ELECTROCHEMISTRY

By

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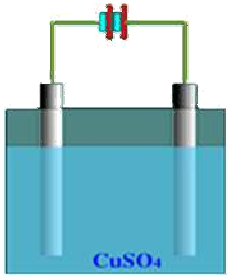
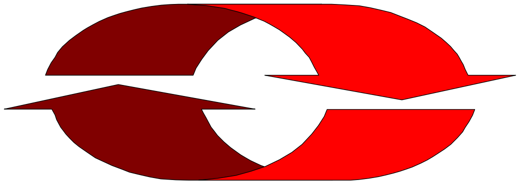
Electrochemistry



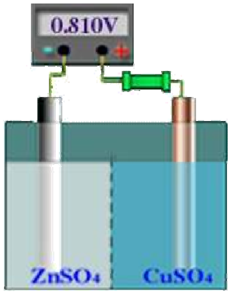
Electrolysis



Electric energy

Chemical energy

Galvanic cell



Electrochemistry

The study of the interchange of chemical and electrical energy.

Chemical Energy ↔ Electrical energy

I: A science studying the relationship between chemical energy and electrical energy and the rules of conversion of two energies.

II: Electrochemistry is the study of solutions of electrolytes and of phenomena occurring at electrodes immersed in these solutions.

Electron Transfer Reactions

➔Electron transfer reactions are oxidation-reduction or Redox reactions.

➔Results in the generation of an electric current (electricity) or be caused by imposing an electric current.

➔Therefore, this field of chemistry is often called ELECTROCHEMISTRY.

Electrochemical processes are oxidation-reduction reactions in which:

- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur

$$2\overset{0}{\mathrm{Mg}}\,(s) + \overset{0}{\mathrm{O}}_2\,(g) \longrightarrow 2\overset{2+}{\mathrm{Mg}}\overset{2-}{\mathrm{O}}\,(s)$$

$2\mathrm{Mg} \longrightarrow 2\mathrm{Mg}^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$\mathrm{O}_2 + 4e^- \longrightarrow 2\mathrm{O}^{2-}$ ***Reduction*** half-reaction (gain e^-)

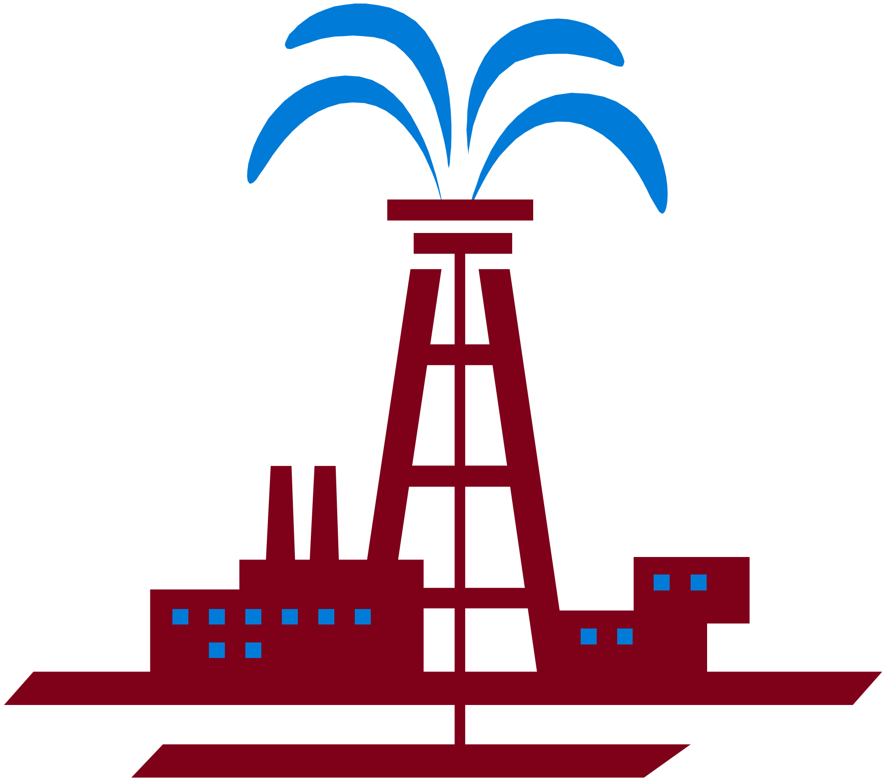
Terminology for Redox Reactions

- ➔OXIDATION—loss of electron(s) by a species; increase in oxidation number; increase in oxygen.
- ➔REDUCTION—gain of electron(s); decrease in oxidation number; decrease in oxygen; increase in hydrogen.
- ➔OXIDIZING AGENT—electron acceptor; species is reduced. (an agent facilitates something; ex. Travel agents don’t travel, they facilitate travel)
- ➔REDUCING AGENT—electron donor; species is oxidized.

Another way to remember

→**OILRIG**

Oxidation
Is
Lose
Reduction
Is
Gain



Review of Oxidation numbers

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.

$$Na, Be, K, Pb, H_2, O_2, P_4 = 0$$

2. In monatomic ions, the oxidation number is equal to the charge on the ion.

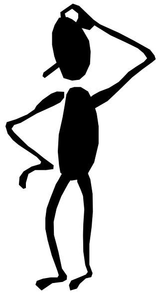
$$Li^+, Li = +1; Fe^{3+}, Fe = +3; O^{2-}, O = -2$$

3. The oxidation number of oxygen *is* **usually** –2. In H_2O_2 and O_2^{2-} it is –1

4. The oxidation number of hydrogen is +1 *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is –1.

5. Group IA metals are +1, IIA metals are +2 and fluorine is always –1.

6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.



Oxidation numbers of all the atoms in HCO_3^- ?

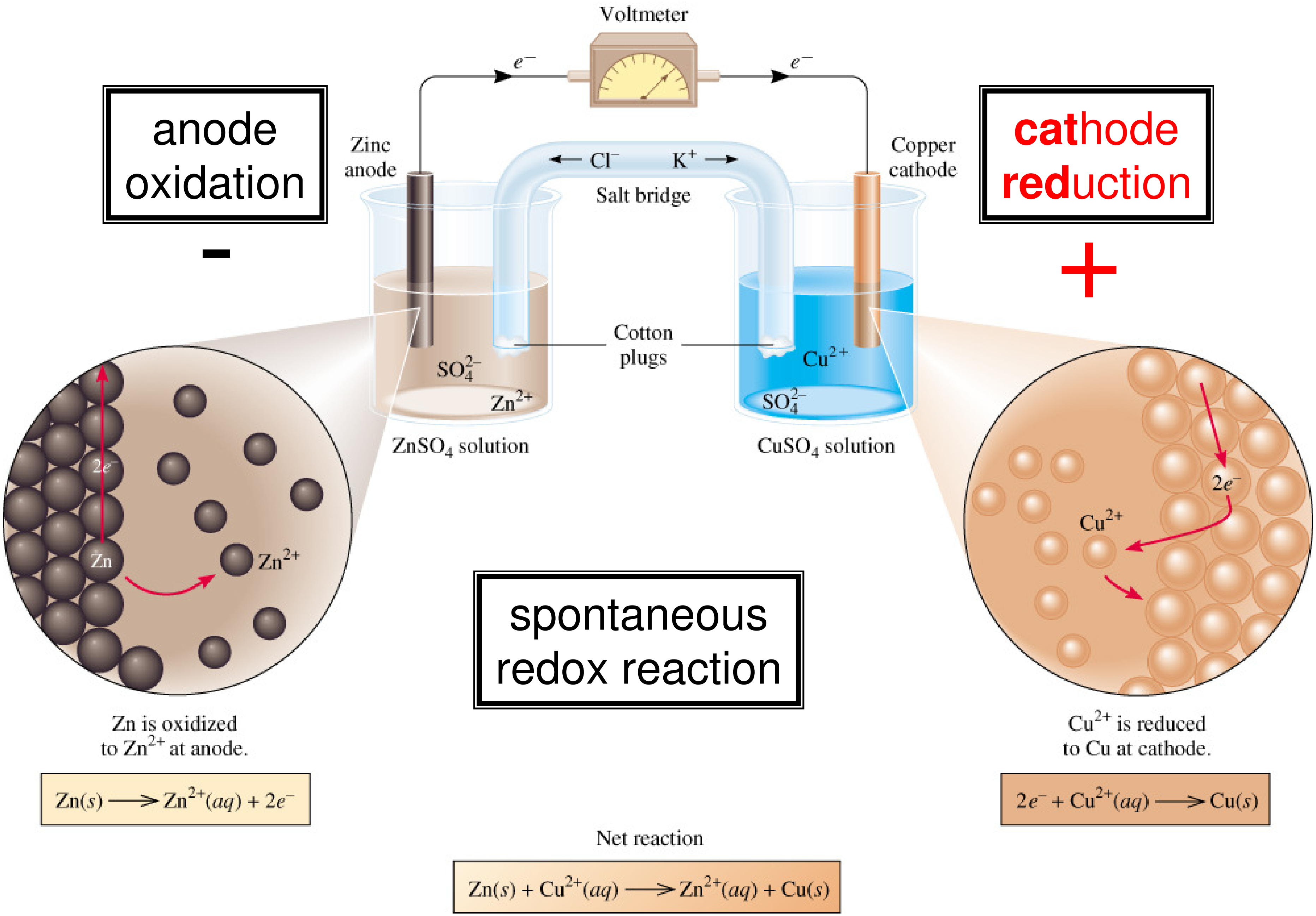
HCO_3^-

O = -2 H = +1

3x(-2) + 1 + ? = -1

C = +4

Galvanic Cells



anode
oxidation

−

cathode
reduction

+

spontaneous
redox reaction

Zn is oxidized to Zn^{2+} at anode.

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cu^{2+} is reduced to Cu at cathode.

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

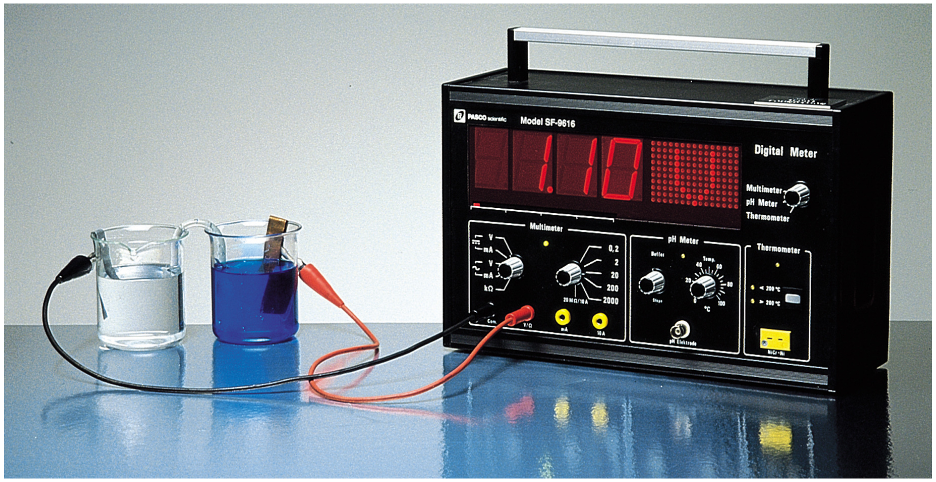
Net reaction

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

Galvanic Cells

The difference in electrical potential between the anode and cathode is called:

- *cell voltage*
- *electromotive force (emf)*
- *cell potential*



Cell Diagram

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

$$Zn\,(s)\,|\,Zn^{2+}\,(1\,M)\,||\,Cu^{2+}\,(1\,M)\,|\,Cu\,(s)$$

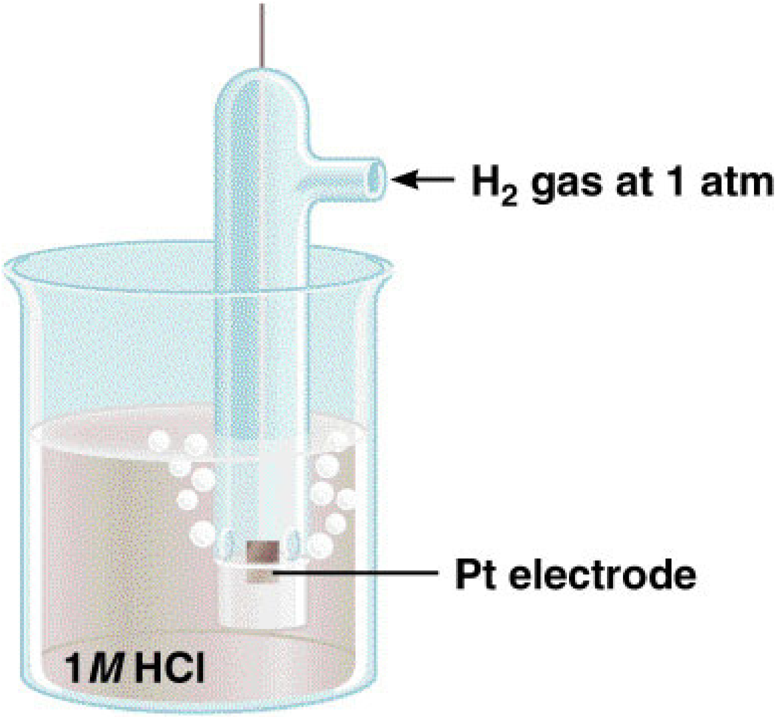
$[Cu^{2+}] = 1\ M$ & $[Zn^{2+}] = 1\ M$

anode cathode

$$\boxed{E^0_{cell} = E^0_{cathode} + E^0_{anode}}$$

Standard Electrode Potentials

Standard reduction potential (E^0) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.

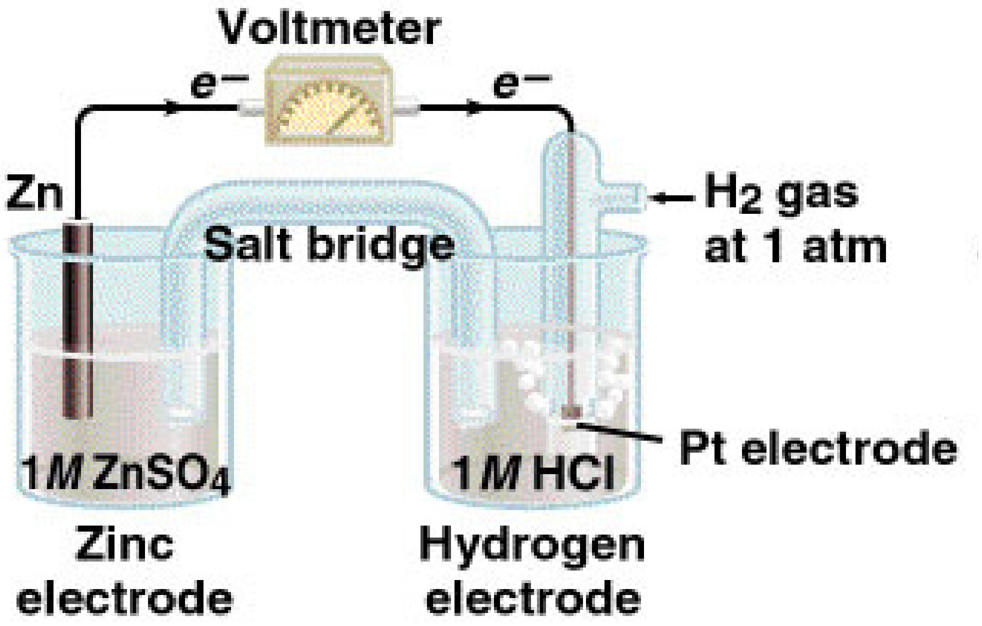


Reduction Reaction

$$2e^- + 2H^+ (1\ M) \longrightarrow H_2\ (1\ atm)$$

$$E^0 = 0\ \mathrm{V}$$

(SHE) or NHE



Standard emf (E^0_{cell})

$$\boxed{E^0_{cell} = E^0_{cathode} + E^0_{anode}}$$

$E^0 = E_{cathode}$ - Eanode

If the reaction is backwards, be sure to flip the sign!

