Chapter 11: Oxidations and Reductions

11.1: Oxidation is the Loss of Electrons and Reduction is the Gain of Electrons

Reduction-Oxidation Reactions (***Redox*** **Rxn**): - chemical reactions where there is a transfer of electron(s).

Oxidation Reactions: - reactions that **LOSE Electrons** (**LEO** – "Losing Electrons" – Oxidation).
- an **INCREASE in the number of Oxygen Atoms in the species** is also a sign of an oxidation reaction.

Examples:

$Fe_{(s)} \rightarrow Fe^{3+}_{(aq)} + 3e^-$ **(Lost 3 Electrons - Oxidation)**

$2\ Cr^{3+}_{(aq)} + 7\ H_2O_{(l)} \rightarrow Cr_2O_7^{2-}_{(aq)} + 14\ H^+_{(aq)} + 6e^-$ **(Lost 6 Electrons – Oxidation)**

Reduction Reactions: - reactions that **GAIN Electrons** (**GER** – "Gaining Electrons" – Reduction).
- a **DECREASE in the number of Oxygen Atoms in the species** is also a sign of a reduction reaction.

Examples:

$F_{2\,(g)} + 2e^- \rightarrow 2\ F^-_{(aq)}$ **(Gained 2 Electrons - Reduction)**

$MnO_4^-_{(aq)} + 8\ H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4\ H_2O_{(l)}$ **(Gained 5 Electrons - Reduction)**

Half-Reactions: - part of the redox reaction where it shows either the oxidation reaction or the reduction reaction.
- electrons are usually present in either side of the half-reaction.
- **Oxidation half-reaction has Electrons on the Product Side (Losing Electrons).**
- **Reduction half-reaction has Electrons on the Reactant Side (Gaining Electrons).**

Oxidizing Agent: - a chemical species that **Accepts (Gains) Electrons from an Oxidized species**.
- it helps another species to oxidize but itself being reduced (gained electrons).
- **non-metal elements**, especially **halogens** (F_2, Cl_2, Br_2 and I_2), and **oxyanions** like (ClO_4^-, MnO_4^- and $Cr_2O_7^{2-}$) tend to be **good oxidizing agent**.
- in another words, **Reducing Species = Oxidizing Agent (GER-OA)**

Reducing Agent: - a chemical species that **Donates (Lose) Electrons from a Reduced species**.
- it helps another species to reduce but itself being oxidized (lost electrons).
- **metal elements** (Sn, Cu, Zn, Cr), especially in the **alkali metals, and alkaline earths** (Li, K, Na, Ca, Mg) tend to be **good reducing agent**.
- in another words, **Oxidizing Species = Reducing Agent (LEO-RA)**

Chemical Species that are BOTH Oxidizing Agent and Reducing Agent: - some of the transition metals have more than one monoatomic ionic charges can have the intermediate charge species act as reducing agent as well as oxidizing agent.

Examples: Iron (II), Chromium (II) and Tin (II)

$Fe^{3+} \rightarrow Fe^{2+} \rightarrow Fe_{(s)}$

$Fe^{3+} + e^- \rightarrow \underline{Fe^{2+}}$ $E° = +0.77$ V

$\underline{Fe^{2+}} + 2e^- \rightarrow Fe_{(s)}$ $E° = -0.44$ V

$Cr^{3+} \rightarrow Cr^{2+} \rightarrow Cr_{(s)}$

$Cr^{3+} + e^- \rightarrow \underline{Cr^{2+}}$ $E° = -0.41$ V

$\underline{Cr^{2+}} + 2e^- \rightarrow Cr_{(s)}$ $E° = -0.91$ V

$Sn^{4+} \rightarrow Sn^{2+} \rightarrow Sn_{(s)}$

$Sn^{4+} + 2e^- \rightarrow \underline{Sn^{2+}}$ $E° = +0.15$ V

$\underline{Sn^{2+}} + 2e^- \rightarrow Sn_{(s)}$ $E° = -0.14$ V

$H_2O_{(l)}$ as an Oxidizing Agent (Left Side of the Table)

$2\,H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2\,OH^-$ $E° = -0.83$ V

$H_2O_{(l)}$ as an Reducing Agent (Right Side of the Table)

