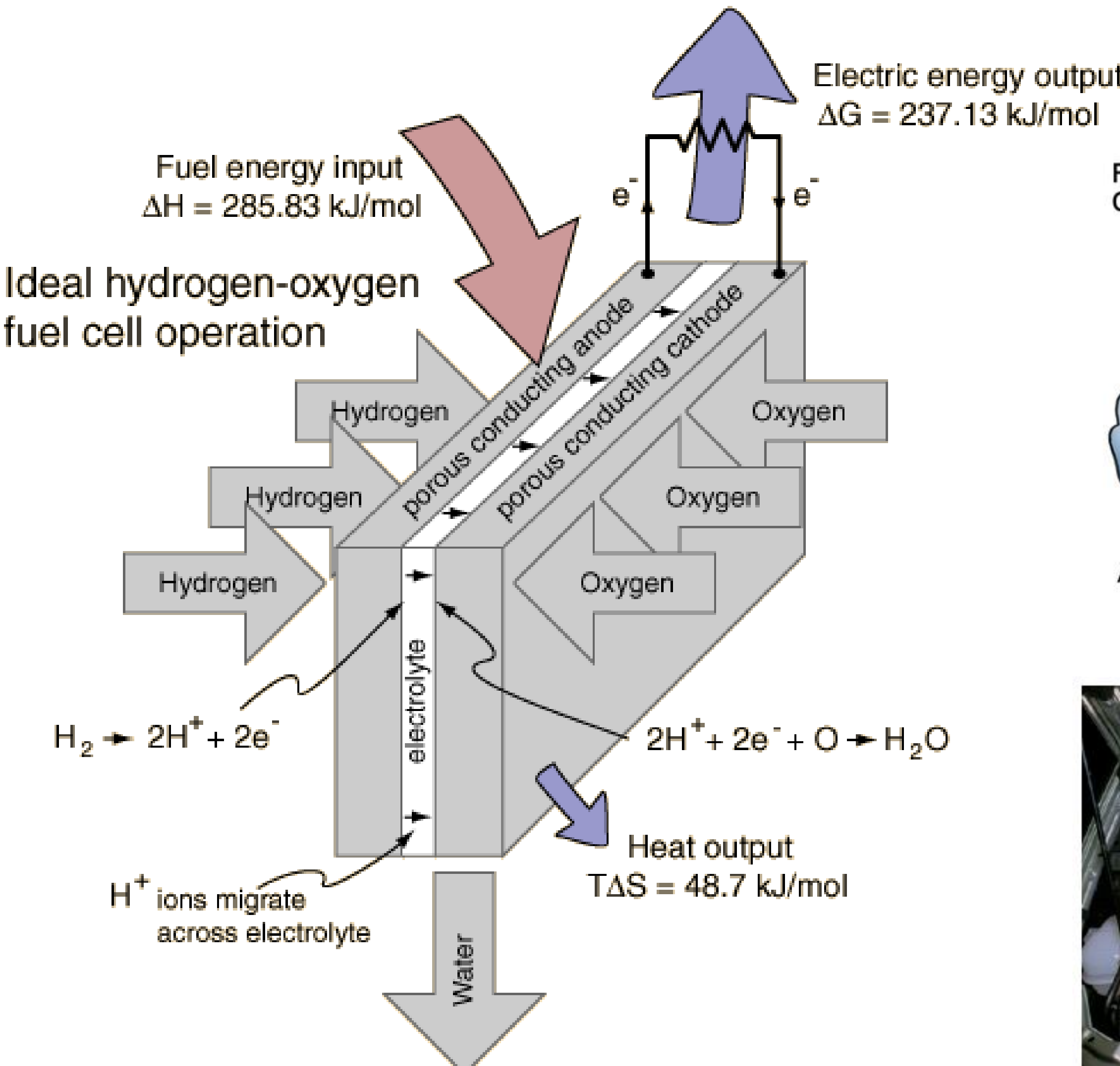
$$\mathrm{Pb}(s) + \mathrm{SO_4^{2-}} \longrightarrow \mathrm{PbSO_4}(s) + 2\,e^- \qquad \text{(anode)}$$

$$\mathrm{PbO_2}(s) + \mathrm{SO_4^{2-}} + 4\,\mathrm{H_3O^+} + 2\,e^- \longrightarrow \mathrm{PbSO_4}(s) + 6\,\mathrm{H_2O}(\ell) \qquad \text{(cathode)}$$

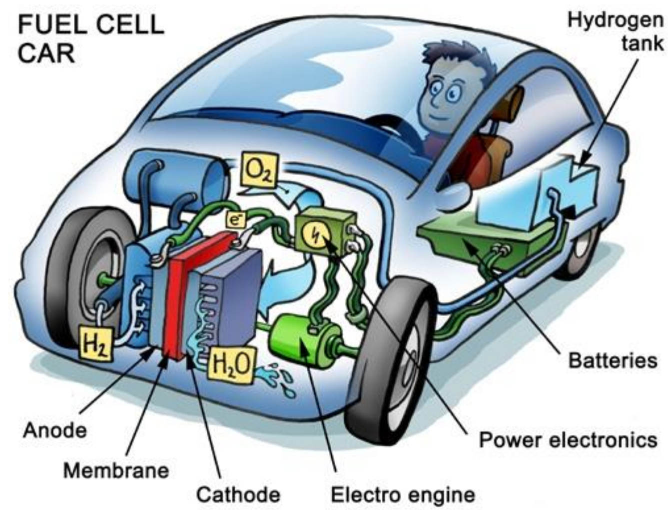
$$\mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\,\mathrm{SO_4^{2-}} + 4\,\mathrm{H_3O^+} \longrightarrow 2\,\mathrm{PbSO_4}(s) + 6\,\mathrm{H_2O}(\ell)$$



- Fuel cell



Electric energy output
ΔG = 237.13 kJ/mol
Fuel energy input
ΔH = 285.83 kJ/mol
e-
e-
Ideal hydrogen-oxygen
fuel cell operation
porous conducting anode
porous conducting cathode
Hydrogen
Hydrogen
Hydrogen
Oxygen
Oxygen
Oxygen
electrolyte
H2 → 2H+ + 2e-
2H+ + 2e- + O → H2O
Heat output
TΔS = 48.7 kJ/mol
H+ ions migrate
across electrolyte
Water



FUEL CELL
CAR
Hydrogen
tank
O2
e-
H2
H2O
Batteries
Anode
Membrane
Cathode
Electro engine
Power electronics

FUEL CELL