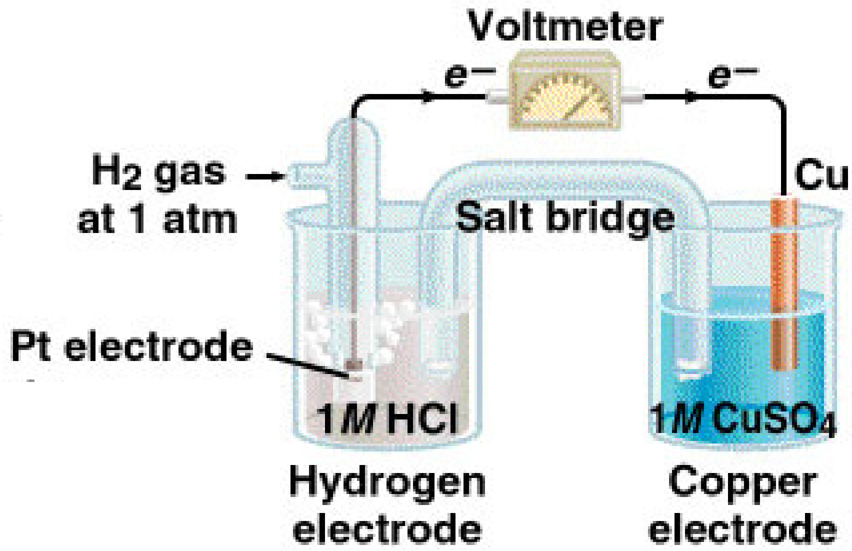
Zn (s) | Zn^{2+} (1 M) || H^+ (1 M) | H_2 (1 atm) | Pt (s)

$$E^0_{cell} = E^0_{H^+/H_2} + E^0_{Zn\ /Zn^{+2}}$$

Zn^{2+} (1 M) + $2e^-$ $\longrightarrow$ Zn $E^0 = -0.76$ V

So $E^o_{Zn/Zn^{+2}} = + 0.76\ V$ $E^0_{cell} = 0 + 0.76\ V = 0.76$ V

$E^0_{cell} = 0.34$ V



$$E^0_{cell} = E^0_{cathode} + E^0_{anode}$$

$$E^0_{cell} = E^0_{Cu^{2+}/Cu} + E^0_{H_2/H+}$$

$$0.34 = E^0_{Cu^{2+}/Cu} + - 0$$

$$E^0_{Cu^{2+}/Cu} = 0.34 \text{ V}$$

Pt (*s*) | H_2 (1 *atm*) | H^+ (1 *M*) || Cu^{2+} (1 *M*) | Cu (*s*)

Anode (oxidation): H_2 (1 *atm*) $\longrightarrow$ $2H^+$ (1 *M*) + $2e^-$

Cathode (reduction): $2e^-$ + Cu^{2+} (1 *M*) $\longrightarrow$ Cu (s)

H_2 (1 *atm*) + Cu^{2+} (1 *M*) $\longrightarrow$ Cu (*s*) + $2H^+$ (1 *M*)

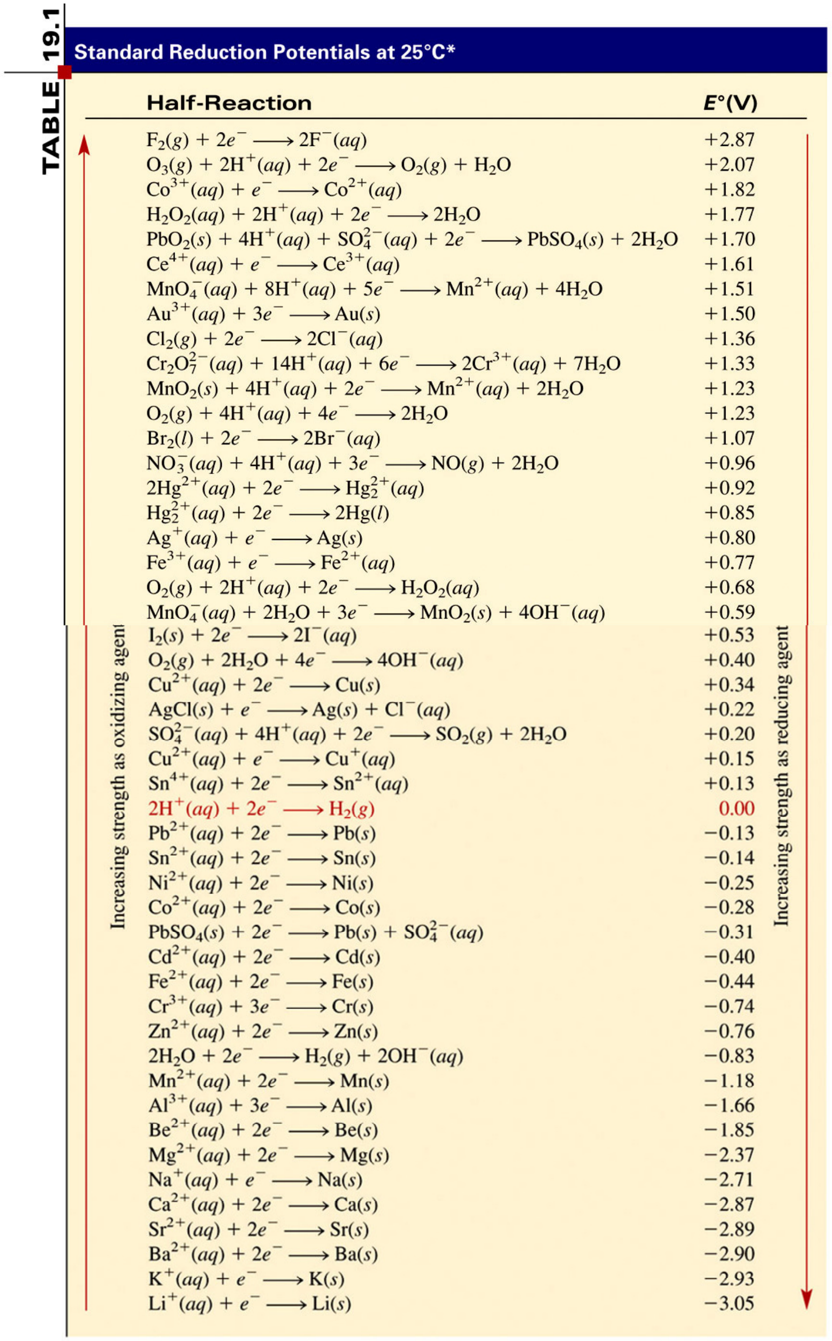


TABLE 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

*For all half-reactions the concentration is 1 *M* for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

- E^0 is for the reaction as written
- The more positive E^0 the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of E^0 changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E^0

QUESTION

What is the standard emf of an electrochemical cell made of a Cd electrode in a 1.0 *M* $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 *M* $Cr(NO_3)_3$ solution?

$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$ $E^0 = -0.40\ V$ Cd is the stronger oxidizer

$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$ $E^0 = -0.74\ V$ Cd will oxidize Cr

Anode (oxidation): $Cr(s) \longrightarrow Cr^{3+}(1\ M) + \boxed{3e^-}$ x 2

Cathode (reduction): $\boxed{2e^-} + Cd^{2+}(1\ M) \longrightarrow Cd(s)$ x 3

$$2Cr(s) + 3Cd^{2+}(1\ M) \longrightarrow 3Cd(s) + 2Cr^{3+}(1\ M)$$

$$E^0_{cell} = E^0_{cathode} + E^0_{anode}$$

$$E^0_{cell} = -0.40 + (+0.74)$$

$$E^0_{cell} = 0.34\ V$$

Spontaneity of Redox Reactions

$\Delta G = -nFE_{cell}$ n = number of moles of electrons in reaction

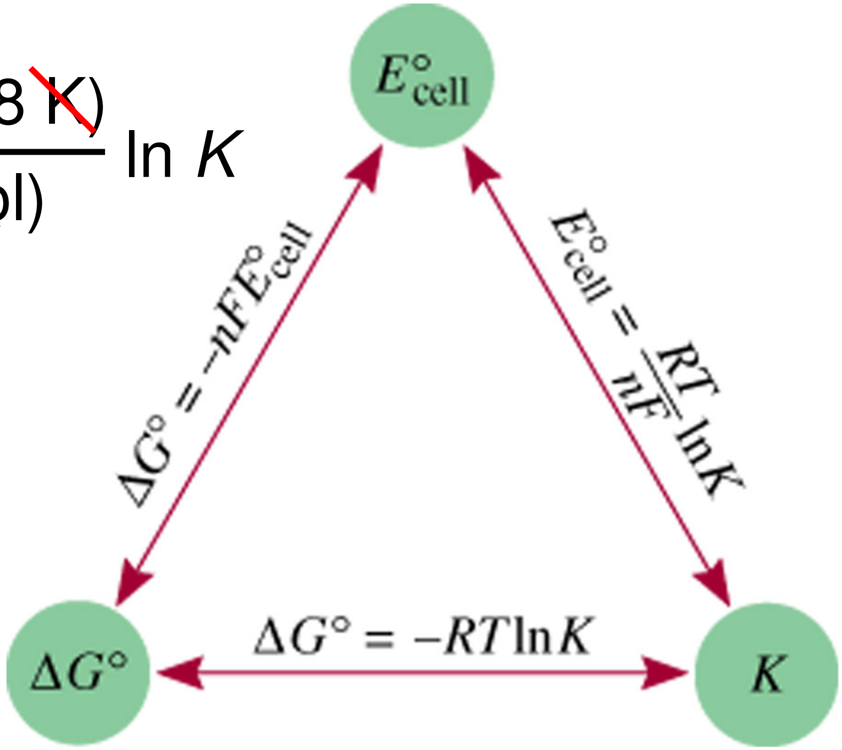
$\Delta G^0 = -nFE^0_{cell}$ $F = 96{,}500 \dfrac{\text{J}}{\text{V} \cdot \text{mol}} = 96{,}500 \text{ C/mol}$

$\Delta G^0 = -RT \ln K = -nFE^0_{cell}$

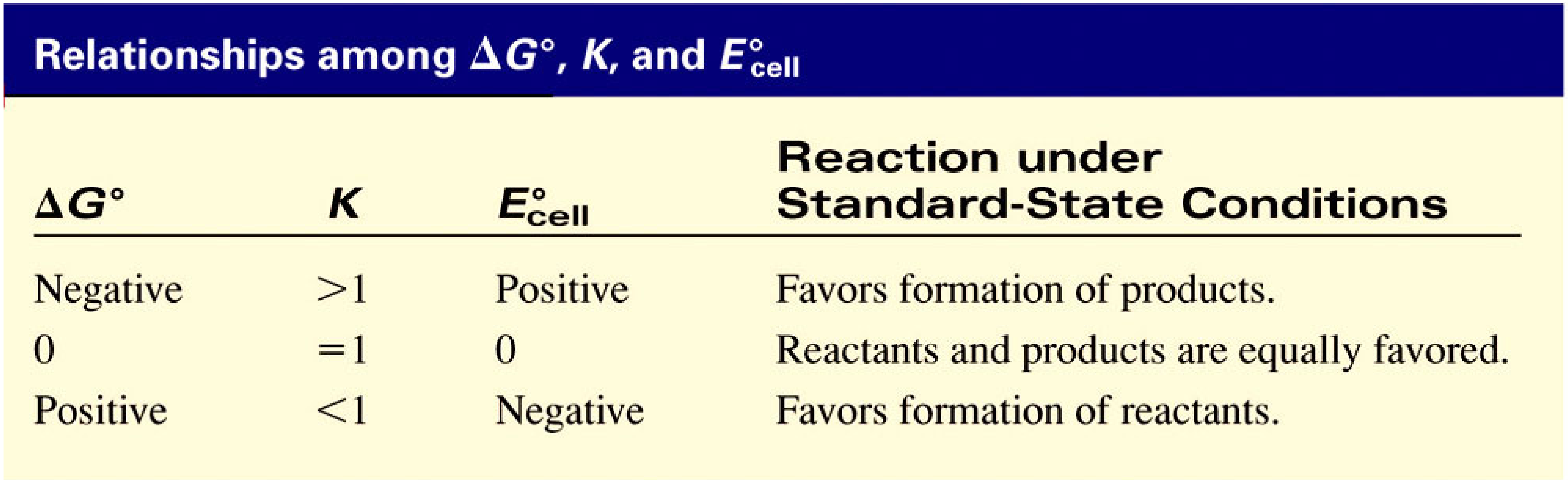
$$E^0_{cell} = \frac{RT}{nF} \ln K = \frac{(8.314\ \cancel{\text{J}}/\cancel{\text{K}}\cdot\cancel{\text{mol}})(298\ \cancel{\text{K}})}{n\,(96{,}500\ \cancel{\text{J}}/\text{V}\cdot\cancel{\text{mol}})} \ln K$$

$$E^0_{cell} = \frac{0.0257\ \text{V}}{n} \boxed{\ln} K$$

$$E^0_{cell} = \frac{0.0592\ \text{V}}{n} \boxed{\log} K$$

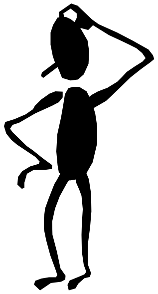


Spontaneity of Redox Reactions



Relationships among $\Delta G°$, K, and $E°_{cell}$

$\Delta G°$	K	$E°_{cell}$	Reaction under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.



What is the equilibrium constant for the following reaction at 25^0C? Fe^{2+} (*aq*) + 2Ag (*s*) $\rightleftharpoons$ Fe (*s*) + $2Ag^+$ (*aq*)

$$E^0_{\text{cell}} = \frac{0.0257\ \text{V}}{n} \ln K$$

Oxidation: $2Ag \longrightarrow 2Ag^+ + \boxed{2e^-}$

Reduction: $\boxed{2e^-} + Fe^{2+} \longrightarrow Fe$

$n = 2$

$$E^0 = E^0_{Fe^{2+}/Fe} + E^0_{Ag\ /Ag^+}$$

$$E^0 = -0.44 + -0.80$$

$$E^0 = -1.24\ \text{V}$$

$$K = \exp\left[\frac{E^0_{cell}\ \text{x}\ n}{0.0257\ \text{V}}\right] = \exp\left[\frac{-1.24\ \text{V x 2}}{0.0257\ \text{V}}\right]$$

$$K = 1.23 \times 10^{-42}$$

The Effect of Concentration on Cell Emf

$\Delta G = \Delta G^0 + RT \ln Q \qquad \Delta G = -nFE \qquad \Delta G^0 = -nFE^0$

$$-nFE = -nFE^0 + RT \ln Q$$

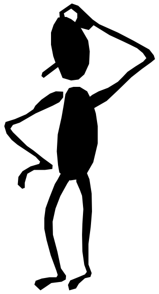
NERNST EQUATION

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E = E^0 - \frac{0.0257\ \mathrm{V}}{n} \ln Q$$

At 298K

$$E = E^0 - \frac{0.0592\ \mathrm{V}}{n} \log Q$$



Will the following reaction occur spontaneously at 25^0C if $[Fe^{2+}] = 0.60\ M$ and $[Cd^{2+}] = 0.010\ M$?

$Fe^{2+}\ (aq) + Cd\ (s) \rightleftharpoons Fe\ (s) + Cd^{2+}\ (aq)$

Oxidation: $Cd \longrightarrow Cd^{2+} + \boxed{2e^-}$

Reduction: $\boxed{2e^-} + Fe^{2+} \longrightarrow 2Fe$

$n = 2$

$$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Cd^{2+}/Cd}$$

$$E^0 = -0.44 - (-0.40)$$

$$E^0 = -0.04\ \text{V}$$

$$E = E^0 - \frac{0.0257\ \text{V}}{n} \ln Q$$

$$E = -0.04\ \text{V} - \frac{0.0257\ \text{V}}{2} \ln \frac{0.010}{0.60}$$

$$E = 0.013$$

$E > 0$ Spontaneous

➔Using the Nernst equation, we can calculate the potential of a cell in which some or all of the components are not in their standard state.

Problem: The **E** $^{o}_{cell}$ is 0.48 V for the galvanic cell based on the reaction $2Al(s) + 3Mn^{2+}(aq) \rightarrow 2Al^{3+} + 3Mn(s)$

- **Consider a cell in which $[Mn^{2+}] = 0.50M$ and $[Al^{3+}] = 1.50M$**
- **Cell potential can be calculated using Nernst equation:**
  - » $E = E^{o} - \frac{0.0591}{n} \log(Q)$

$$Q = \frac{[Al^{3+}]^2}{[Mn^{2+}]^3} = \frac{(1.50)^2 \quad (ox)}{(0.50)^3 \quad (red)}$$

Half cells: $(Al \rightarrow Al^{3+} + 3e^-)\,2$

$(Mn^{2+} + 2e^- \rightarrow Mn)3$

$n=6$

The cell potential from the Nernst is the maximum potential before any current flow occurs

As the cell discharges and current flows from anode to cathode, the concentrations will change and the

E_{cell} will change.

The cell will spontaneously discharge until it reaches equilibrium at which point Q = K and $E_{cell} = 0$

Concentration cells

- A cell in which both compartments have the same components but at different concentrations

- The difference in concentration is the only factor that produces cell potential in this case

- Typically, voltages are very small

Concentration Cells

- ➔ We can use the Nernst equation to generate a cell that has an emf based solely on difference in concentration.
- ➔ One compartment will consist of a concentrated solution, while the other has a dilute solution.
- ➔ Example: 1.00 M $Ni^{2+}(aq)$ and 1.00×10^{-3} M $Ni^{2+}(aq)$.
- ➔ The cell tends to equalize the concentrations of $Ni^{2+}(aq)$ in each compartment.
- ➔ The concentrated solution has to reduce the amount of $Ni^{2+}(aq)$ (to $Ni(s)$), so must be the cathode.