$O_{2\,(g)} + 4\,H^+ + 4e^- \rightarrow 2\,H_2O_{(l)}$ $E° = +1.23$ V

Balancing Redox Reaction by Half-Reaction Method (For Reactions that are on the Table):

1. **List all the species available** and **identify** them as **oxidizing agents** or **reducing agents** or **both**.
2. **Select the Strongest Oxidizing Agent (SOA) and the Strongest Reducing Agent (SRA) from the Reduction Potential Table (next page).**
3. **Copy the half-reaction for the Strongest Oxidizing Agent. FLIP and COPY the half-reaction of the Strongest Reducing Agent.**
4. **Combine the redox half-reactions by balancing the electrons. There should be electrons on the product side of the oxidation half-reaction and the reactant side of the reduction half-reaction.**

Example 1: Balance the following redox reaction by first selecting the strongest oxidizing and reducing agents and writing the half-reactions.

a. A piece of zinc metal is placed in a solution of silver nitrate solution.

	SOA		OA
Zn,	**Ag^+,**	NO_3^-,	H_2O
SRA			RA

NO_3^- can only be considered as Oxidizing Agents if and only if H^+ is present (acidified).

Reduction Half-Rxn: $2\,(\,Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}\,)$

Oxidation Half-Rxn: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\,e^-$

$$\mathbf{2\,Ag^+_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\,Ag_{(s)}}$$

b. A solution of acidify potassium dichromate is reacted with an iron (II) nitrate solution.

OA	**SOA**	OA	OA	OA	OA
K^+,	**$Cr_2O_7^{2-}$,**	H^+,	Fe^{2+},	NO_3^-,	H_2O
			SRA		RA

$Cr_2O_7^{2-}$ and NO_3^- can only be considered as Oxidizing Agents if and only if H^+ is present (acidified).

Reduction Half-Rxn: $Cr_2O_7^{2-}{}_{(aq)} + 14\,H^+_{(aq)} + 6e^- \rightarrow 2\,Cr^{3+}_{(aq)} + 7\,H_2O_{(l)}$

Oxidation Half-Rxn: $6\,(\,Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-\,)$

$$\mathbf{Cr_2O_7^{2-}{}_{(aq)} + 14\,H^+_{(aq)} + 6\,Fe^{2+}_{(aq)} \rightarrow 6\,Fe^{3+}_{(aq)} + 2\,Cr^{3+}_{(aq)} + 7\,H_2O_{(l)}}$$

c. Tin metal is undergoing corrosion with the presence of oxygen and water.

	SOA	OA
Sn,	**O_2,**	H_2O
SRA		RA

There are other reduction half-reactions involving O_2, but they require H^+, which we don't have. We have to use the O_2 reduction half reaction that contains H_2O.

Reduction Half-Rxn: $O_{2\,(g)} + 2\,H_2O_{(l)} + 4e^- \rightarrow 4\,OH^-_{(aq)}$

Oxidation Half-Rxn: $2\,(\,Sn_{(s)} \rightarrow Sn^{2+}_{(aq)} + 2e^-\,)$

$$\mathbf{O_{2\,(g)} + 2\,H_2O_{(l)} + 2\,Sn_{(s)} \rightarrow 2\,Sn^{2+}_{(aq)} + 4\,OH^-_{(aq)}}$$

Table of Selected Standard Electrode Potentials*

Oxidizing Agents: Strongest (top) ↑ Weakest (bottom)

Reducing Agents: Weakest (top) ↓ Strongest (bottom)