Concentration Cells

- Since the two half-reactions are the same, *E*° will be zero.

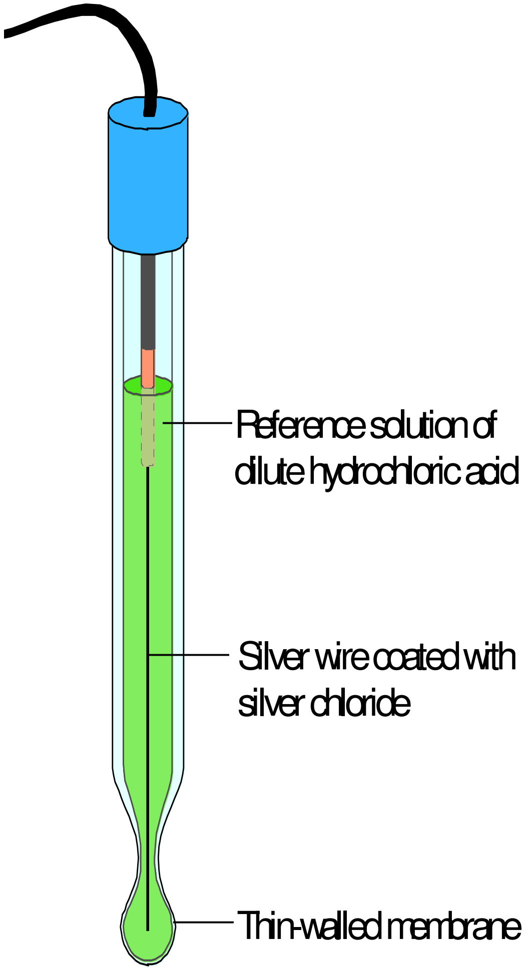
$$E = E° - \frac{0.0592}{n} \log Q$$

$$= 0\ \mathrm{V} - \frac{0.0592}{2} \log \frac{[\mathrm{Ni}^{2+}]_{\mathrm{dilute}}}{[\mathrm{Ni}^{2+}]_{\mathrm{concentrated}}}$$

$$= 0\ \mathrm{V} - \frac{0.0592}{2} \log \frac{1.00 \times 10^{-3}\, M}{1.00\, M}$$

$$= +0.0888\ \mathrm{V}$$

Measurement of pH



Ion selective electrodes are glass electrodes that measures a change in potential when $[H^+]$ varies. Used to measure pH.

Calculate the pH of the following half cell solution. Pt.H_2 (1atm) / HCl; E =0.25 V.

Solution :

$$H_2 \longrightarrow 2H^+ + 2e\text{-}1 \quad E = 0.25$$

$$2H^+ + 2e \longrightarrow H_2 \quad E = -0.25$$

$$-0.25 = 0 - \frac{0.059}{2} (\log 1 - 2 \log [H^+])$$

$$2\,pH = \frac{0.25 \times 2}{0.059} = 4.23$$

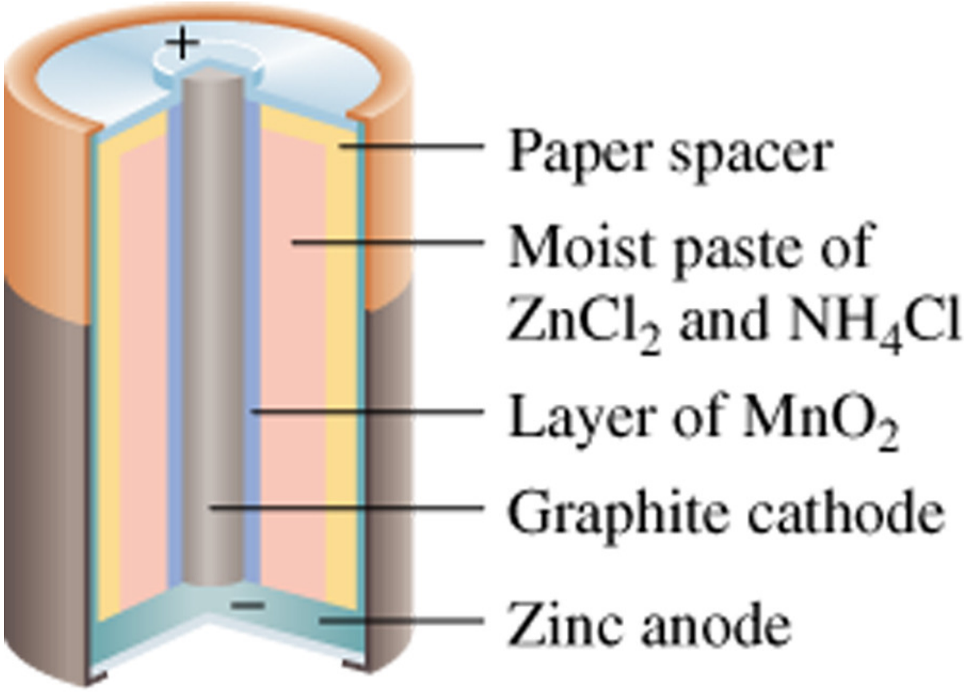
Battery: A system which converts chemical energy into electrical energy

More correctly, a battery is an electrochemical cell: Galvanic Cells convert the energy from spontaneous chemical reactions into electricity

Batteries

Dry cell

Leclanché cell



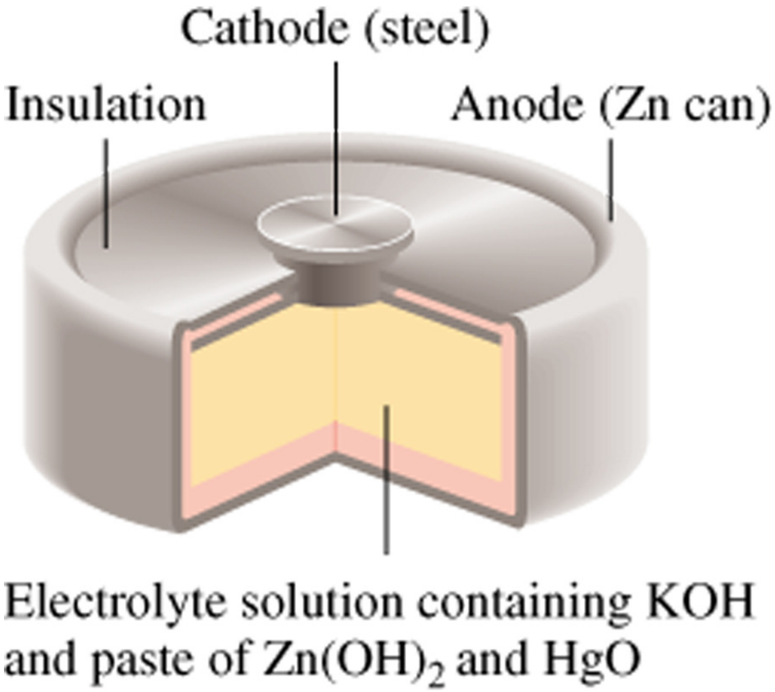
Anode: $\mathrm{Zn}\ (s) \longrightarrow \mathrm{Zn}^{2+}\ (aq) + 2e^-$

Cathode: $2\mathrm{NH}_4^+\ (aq) + 2\mathrm{MnO}_2\ (s) + 2e^- \longrightarrow \mathrm{Mn}_2\mathrm{O}_3\ (s) + 2\mathrm{NH}_3\ (aq) + \mathrm{H}_2\mathrm{O}\ (l)$

$$\mathrm{Zn}\ (s) + 2\mathrm{NH}_4\ (aq) + 2\mathrm{MnO}_2\ (s) \longrightarrow \mathrm{Zn}^{2+}\ (aq) + 2\mathrm{NH}_3\ (aq) + \mathrm{H}_2\mathrm{O}\ (l) + \mathrm{Mn}_2\mathrm{O}_3\ (s)$$

Batteries

Mercury Battery



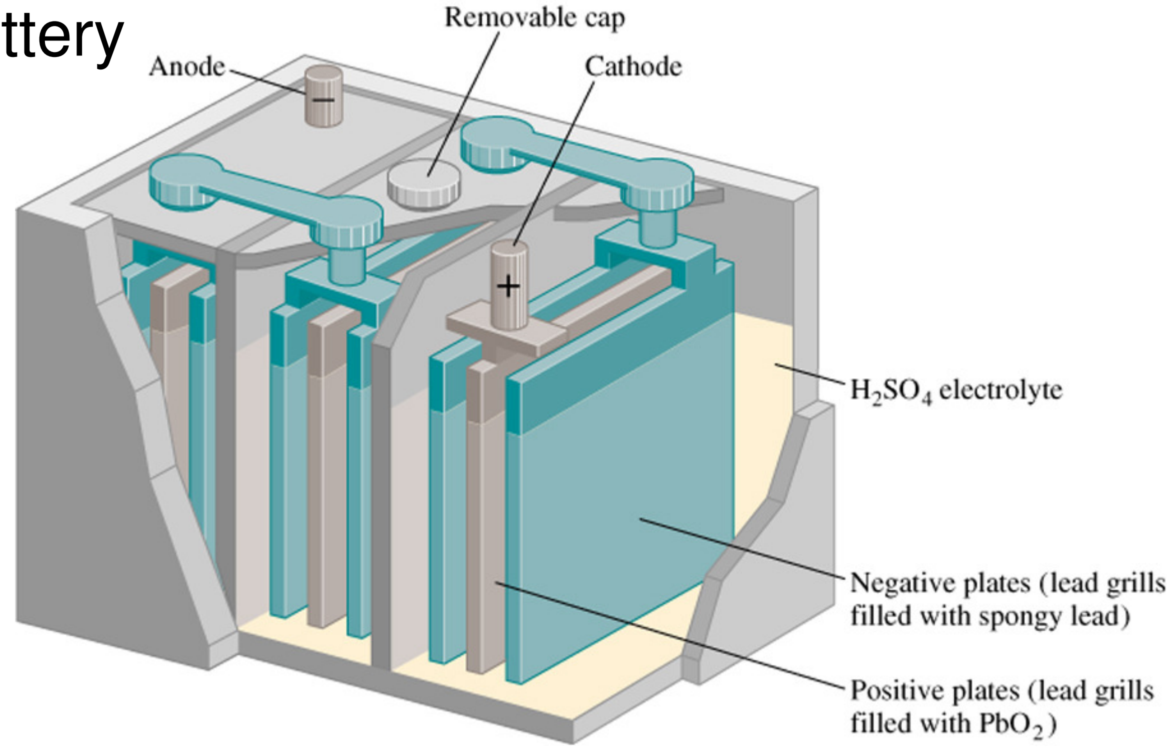
Anode: $Zn(Hg) + 2OH^- (aq) \longrightarrow ZnO (s) + H_2O (l) + 2e^-$

Cathode: $HgO (s) + H_2O (l) + 2e^- \longrightarrow Hg (l) + 2OH^- (aq)$

$Zn(Hg) + HgO (s) \longrightarrow ZnO (s) + Hg (l)$

Batteries

Lead storage battery

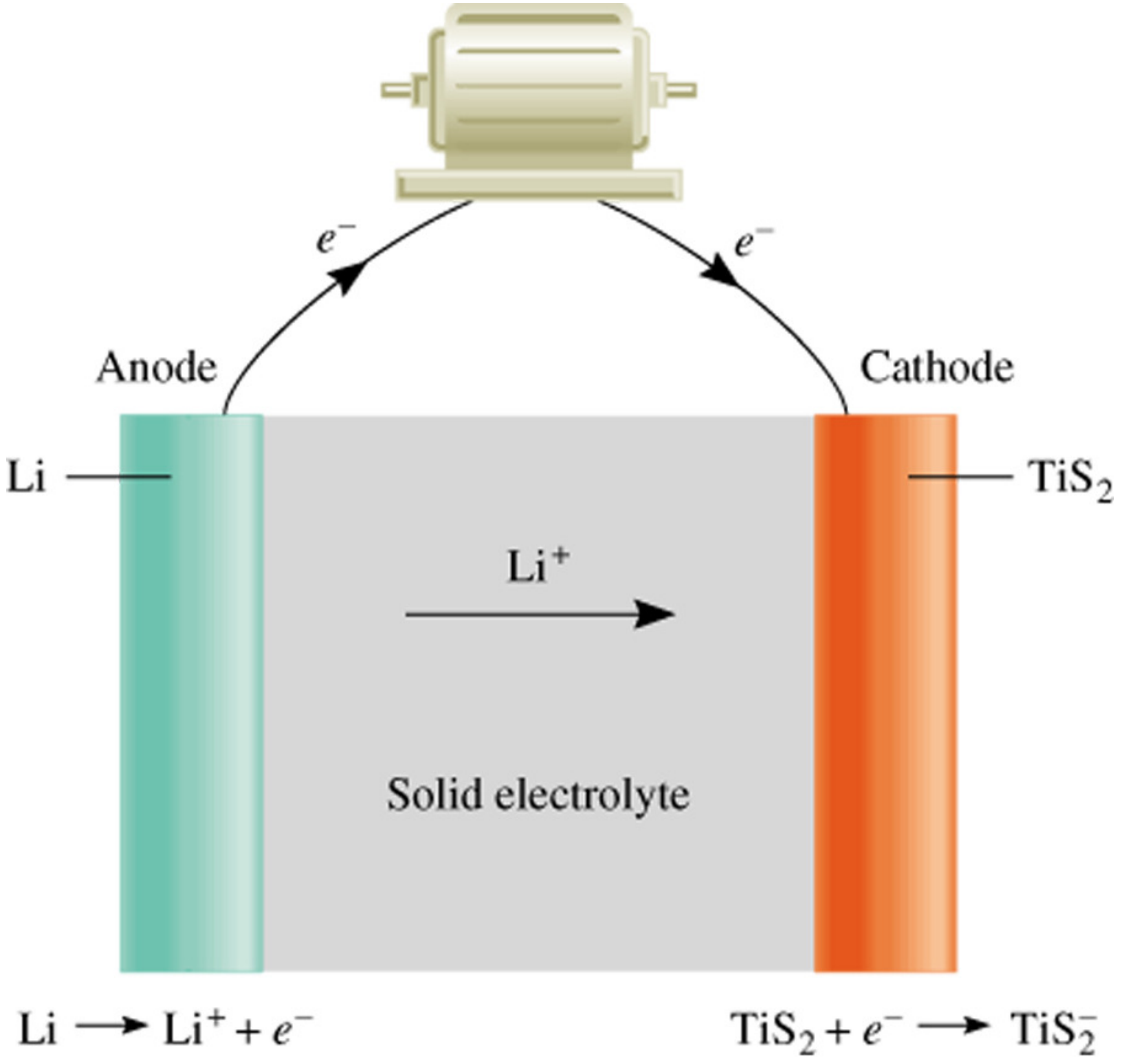


Anode: $Pb\ (s) + SO_4^{2-}\ (aq) \longrightarrow PbSO_4\ (s) + 2e^-$

Cathode: $PbO_2\ (s) + 4H^+\ (aq) + SO_4^{2-}\ (aq) + 2e^- \longrightarrow PbSO_4\ (s) + 2H_2O\ (l)$

$$Pb\ (s) + PbO_2\ (s) + 4H^+\ (aq) + 2SO_4^{2-}\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$$

Solid State Lithium Battery



Fuel Cell

- ➔ **It is a device in which energy from the combustion of fuel is directly converted into electrical energy**
- ➔ **Common example of fuel cell is H_2-O_2 fuel cell**
- ➔ **This cell is also known as Bacon cell**

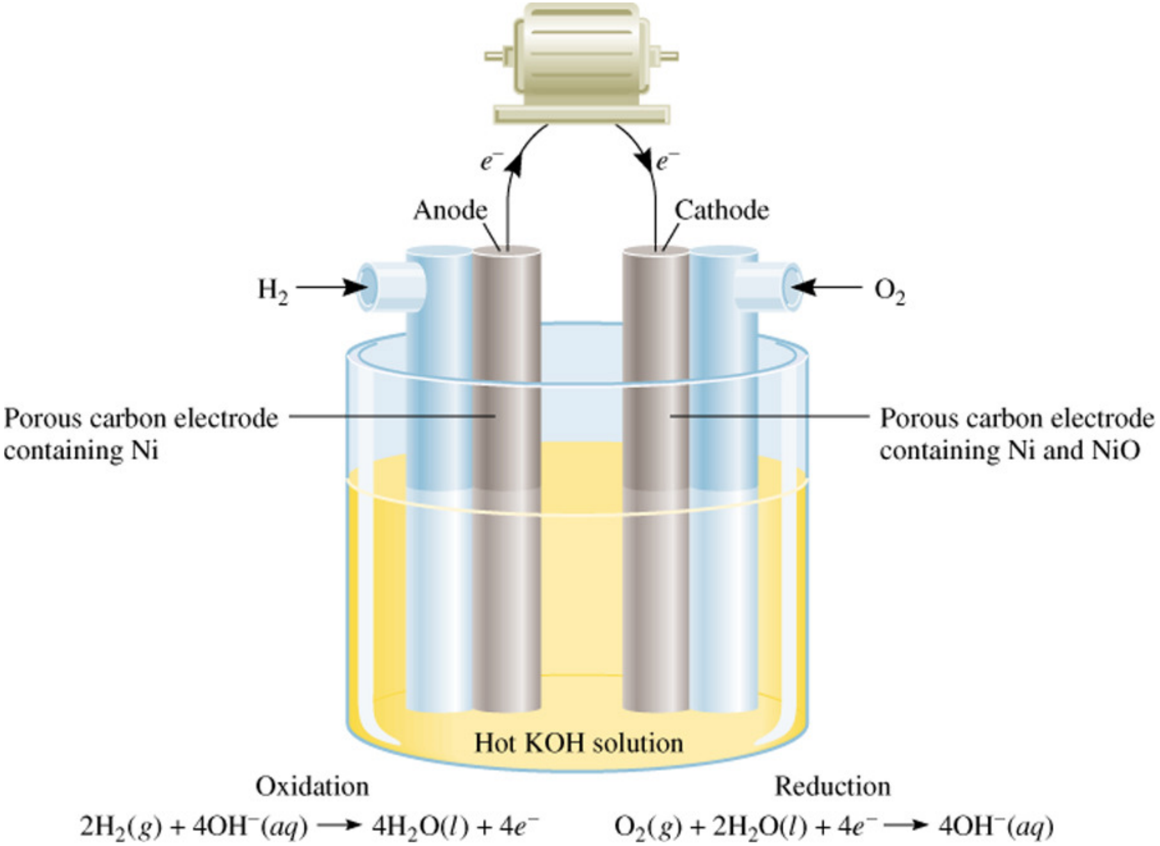
The reactions taking place at electrodes are:

At anode

$$H_2 + 2OH^-(aq) \xrightarrow{\quad} 2H_2O(l) + 2e^-)X2$$

At cathode

$$O2 + H_2O(l) + 4\ e^- \xrightarrow{\quad} 4\ OH^-(aq)$$



A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning

Anode: $2H_2\ (g) + 4OH^-\ (aq) \longrightarrow 4H_2O\ (l) + 4e^-$

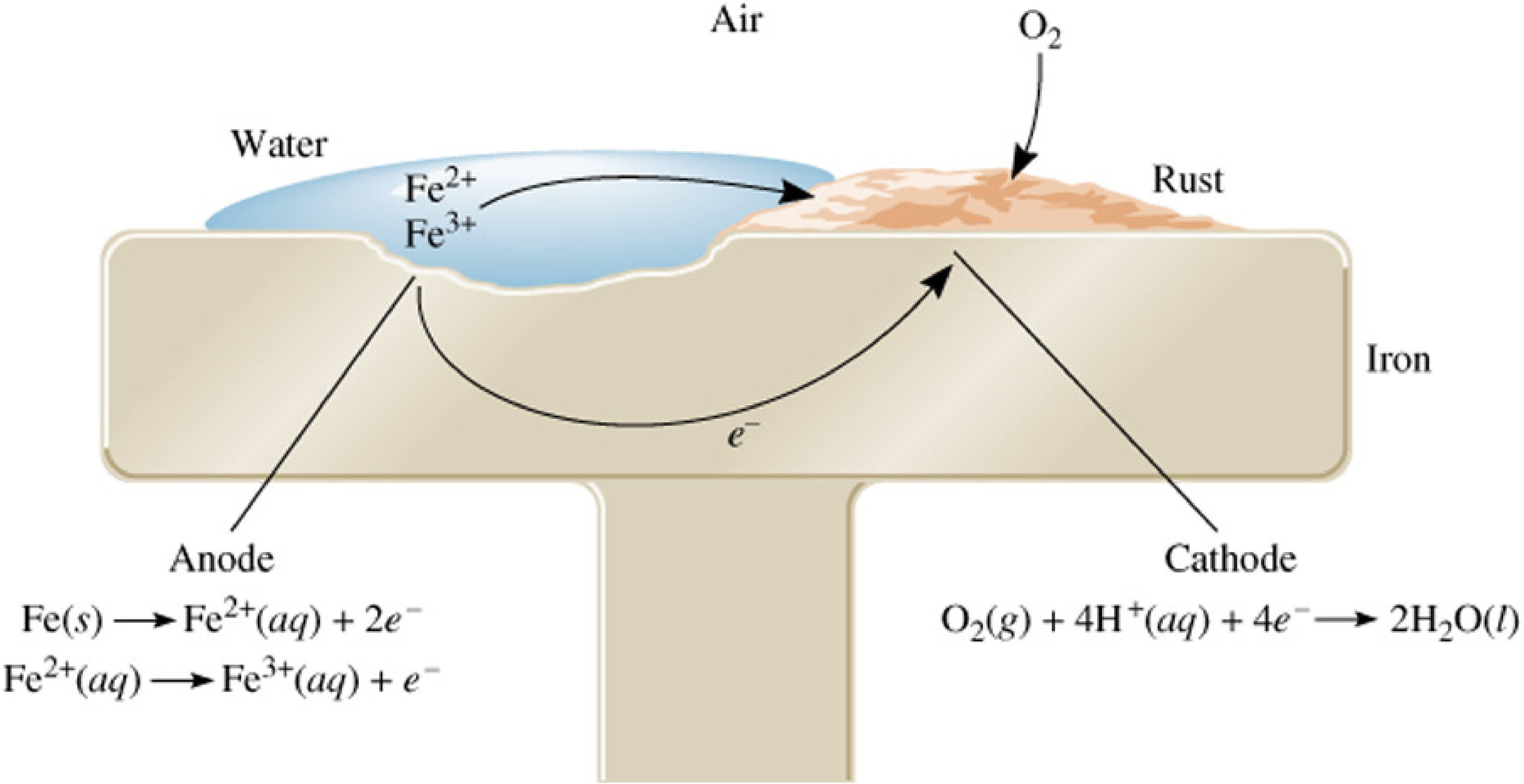
Cathode: $O_2\ (g) + 2H_2O\ (l) + 4e^- \longrightarrow 4OH^-\ (aq)$

$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l)$

Advantages of a fuel cell

- ➔It works continuously as long as gases are supplied
- ➔High efficiency
- ➔Pollution free working

Corrosion



$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

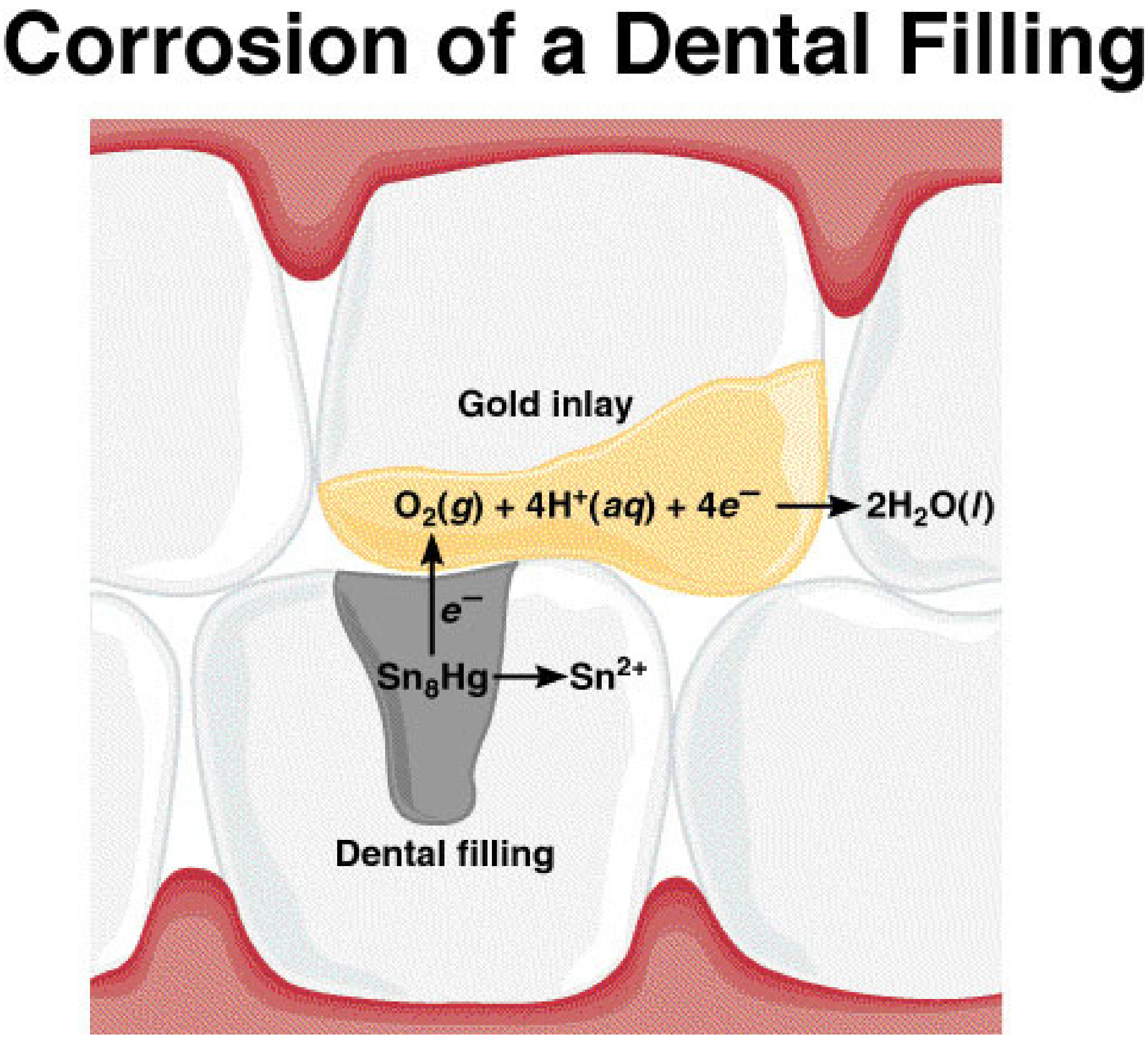
$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$

$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

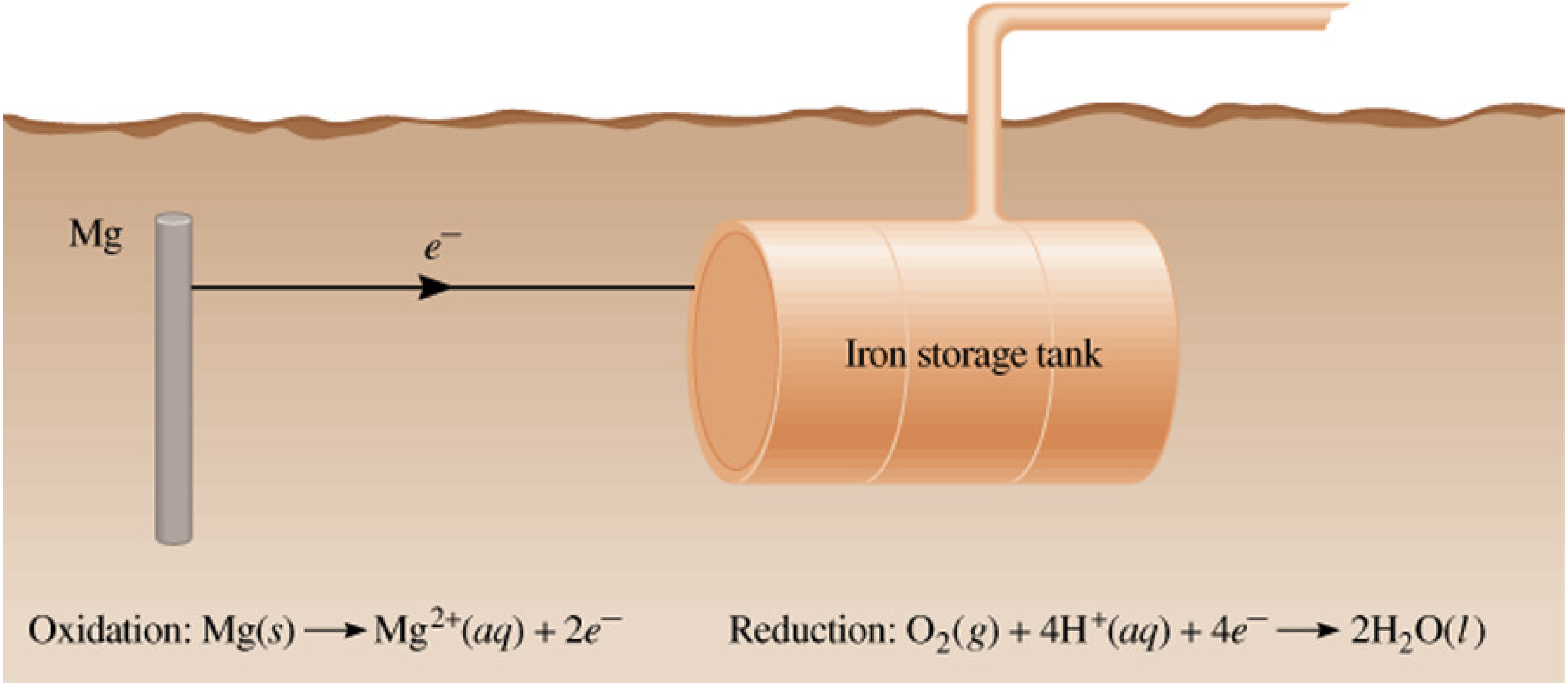
Chemistry In Action: Dental Filling Discomfort

Hg_2^{2+}/Ag_2Hg_3 0.85 V

Sn^{2+}/Ag_3Sn -0.05 V



Cathodic Protection of an Iron Storage Tank



Oxidation: $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

Electrolysis

- ➔Previously our lectures on electrochemistry were involved with voltaic cells i.e. cells with $E_{cell} > 0$ and $\Delta G < 0$ that were spontaneous reactions.

- ➔Today we discuss electrochemical cells where $E_{cell} < 0$ and $\Delta G > 0$ that are non-spontaneous reactions and require electricity for the reactions to take place. We can take a voltaic cell and reverse the electrodes to make an electrochemical cell.

Electrolysis

- ➔**Define electrolysis?**
- ➔Some examples.
- ➔What are the values of ΔG and E_{cell}?
- ➔Electrolysis of water.
- ➔Some industrial applications.

Electrolysis

- ➔ The splitting (lysing) of a substance or decomposing by forcing a current through a cell to produce a chemical change for which the cell potential is negative.

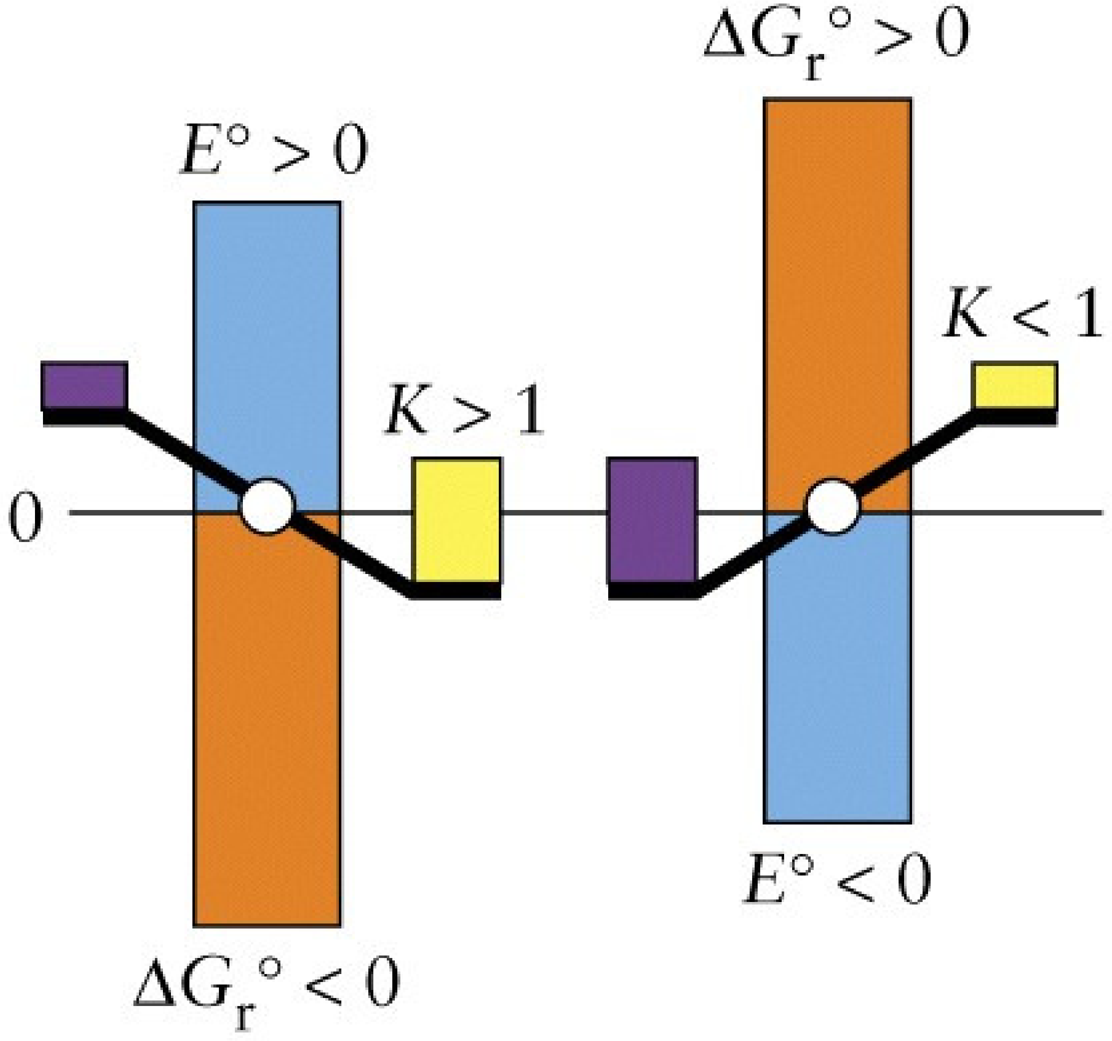
Two Types of Cells

- ➔ Cell 1: does work by releasing free energy from a spontaneous reaction to produce electricity such as a battery.