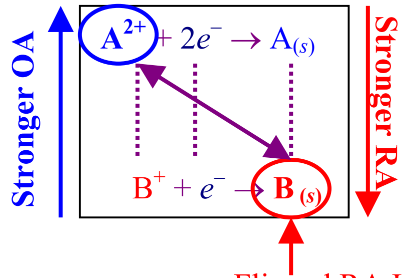
Reduction Half-Reaction	Electrical Potential (V) E°
$F_{2(g)} + 2e^- \rightleftharpoons 2F^-_{(aq)}$	+2.87
$PbO_{2(s)} + SO_{4(aq)}^{2-} + 4H^+_{(aq)} + 2e^- \rightleftharpoons PbSO_{4(s)} + 2H_2O_{(l)}$	+1.69
$MnO_{4(aq)}^- + 8H^+_{(aq)} + 5e^- \rightleftharpoons Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.51
$Au^{3+}_{(aq)} + 3e^- \rightleftharpoons Au_{(s)}$	+1.50
$ClO_{4(aq)}^- + 8H^+_{(aq)} + 8e^- \rightleftharpoons Cl^-_{(aq)} + 4H_2O_{(l)}$	+1.39
$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$	+1.36
$2HNO_{2(aq)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons N_2O_{(g)} + 3H_2O_{(l)}$	+1.30
$Cr_2O_{7(aq)}^{2-} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.23
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(l)}$	+1.23
$MnO_{2(aq)} + 4H^+_{(aq)} + 2e^- \rightleftharpoons Mn^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.22
$Br_{2(l)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$	+1.07
$Hg^{2+}_{(aq)} + 2e^- \rightleftharpoons Hg_{(l)}$	+0.85
$OCl^-_{(aq)} + H_2O_{(l)} + 2e^- \rightleftharpoons Cl^-_{(aq)} + 2OH^-_{(aq)}$	+0.84
$2NO_{3(aq)}^- + 4H^+_{(aq)} + 2e^- \rightleftharpoons N_2O_{4(g)} + 2H_2O_{(l)}$	+0.80
$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2O_{2(l)}$	+0.70
$I_{2(s)} + 2e^- \rightleftharpoons 2I^-_{(aq)}$	+0.54
$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightleftharpoons 4OH^-_{(aq)}$	+0.40
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$SO_{4(aq)}^{2-} + 4H^+_{(aq)} + 2e^- \rightleftharpoons H_2SO_{3(aq)} + H_2O_{(l)}$	+0.17
$Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)}$	+0.15
$S_{(s)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2S_{(aq)}$	+0.14
$AgBr_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Br^-_{(aq)}$	+0.07
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$	0.00
$Pb^{2+}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)}$	−0.13
$Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)}$	−0.14
$AgI_{(s)} + e^- \rightleftharpoons Ag_{(s)} + I^-_{(aq)}$	−0.15
$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$	−0.26
$Co^{2+}_{(aq)} + 2e^- \rightleftharpoons Co_{(s)}$	−0.28
$PbSO_{4(s)} + 2e^- \rightleftharpoons Pb_{(s)} + SO_{4(aq)}^{2-}$	−0.36
$Se_{(s)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2Se_{(aq)}$	−0.40
$Cd^{2+}_{(aq)} + 2e^- \rightleftharpoons Cd_{(s)}$	−0.40
$Cr^{3+}_{(aq)} + e^- \rightleftharpoons Cr^{2+}_{(aq)}$	−0.41
$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$	−0.45
$NO_{2(aq)}^- + H_2O_{(l)} + e^- \rightleftharpoons NO_{(g)} + 2OH^-_{(aq)}$	−0.46
$Ag_2S_{(s)} + 2e^- \rightleftharpoons 2Ag_{(s)} + S^{2-}_{(aq)}$	−0.69
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	−0.76
$2H_2O_{(l)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)}$	−0.83
$Cr^{2+}_{(aq)} + 2e^- \rightleftharpoons Cr_{(s)}$	−0.91
$Se_{(s)} + 2e^- \rightleftharpoons Se^{2-}_{(aq)}$	−0.92
$SO_{4(aq)}^{2-} + H_2O_{(l)} + 2e^- \rightleftharpoons SO_{3(aq)}^{2-} + 2OH^-_{(aq)}$	−0.93
$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$	−1.66
$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$	−2.37
$Na^+_{(aq)} + e^- \rightleftharpoons Na_{(s)}$	−2.71
$Ca^{2+}_{(aq)} + 2e^- \rightleftharpoons Ca_{(s)}$	−2.87
$Ba^{2+}_{(aq)} + 2e^- \rightleftharpoons Ba_{(s)}$	−2.91
$K^+_{(aq)} + e^- \rightleftharpoons K_{(s)}$	−2.93
$Li^+_{(aq)} + e^- \rightleftharpoons Li_{(s)}$	−3.04

*For 1.0 mol/L solutions at 298.15 K (25°C) and a pressure of 101.325 kPa

Procedure to Predict Spontaneity Redox Reactions Under Standard Conditions:

1. Locate the chemical species on the Table of Relative Strength of Standard Reduction Potentials. There should be one on the Left Side of the table and one on the right side. The reactions represent the reduction and oxidation half-reactions of the redox reaction.