- ➔ Cell 2: does work by absorbing free energy from a source of electricity to drive a non-spontaneous reaction such as electroplating.

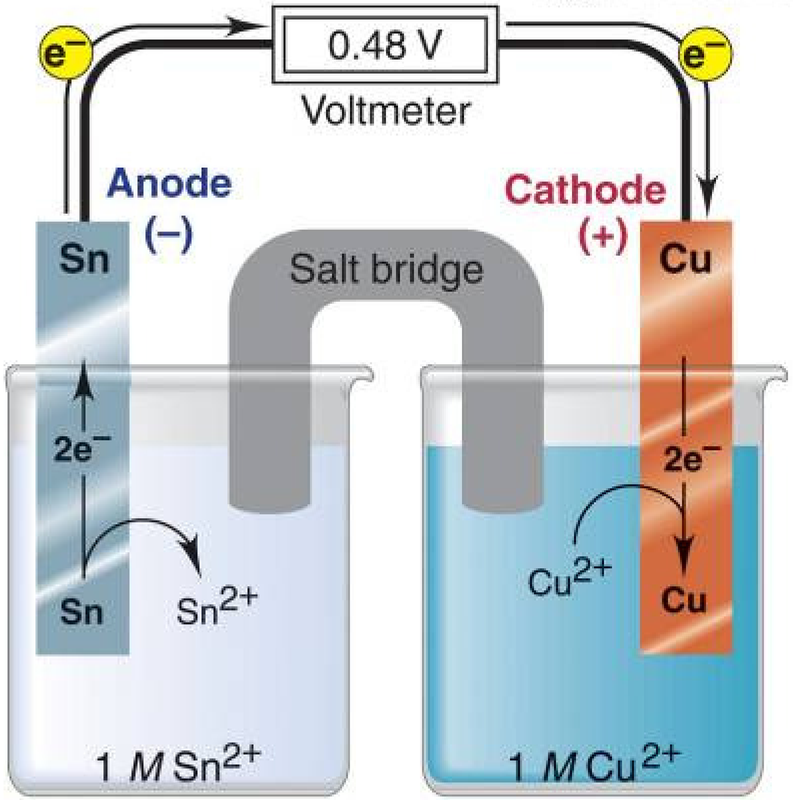
Voltaic

Electrolytic



Comparison of Voltaic and Electrolytic Cells

			Electrode		
CELL TYPE	**ΔG**	**E_{cell}**	**Name**	**Process**	**Sign**
Voltaic	<0	>0	Anode	Oxidation	-
Voltaic	<0	>0	Cathode	Reduction	+
Electrolytic	>0	<0	Anode	Oxidation	+
Electrolytic	>0	<0	Cathode	Reduction	-

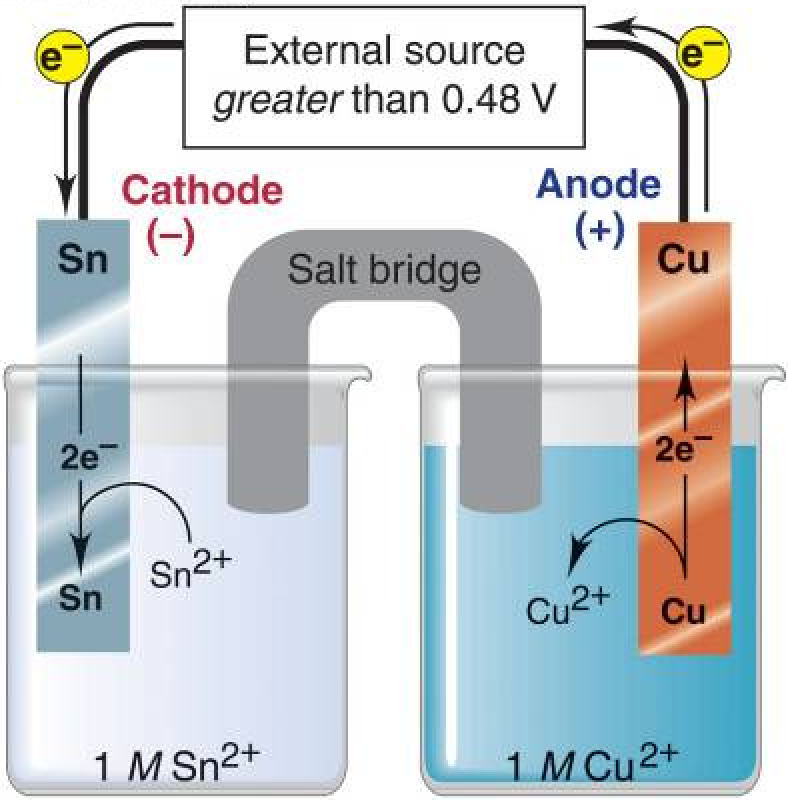


Oxidation half-reaction
$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$

Reduction half-reaction
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall (cell) reaction
$Sn(s) + Cu^{2+}(aq) \longrightarrow Sn^{2+}(aq) + Cu(s)$

A Voltaic cell



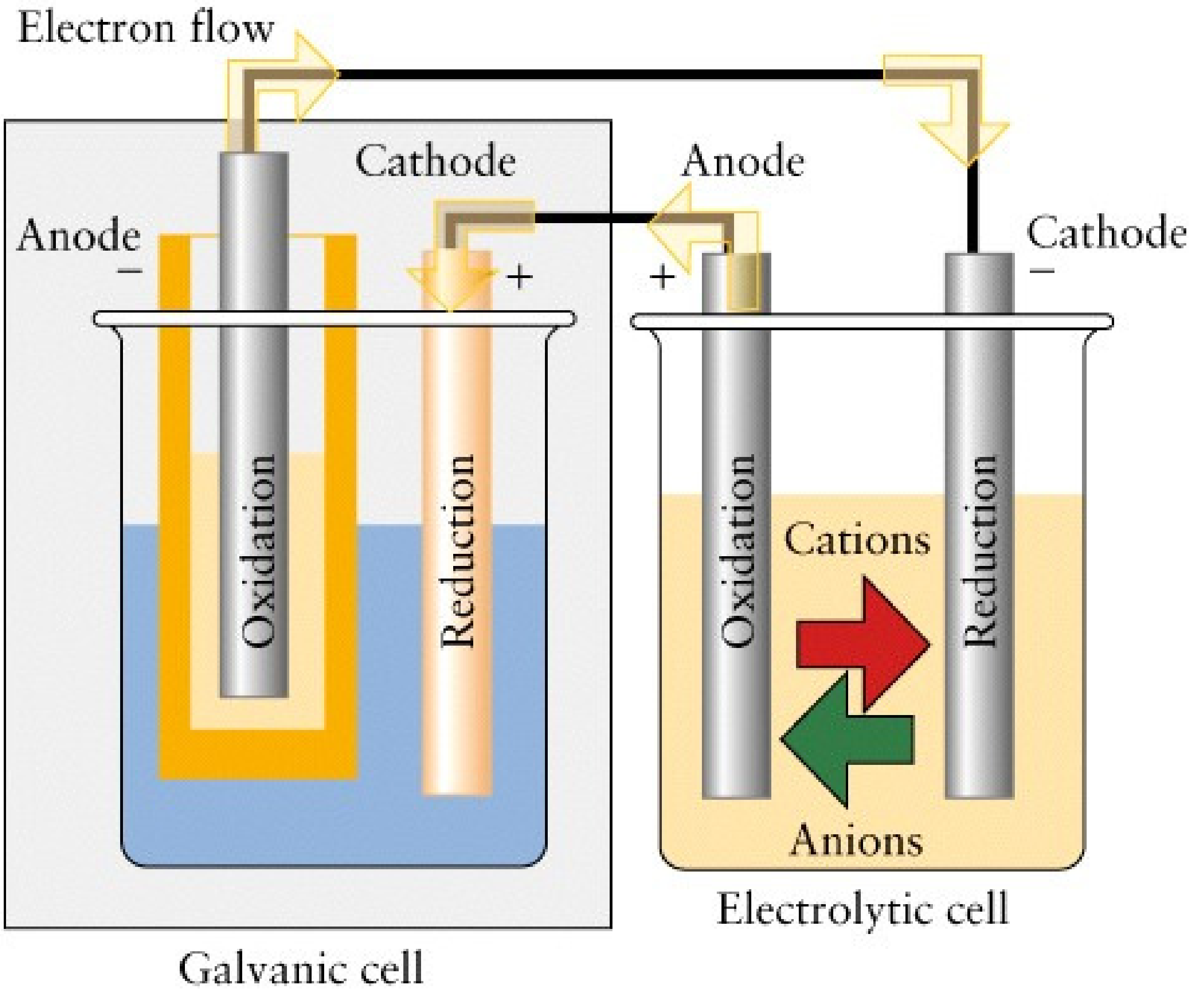
Oxidation half-reaction
$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Reduction half-reaction
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$

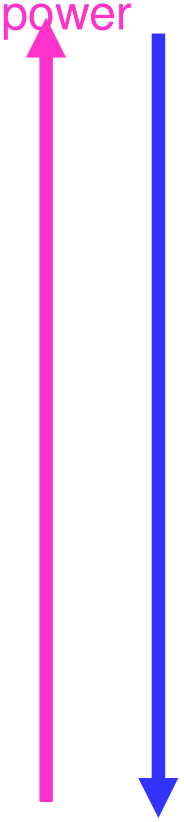
Overall (cell) reaction
$Cu(s) + Sn^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Sn(s)$

B Electrolytic cell

A voltaic (Galvanic) cell can power an electrolytic cell



Half-Reaction	**E^0 (V)**
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

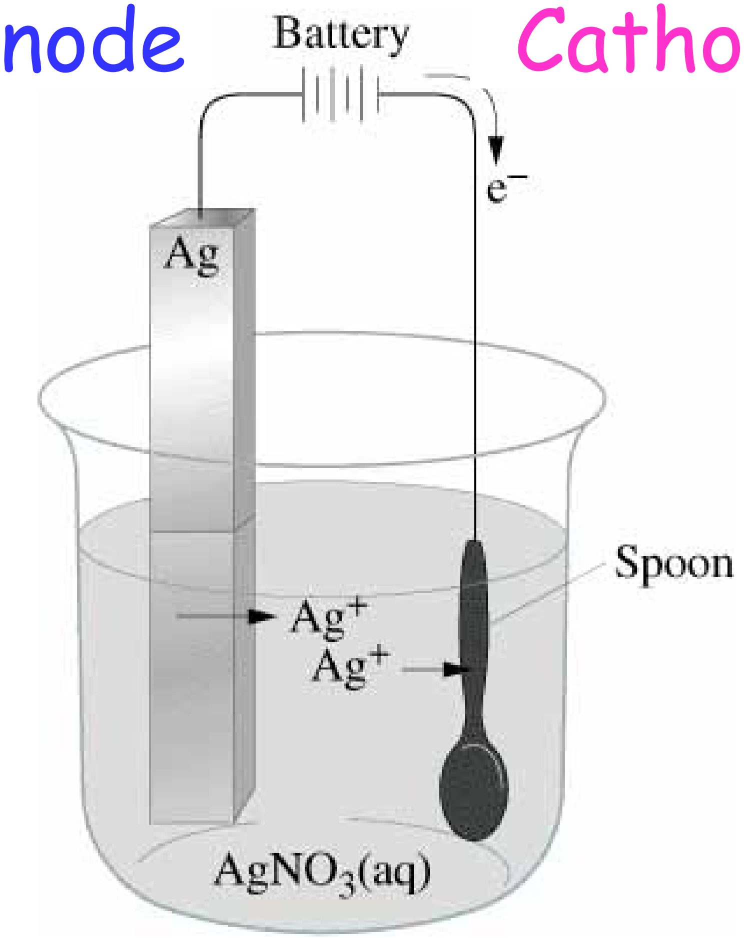


Increase oxidizing power

Increase reducing power

Electrolysis

Anode Cathode



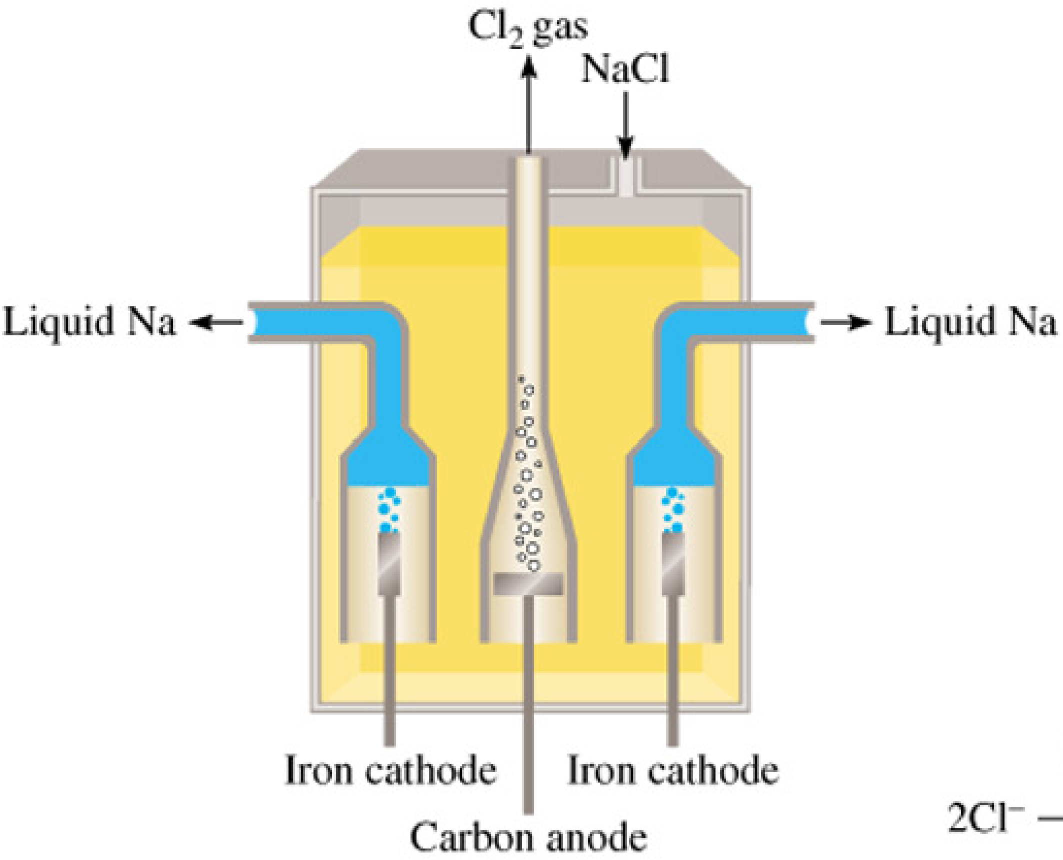
At Anode: Oxidation

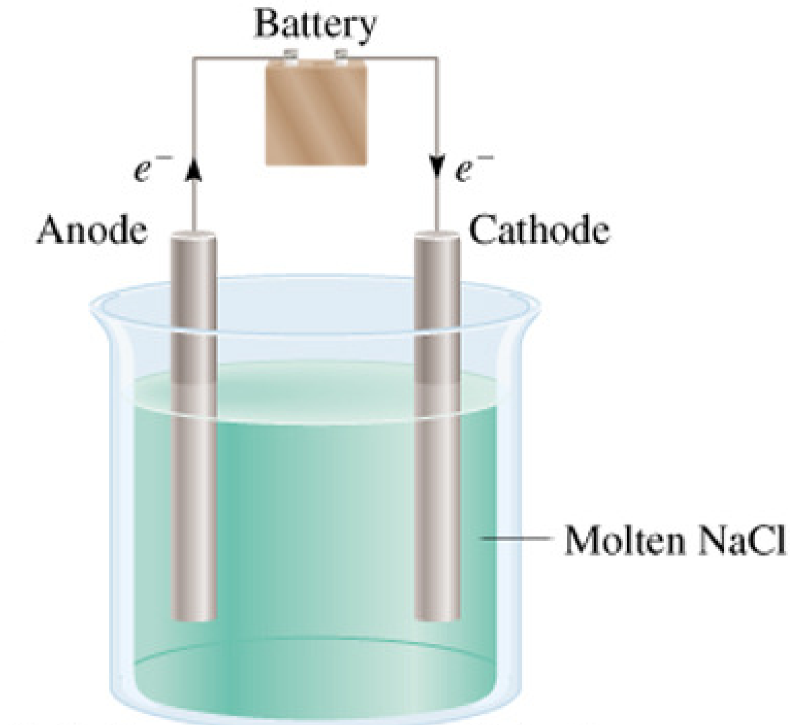
$$Ag \longrightarrow Ag^+ + e^-$$

At Cathode: Reduction

$$Ag^+ + e^- \longrightarrow Ag$$

Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.





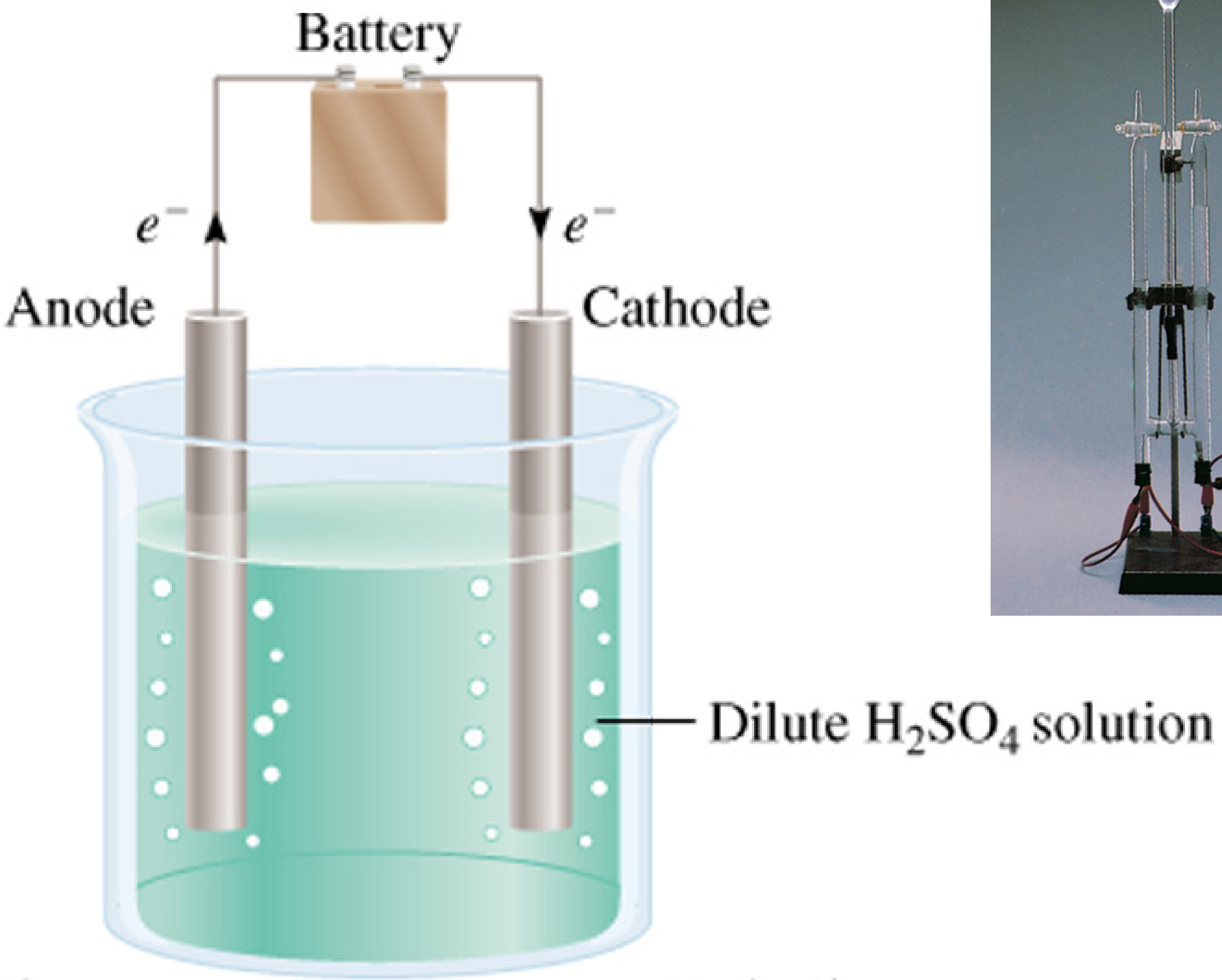
Oxidation

$2Cl^- \longrightarrow Cl_2(g) + 2e^-$

Reduction

$2Na^+ + 2e^- \longrightarrow 2Na(l)$

Electrolysis of Water



Oxidation

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Reduction

$4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$

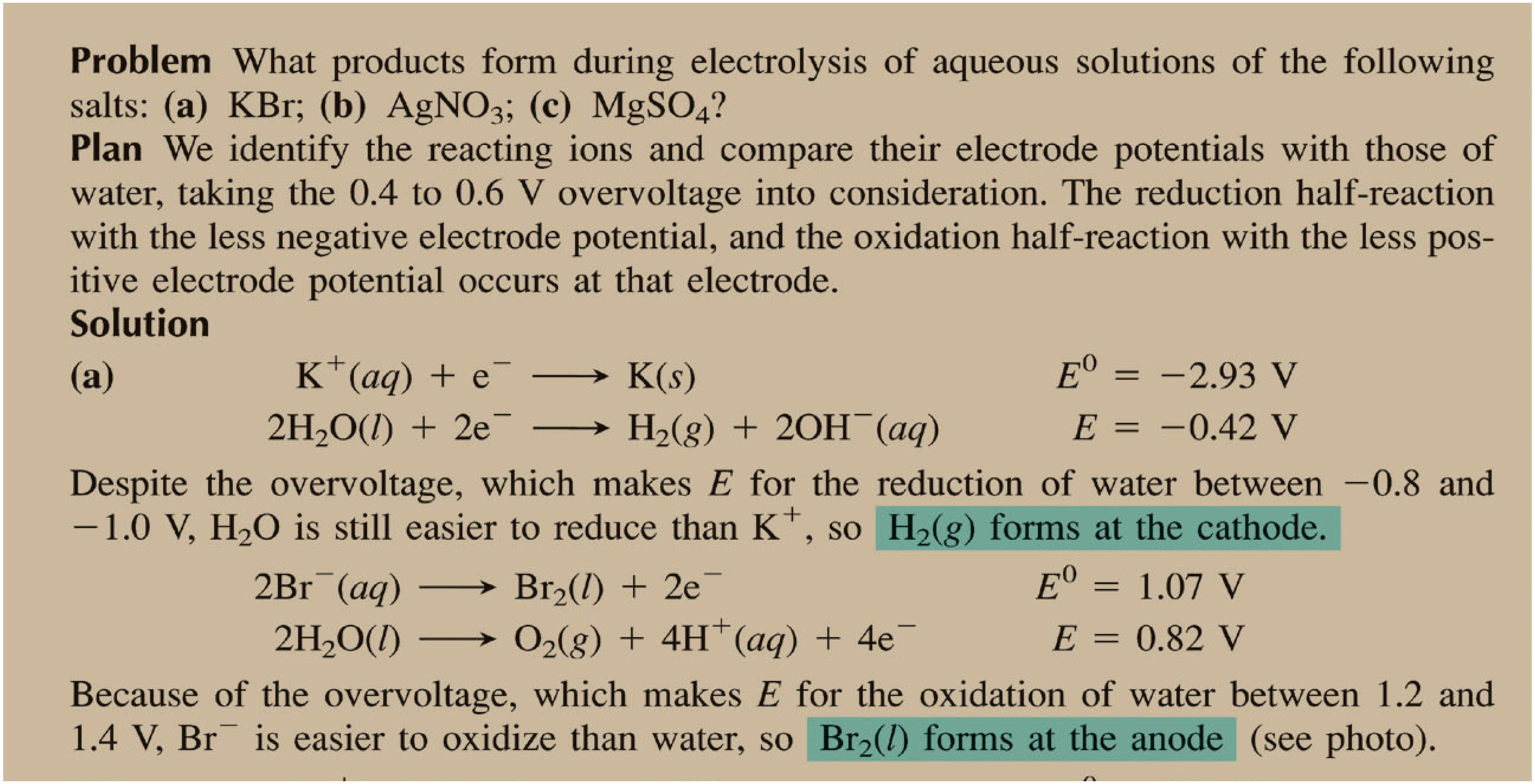
Electrolysis of water

- At the anode (oxidation):
- $2H_2O(l) + 2e^- = H_2(g) + 2OH^-(aq)$ E=-0.42V
- At the cathode (reduction):
- $2H_2O(l) = O_2(g) + 4H^+(aq) + 4e^-$ E= 0.82V
- Overall reaction after multiplying anode reaction by 2,
- $2H_2O(l) = 2H_2(g) + O_2(g)$
- $E^o_{cell} = -0.42 - 0.82 = -1.24$ V

Electrolysis products

- ➔Metal>Higher I.E.> gains electrons more easily > stronger oxidizing agent > reduced at cathode

- ➔Non metal > less electro negativity> holds the electrons less tightly>loose electrons easily> stronger reducing agent > oxidized at anode



Problem What products form during electrolysis of aqueous solutions of the following salts: **(a)** KBr; **(b)** $AgNO_3$; **(c)** $MgSO_4$?

Plan We identify the reacting ions and compare their electrode potentials with those of water, taking the 0.4 to 0.6 V overvoltage into consideration. The reduction half-reaction with the less negative electrode potential, and the oxidation half-reaction with the less positive electrode potential occurs at that electrode.

Solution

(a)

$$K^+(aq) + e^- \longrightarrow K(s) \qquad E^0 = -2.93\ V$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E = -0.42\ V$$

Despite the overvoltage, which makes E for the reduction of water between −0.8 and −1.0 V, H_2O is still easier to reduce than K^+, so $H_2(g)$ forms at the cathode.

$$2Br^-(aq) \longrightarrow Br_2(l) + 2e^- \qquad E^0 = 1.07\ V$$

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E = 0.82\ V$$

Because of the overvoltage, which makes E for the oxidation of water between 1.2 and 1.4 V, Br^- is easier to oxidize than water, so $Br_2(l)$ forms at the anode (see photo).

(b) $Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E^0 = 0.80\ V$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E = -0.42\ V$$

As the cation of an inactive metal, Ag^+ is a better oxidizing agent than H_2O, so Ag forms at the cathode. NO_3^- cannot be oxidized, because N is already in its highest (+5) oxidation state. Thus, O_2 forms at the anode:

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$

(c) $Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$ $E^0 = -2.37\ V$

Like K^+ in part (a), Mg^{2+} cannot be reduced in the presence of water, so H_2 forms at the cathode. The SO_4^{2-} ion cannot be oxidized because S is in its highest (+6) oxidation state. Thus, H_2O is oxidized, and O_2 forms at the anode:

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$

Electrolysis: Consider the electrolysis of a solution that is 1.00 M in each of $CuSO_4(aq)$ and $NaCl(aq)$

➔ **Oxidation possibilities follow.**

➔ $2Cl^-(aq) = Cl_2(g) + 2e^-$ $E° = -1.358$ V

➔ $2SO_4^{2-}(aq) = S_2O_8^{2-}(aq) + 2e^-$ $E° = -2.01$ V

➔ $2H_2O = 4H^+(aq) + O_2(g) + 4e^-$ $E° = -1.229$ V

➔ **Reduction possibilities follow:**

➔ $Na^+(aq) + e^- = Na(s)$ $E° = -2.713$ V

➔ $Cu^{2+}(aq) + 2e^- = Cu(s)$ $E° = +0.337$ V

➔ $2H_2O + 2e^- = H_2(g) + 2OH^-(aq)$ $E° = +0.828$ V

Electrolysis

- We would choose the production of $O_2(g)$ and $Cu(s)$.
- But the voltage for producing $O_2(g)$ from solution is considerably higher than the standard potential, because of the high activation energy needed to form $O_2(g)$.
- The voltage for this half cell seems to be closer to −1.5 V in reality.
- The result then is the production of $Cl_2(g)$ and $Cu(s)$.

  anode, oxidation: $2Cl^-(aq) = Cl_2(g) + 2e^-$ $E° = -1.358$ V
- cathode, reduction: $Cu^{2+}(aq) + 2e^- = Cu(s)$ $E° = +0.337$ V
- overall: $CuCl_2(aq) : Cu(s) + Cl_2(g)$ $E = -1.021$ V
- We must apply a voltage of more than +1.021 V to cause this reaction to occur.

Products of Electrolysis

	Type of Electrode	At Anode	At Cathode
Molten NaCl		**Cl_2**	**Na**
Aqueous NaCl		**Cl_2**	**H_2**
Aqueous CuBr		**Br_2**	**Cu**
Aqueous $CuSO_4$		**Cu dissolves**	**Cu deposited**
Aqueous $CuSO_4$	**Pt. Electrodes**	**O_2**	**Cu**

Stoichiometry of electrolysis: Relation between amounts of charge and product

- ➔Faraday's law of electrolysis relates to the amount of substance produced at each electrode is directly proportional to the quantity of charge flowing through the cell (half reaction).

- ➔Each balanced half-cell shows the relationship between moles of electrons and the product.

Faradays Laws

Faraday First Law :

$$M \propto Q \Rightarrow M = ZIT$$

Z is electrochemical constant

$$Na^+Cl \longrightarrow Na + \tfrac{1}{2}Cl_2$$

$$Na^+ + e^- \longrightarrow Na$$

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

Charge on one mole of electrons is 96487 ≈ 96500 C = one Faraday

If n e^- are involved in the electrode reaction, the passage of n-faraday of electricity will liberate one mole of substance

Stoichiometry of Electrolysis

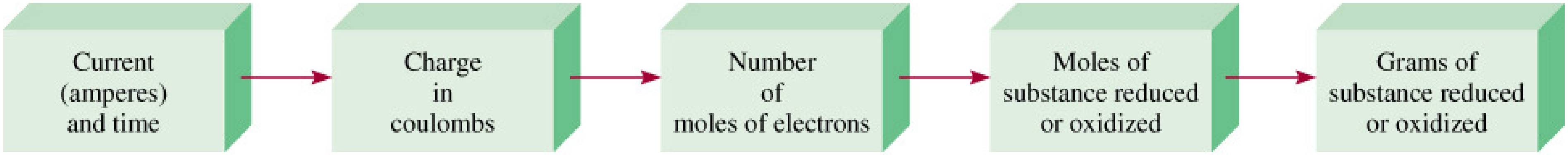
- How much chemical change occurs with the flow of a given current for a specified time?