2. **Spontaneous Reaction**: - redox reactions that **will proceed forward** where chemical energy converts to electrical energy.
   - the **Oxidizing Agent (OA) on the LEFT is HIGHER than the Reducing Agent (RA) on the RIGHT**.
   - **FLIP the Reducing Agent – Oxidation Half-Reaction (LOWER Half-Reaction) and ADD the two half-reactions by balancing the electrons**.



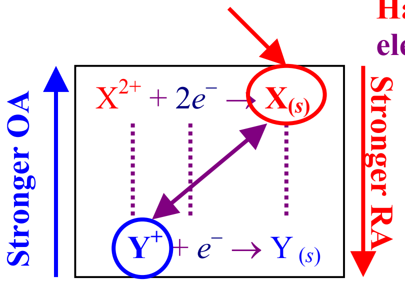
Flipped RA Half-Rxn

A^{2+} will react with $B_{(s)}$

$$\begin{array}{ll} A^{2+} + 2e^- \rightarrow A_{(s)} & \text{(Reduction)} \\ \underline{2\,(B_{(s)} \rightarrow B^+ + e^-)} & \text{(Oxidation)} \\ A^{2+} + 2\,B_{(s)} \rightarrow 2\,B^+ + A_{(s)} & \textbf{(Spontaneous)} \\ \textbf{OA} \quad \textbf{RA} & \end{array}$$

3. **Non-Spontaneous Reaction**: - redox reactions that **will NOT proceed forward** unless there is an eternal energy source to start and maintain the chemical reaction.
   - the **Oxidizing Agent (OA) on the LEFT is LOWER than the Reducing Agent (RA) on the RIGHT**.
   - **FLIP the Reducing Agent – Oxidation Half-Reaction (HIGHER Half-Reaction) and ADD the two half-reactions by balancing the electrons.**

Flipped RA Half-Rxn



$X_{(s)}$ will NOT react with Y^+

$$\begin{array}{ll} 2\,(Y^+ + e^- \rightarrow Y_{(s)}) & \text{(Reduction)} \\ \underline{X_{(s)} \rightarrow X^{2+} + 2e^-} & \text{(Oxidation)} \\ 2\,Y^+ + X_{(s)} \rightarrow \textbf{Non-Spontaneous} & \\ \textbf{OA} \quad \textbf{RA} & \end{array}$$

Example 2: Predict the whether the following reactions will react and write the complete redox reactions.

a. $Br_{2\,(l)}$ with $Ni_{(s)}$

$Br_{2\,(l)} + 2e^- \rightarrow 2\,Br^-_{(aq)}$ $E° = 1.07$ V
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ $E° = -0.25$ V

Since Br_2 (OA) is higher than Ni (RA), the reaction will be spontaneous.

$$\begin{array}{l} Br_{2\,(l)} + 2e^- \rightarrow 2\,Br^-_{(aq)} \\ \underline{Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-} \\ Br_{2\,(l)} + Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2\,Br^-_{(aq)} \end{array}$$

b. $Au_{(s)}$ with $Fe^{3+}_{(aq)}$

$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$ $E° = 1.50$ V
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$ $E° = 0.77$ V

Since Fe^{3+} (OA) is lower than Au (RA), the reaction will be non-spontaneous.

$$\begin{array}{l} 3\,(Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}) \\ \underline{Au_{(s)} \rightarrow Au^{3+}_{(aq)} + 3e^-} \\ 3\,Fe^{3+}_{(aq)} + Au_{(s)} \rightarrow \text{No Reaction} \end{array}$$

Because **gold does not oxidized easily**, this is the main reason why gold is so valuable!

Assignment
11.1 pg. 358 #1 to 5

11.3: The Energy of Flowing Electrons can be Harnessed

Electrochemistry: - the branch of chemistry that studies the relationship between chemical energy and electrical energy.

Electrochemical Cells: - an apparatus that **Converts Chemical Energy *to* Electrical Energy**.
- commonly known as **Galvanic Cells** or **Voltaic Cells**.
- it consists of two containers of solutions (electrolytes) and the electrodes (usually metals called anode and cathode), as well as a connection between these two containers (salt bridge, porous cup, or porous disk), and a wire connecting the two electrodes.