➔current and time → quantity of charge →

➔moles of electrons → moles of analyte →

➔grams of analyte

Electrolysis and Mass Changes



Current (amperes) and time → Charge in coulombs → Number of moles of electrons → Moles of substance reduced or oxidized → Grams of substance reduced or oxidized

charge (Coulombs) = current (Amperes) x time (sec)

$$\boxed{1 \text{ mole } e^- = 96{,}500 \text{ C} = 1 \text{ Faraday}}$$

Problems

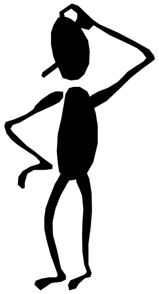
- How much charge is requires for the following reactions?

  i) 1 mol of MnO_4^- to Mn^{2+}

  ii) 1 mol of H_2O to O_2

  iii) Complete oxidation of 90g of water

  iv) Complete reduction of 100 ml Of 0.1 M $KMnO_4$ solution



How much Ca will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

Anode: $2Cl^- (l) \longrightarrow Cl_2 (g) + 2e^-$

Cathode: $Ca^{2+} (l) + \boxed{2e^-} \longrightarrow Ca (s)$

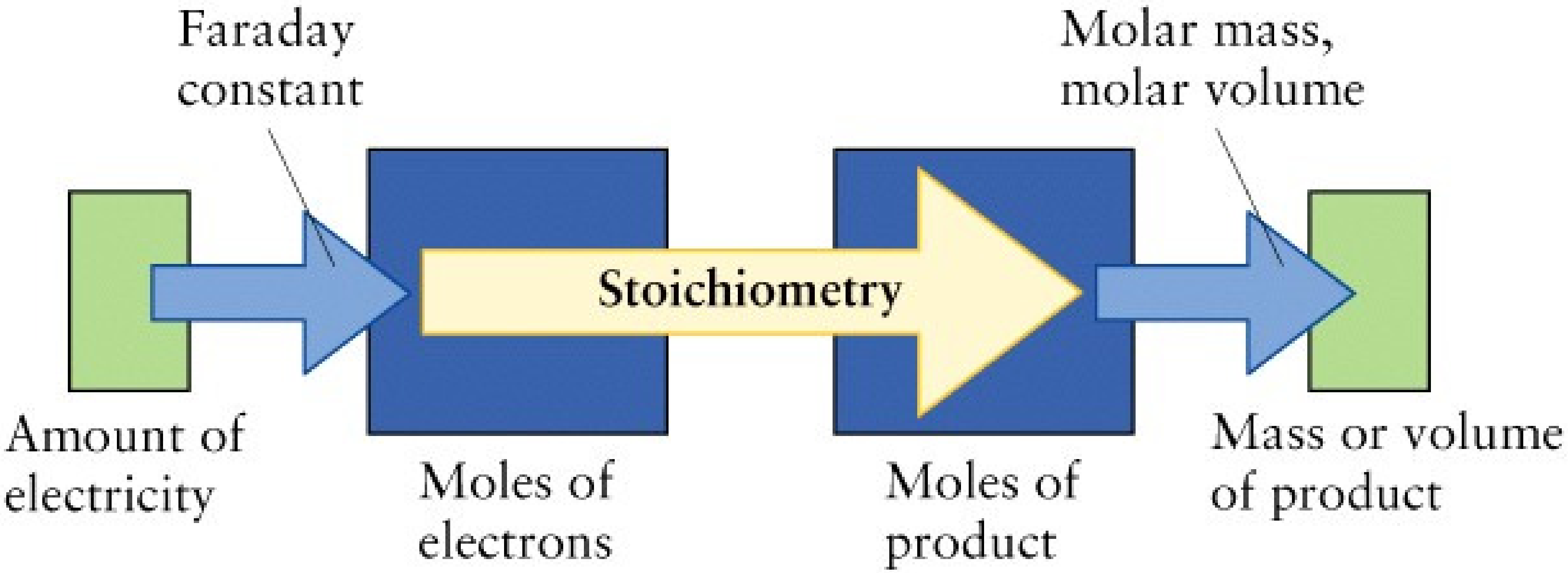
$$Ca^{2+} (l) + 2Cl^- (l) \longrightarrow Ca (s) + Cl_2 (g)$$

2 mole e^- = 1 mole Ca

$$\text{mol Ca} = 0.452 \frac{\cancel{C}}{\cancel{s}} \times 1.5\ \cancel{hr} \times 3600 \frac{\cancel{s}}{\cancel{hr}} \times \frac{1\ \cancel{mol}\ e^-}{96{,}500\ \cancel{C}} \times \frac{1\ \text{mol Ca}}{2\ \cancel{mol}\ e^-}$$

$$= 0.0126\ \text{mol Ca} = 0.50\ \text{g Ca}$$

Doing work with electricity.



Faradays Laws

Faraday Second Law :

When the same amount of electricity is passed through solutions of different electrolytes connected in series, the weights of substances produced at the electrodes are directly proportional to their equivalents weights

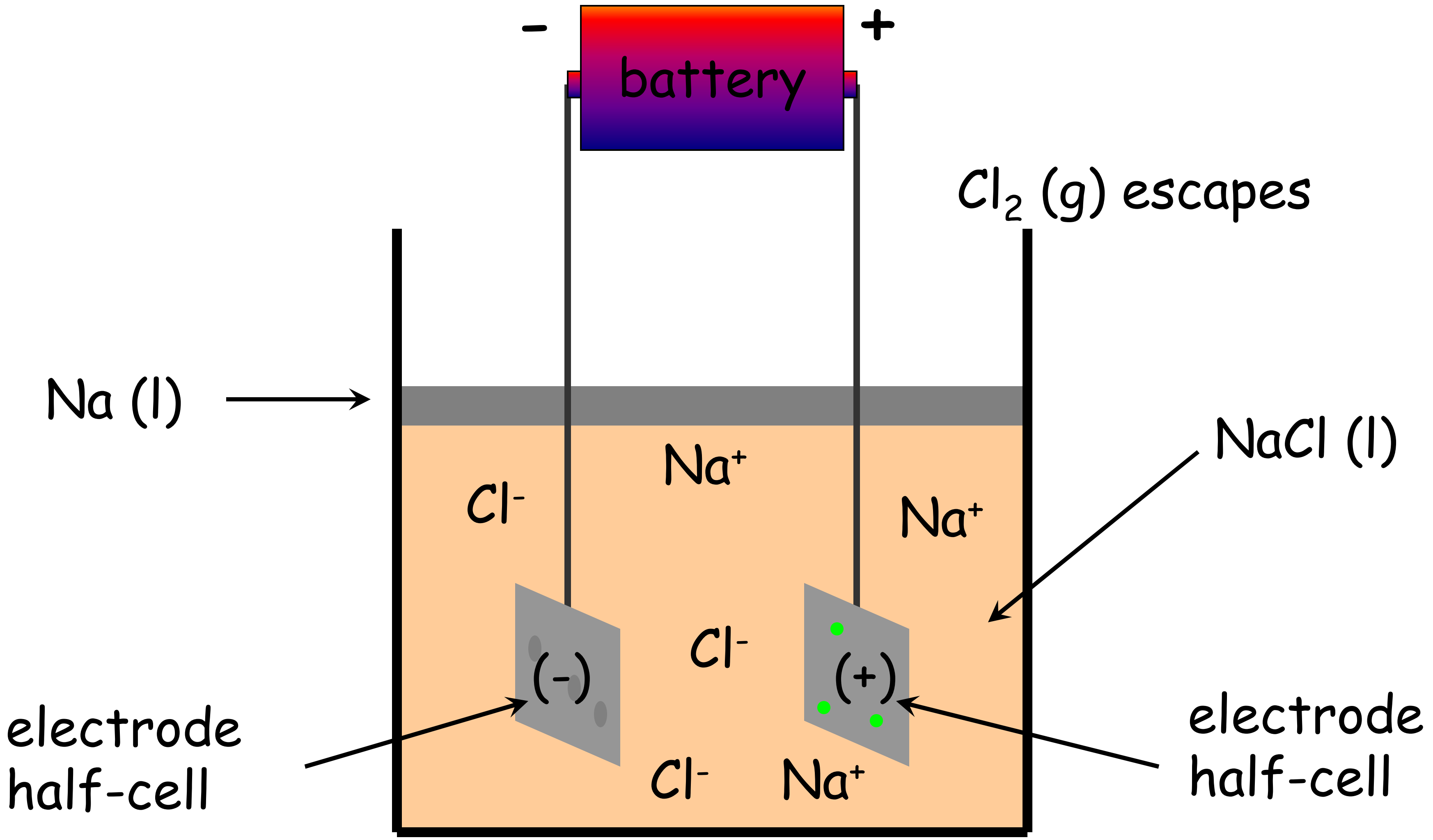
$$\frac{\text{Weight of } M_1 \text{ deposited}}{\text{Weight of } M_2 \text{ deposited}} = \frac{\text{Gram Equivalent weight of } M_1}{\text{Gram Equivalent weight of } M_2}$$

Industrial Applications of Electrolysis

- Production of hydrogen by electrolysis of H_2O.
- Production of Cl_2 by electrolysis of aqueous NaCl solution.
- Manufacture of heavy water
- Electrolytic extraction of metals like Na, K, Mg, Ca, Al etc.
- Electroplating and electrorefining

Molten NaCl

Observe the reactions at the electrodes



- battery +

Cl_2 (g) escapes

Na (l)

NaCl (l)

Na^+ Cl^- Na^+ Cl^- Cl^- Na^+

(-) (+)

electrode half-cell

electrode half-cell

$Na^+ + e^- \rightarrow Na$

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

Molten NaCl Electrolytic Cell

cathode half-cell (-)

REDUCTION $[Na^+ + e^- \rightarrow Na] \times 2$

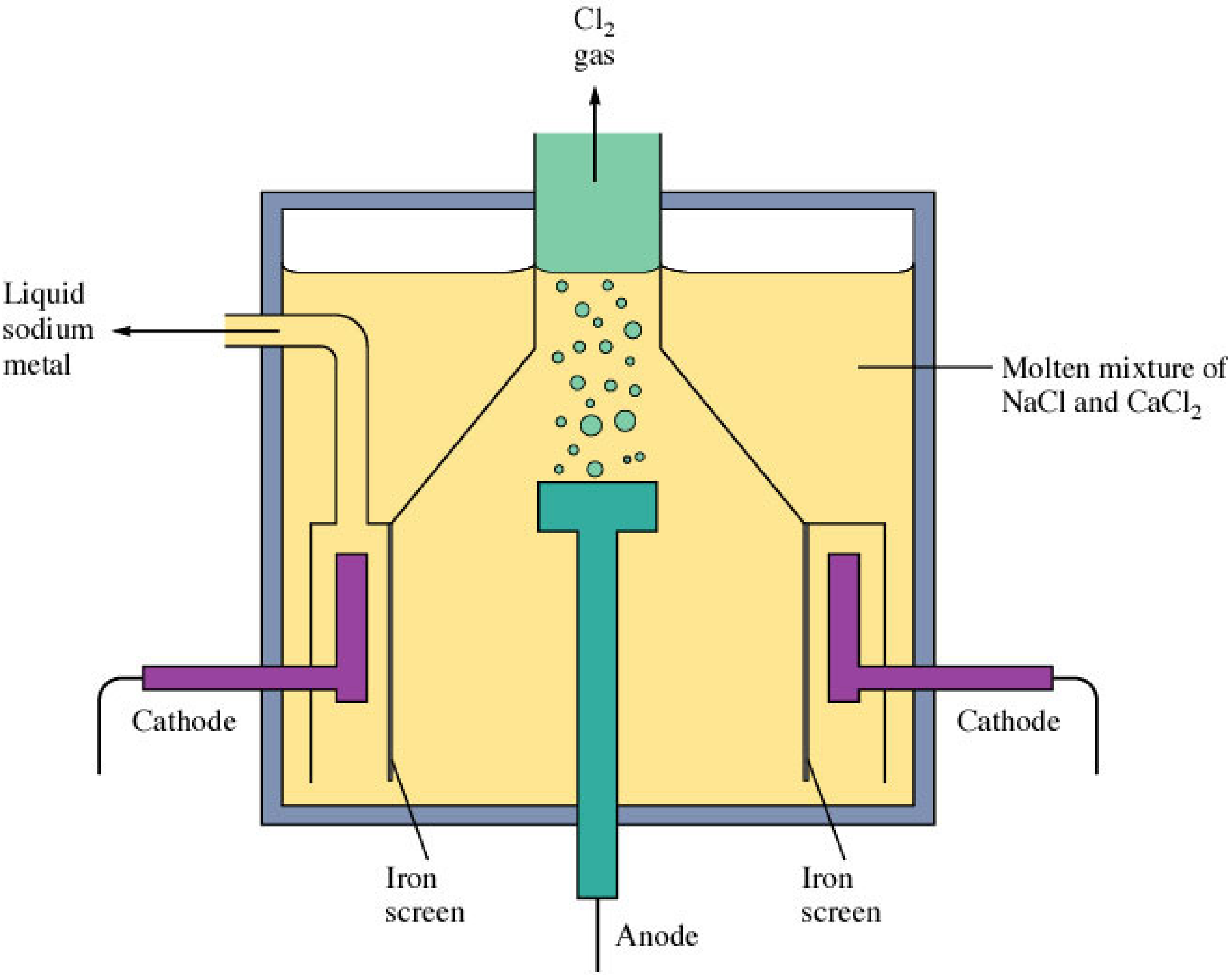
anode half-cell (+)

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

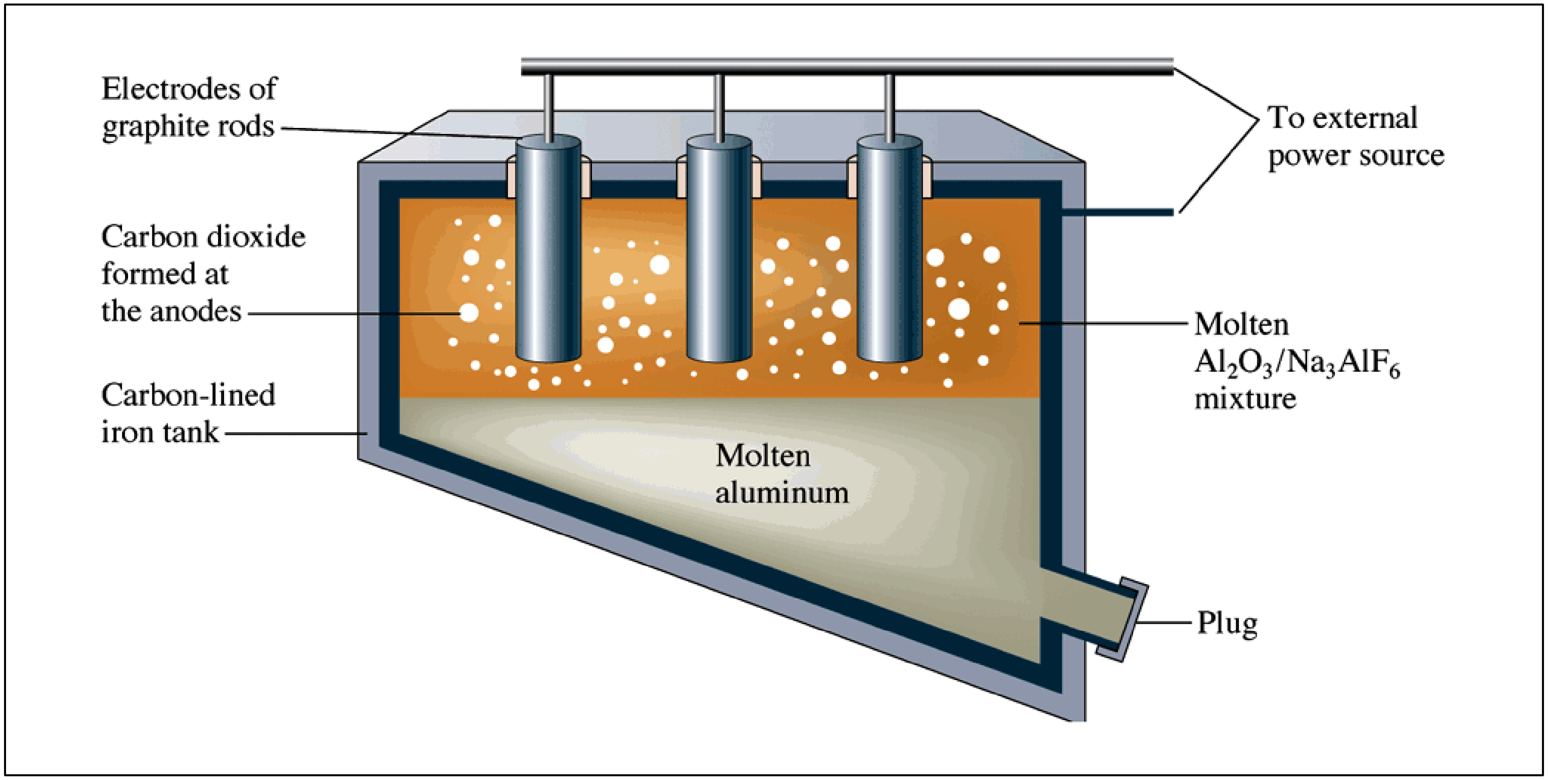
overall cell reaction

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

The Downs Cell for the Electrolysis of Molten Sodium Chloride



A schematic diagram of an electrolytic cell for producing aluminum by the Hall-Heroult process.