Electrodes: - metals or other elements that serve as the site of redox reactions in a galvanic cell.
- in the case of a gaseous or liquid element, a carbon rod or platinum plating (inert material) is used as the solid electrode.

Anode: - the terminal where **oxidation** is taken place and commonly marked as the **Negative terminal**.
(LEOA–RA: Losing Electrons Oxidation Anode – Reducing Agent)

Cathode: - the terminal where **reduction** is taken place and commonly marked as the **Positive terminal**.
(GERC–OA: Gaining Electrons Reduction Cathode – Oxidizing Agent)

Salt Bridge: - an upside down U-tube filled with electrolytes like $KCl_{(aq)}$ to prevent charge build-up. (The ions in the salt bridge do NOT get mixed into the half-cells, nor do the electrolytes in the half-cells travelled into the salt bridge.)
- also serves as the separator between the two half cells.
- other equipment like **porous disk** and **porous cup (clay porcelain cup)** can be used instead of a salt bridge.

Cell Potential (**E_{cell}**): - sometimes called **electromotive force (emf)**.
- the amount of **electrical energy in terms of electric charges**.

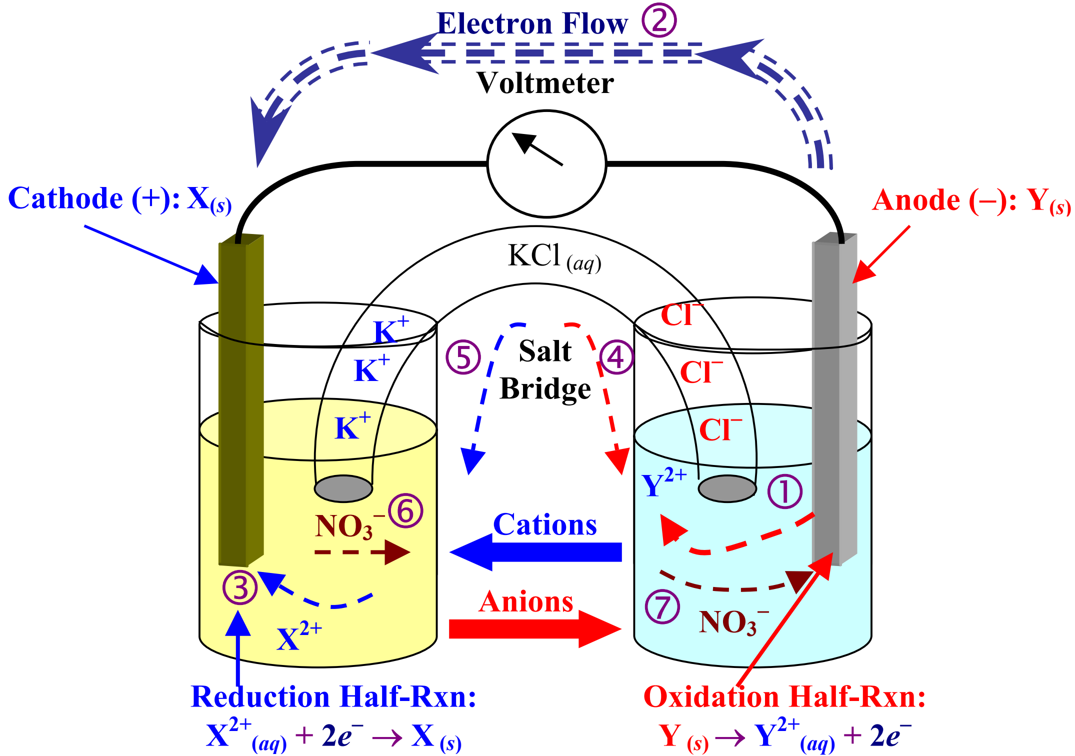
Volts (**V**): - the amount of **work (energy) in J per charge (q) coulomb (unit symbol: C) of electrons** transferred between two potentials (anode and cathode).
- commonly refer to as **potential difference**.

Potentiometer: - a electric device that measures potential difference between the cathode and anode.
- sometimes refer to as a **voltmeter**.