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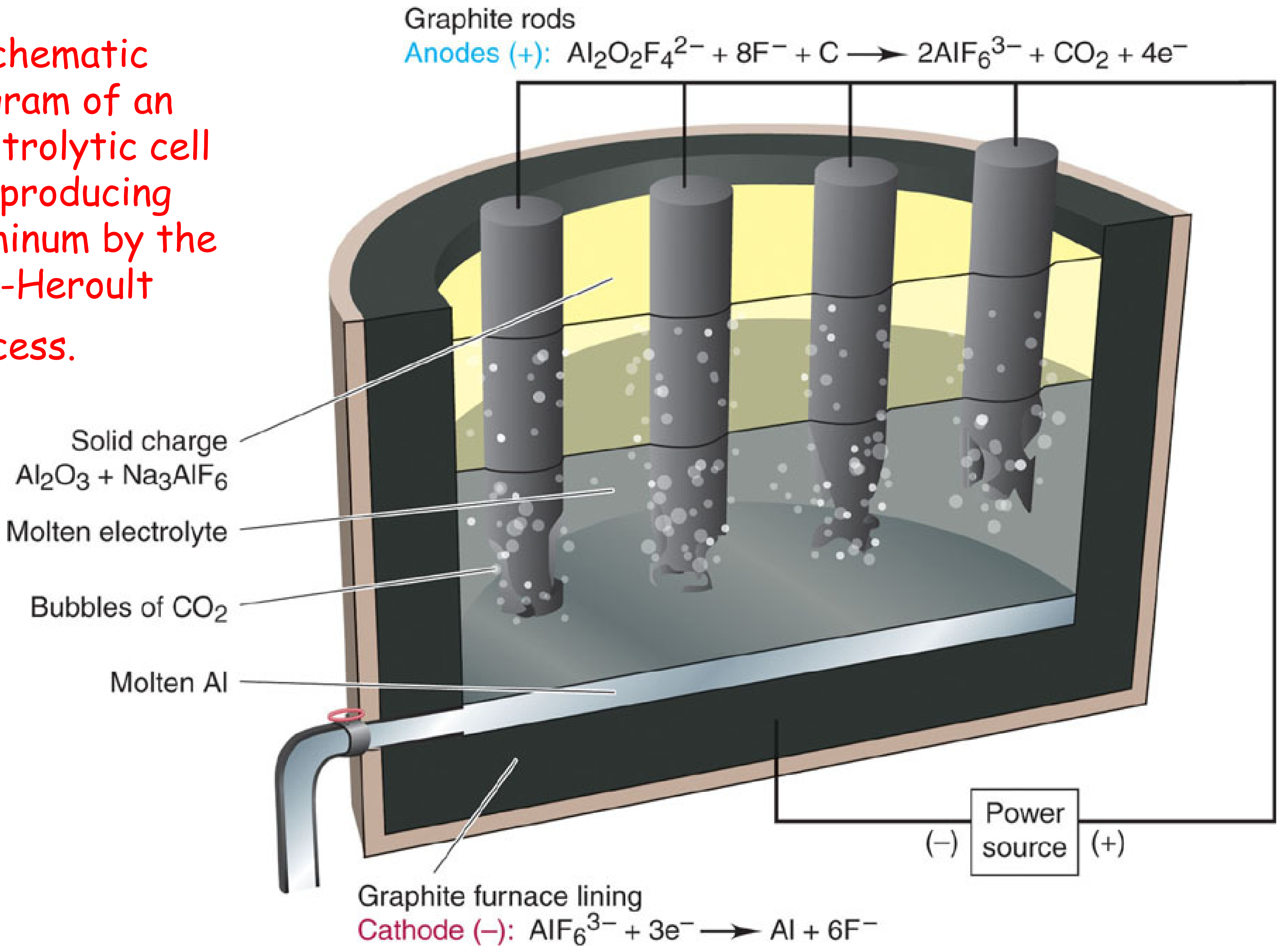
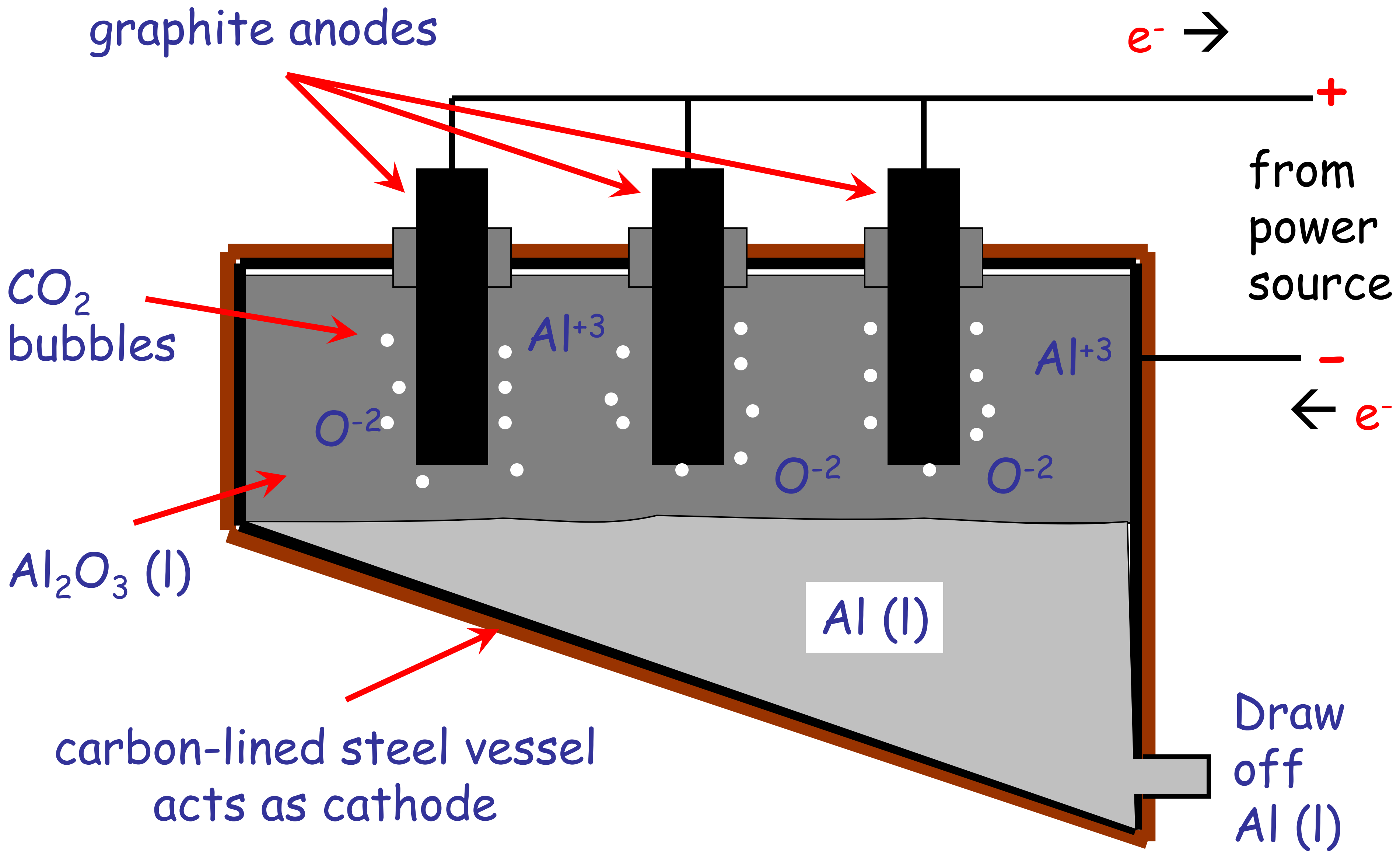




graphite anodes

$e^- \rightarrow$

+

from power source

−

$\leftarrow e^-$

CO_2 bubbles

Al^{+3}

Al^{+3}

O^{-2}

O^{-2}

O^{-2}

Al_2O_3 (l)

Al (l)

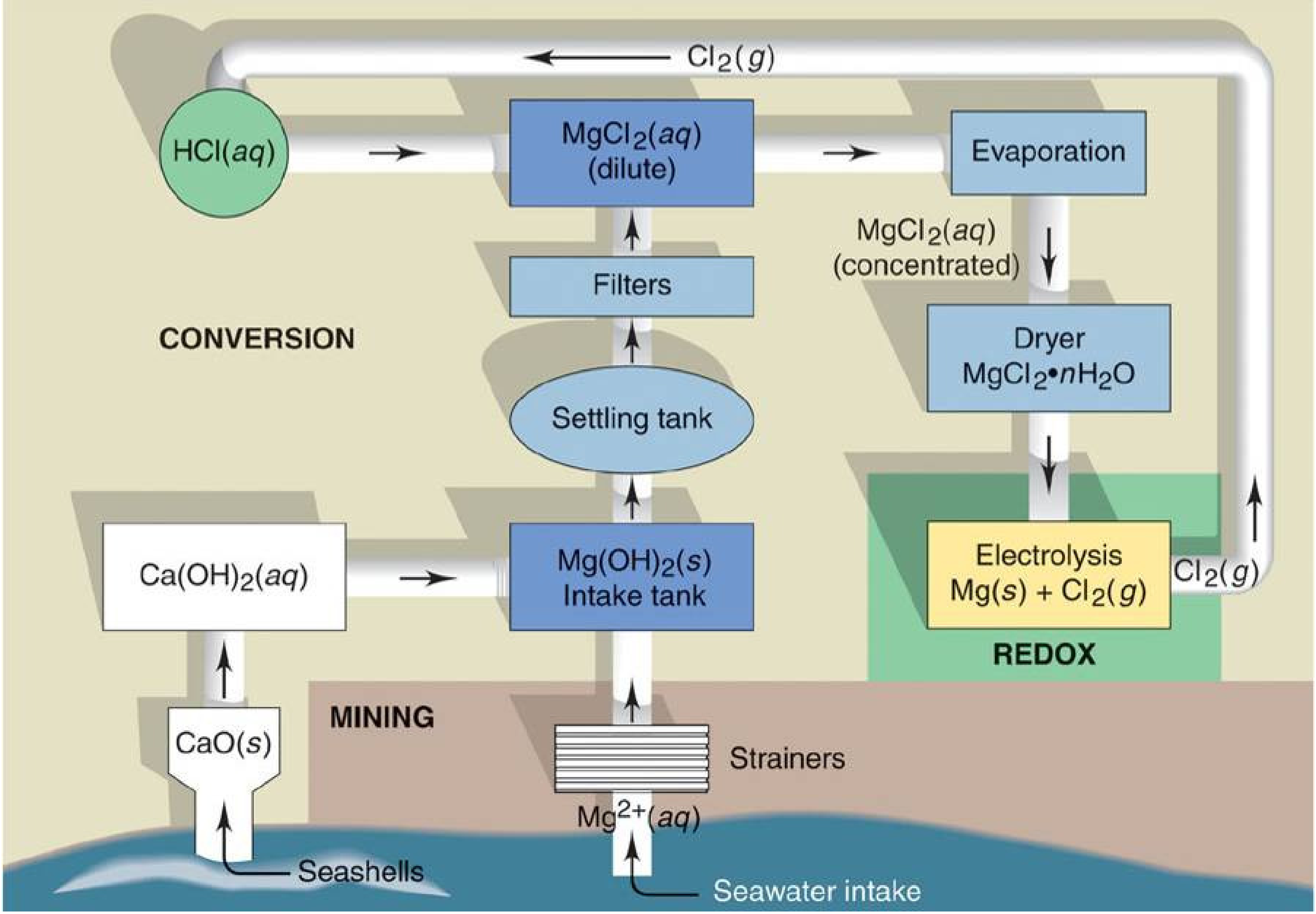
Draw off Al (l)

carbon-lined steel vessel acts as cathode

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

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

Production of solid Mg



Concentration Vs molar conductivity (Λ_m)

The definition and the measurement

➔Conductance *G* in S

$$G = \frac{1}{R} \qquad G = \kappa \frac{A_s}{l}$$

➔*K* in equation is conductivity. **In S m^{-1}**.

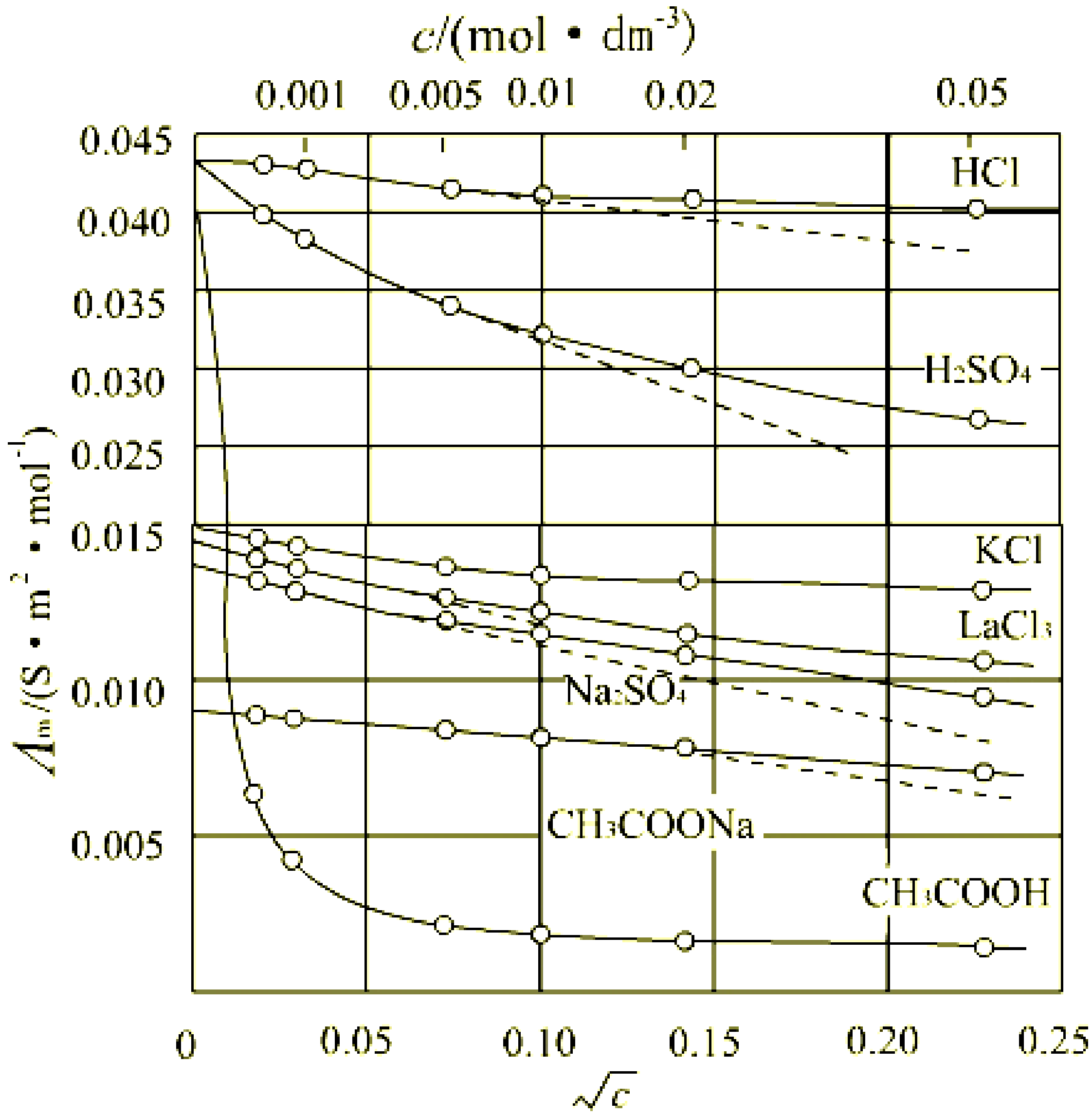
➔Molar conductivity **(in Sm^{2}mol^{-1})**

$$\Lambda_m = \kappa / c$$

Factors affecting the molar conductivity (Λ_m)

- ➔ **Solute – Solute Interaction**
- ➔ **Solute-Solvent Interaction**
- ➔ **Solvent – Solvent Interaction**
- ➔ **Temperature**
- ➔ **Concentration**

Concentration Vs molar conductivity (Λ_m)



Concentration Vs molar conductivity (Λ_m)

- ➔ **Strong Electrolytes:** There is slight increase in molar conductivity with the decrease in concentration.
- ➔ **Weak Electrolytes:** The molar conductivity increases many folds with the decrease in molar conductivity

Concentration Vs molar conductivity (Λ_m)

For strong electrolyte , Kohlrausch observed that Λ_m decreased with concentration according to the expression

$$\Lambda_{\mathrm{m}} = \Lambda_{\mathrm{m}}^{\infty} - A\sqrt{c}$$

Law of the independent migration of ions

➔Kohlrausch discovered relations between the values of Λ_m^∞ for different electrolytes. eg

$$\Lambda_m^\infty(\mathrm{KCl}) = 0.01499\ \mathrm{S \cdot m^2 \cdot mol^{-1}}$$

$$\Lambda_m^\infty(\mathrm{LiCl}) = 0.01150\ \mathrm{S \cdot m^2 \cdot mol^{-1}}$$

$$\Lambda_m^\infty(\mathrm{KNO_3}) = 0.01450\ \mathrm{S \cdot m^2 \cdot mol^{-1}}$$

$$\Lambda_m^\infty(\mathrm{LiNO_3}) = 0.01101\ \mathrm{S \cdot m^2 \cdot mol^{-1}}$$

The difference in for pairs of salts having common ion is always approximately constant.

Applications of Kohlrausch Law

➔To calculate the Λ_m^∞ of weak electrolytes

➔Degree of dissociation $\alpha = \Lambda_m / \Lambda_m^\infty$

➔ Dissociation constant $K = C\alpha^2/1-\alpha$

Lecture summary

- ➔Electrolysis is often the reverse of voltaic cell in that $E_{cell} < 0$, and $\Delta G > 0$ and reaction is non-spontaneous.
- ➔Electrolysis of water and to produce O_2 and H_2.
- ➔**Faraday's law allows us to determine how much current is needed to produce a certain amount of an element.**
- ➔Industrial applications are numerous for producing a variety of solid elements (Al, Mg, Na, etc).