Galvanic Cells

1. **Electrons move *from* Anode (–) *to* Cathode (+).**
2. **Cations move *towards* the Cathode.**
3. **Anions move *towards* the Anode.**

Anode (–): (LEOA–RA: Losing Electrons Oxidation Anode – Reducing Agent)
Cathode (+): (GERC–OA: Gaining Electrons Reduction Cathode – Oxidizing Agent)



(Above) A typical electrochemical cells with a salt bridge using an upside down U-tube.

Check out Voltaic Cell Animations at

(http://www.sgc.peachnet.edu/users/larnold/WWW/courses/1212/rev1212.html)

Galvanic Cell Step by Step

① Y^{2+} leaves $Y_{(s)}$ at the Anode.

② Electrons produced at the Anode (–) move to Cathode (+) causing a potential difference that is measured by the voltmeter.

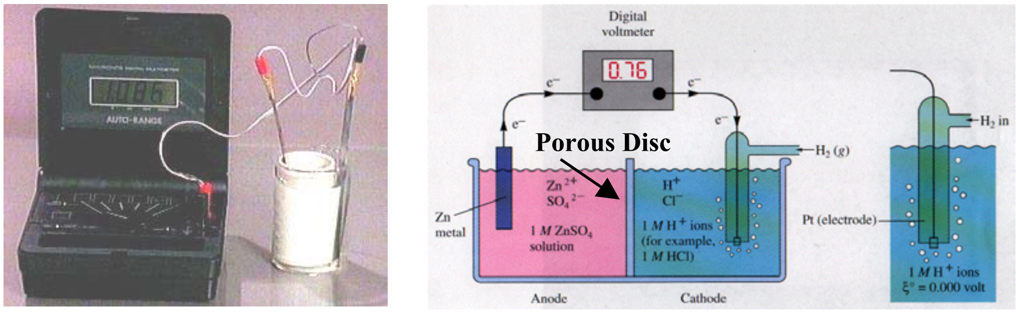
③ Electrons arrived at the Cathode combining with X^{2+} to form $X_{(s)}$.

④ Cl^- from the salt bridge migrate towards the anode half-cells to counteract charge buildup by Y^{2+}

⑤ As a result, K^+ from the salt bridge travel towards the cathode half-cell

⑥ NO_3^- (anions to bring in cations electrolytes into the half-cells) in the cathode half-cell moves toward the salt bridge (and thus towards the anode) because of K^+ charge buildup inside the salt bridge.

⑦ Similarly, NO_3^- in the anode half-cell moves towards the anode because the anode metal is becoming too positive (electrons are leaving at the anode metal).



Galvanic cells using a porous cup (left) and platinum electrode because of the gaseous cathode (right).

Standard Hydrogen Potential: - the reduction potential of hydrogen ions to hydrogen gas is assigned a voltage of 0 at standard conditions (25°C and 1 atm).

$$(2H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)} \qquad E° = 0.00\text{ V})$$

Standard Reduction Potential: - the electric potentials of reduction half-reactions as compared with hydrogen under standard condition (25°C and 1.0 mol/L of electrolytes or 1.0 atm of gaseous element (*see Table pg 140*).

- since the table are of reduction half reactions, the **strongest oxidizing agent is listed on the left and decreasing in strength as one moves down the table**. ($F_{2\,(g)}$ is the most electronegative element, and thereby is the strongest oxidizing agent – likes to gain electrons.)
- conversely, the **weakest reducing agent is listed on the right and increasing as one moves down the table**. (Since Alkali metals like to lose electrons, they make excellent reducing agents.)
- metals are reducing agents as they prefer to lose electrons to become cations (oxidation).
- non-metals (especially halogens) are usually oxidizing agent as they tend to gain electrons to become anions (reduction).
- strong oxidizing for common laboratory agents are acidify MnO_4^- and $Cr_2O_7^{2-}$.

Standard Cell Potential: - the cell potential under standard conditions ($E°_{cell} = E°_{cathode} + E°_{anode}$)

- when Flipping the Reducing Agent's Half-Reaction, **reverse the Sign of $E°$ to obtain $E°_{anode}$**.
- **do NOT Multiply $E°$ when using electrons to balance complete redox reactions**.

Line Notation: - a notation using lines to represent the electrode and electrolytes as well as the half-cell separations of a galvanic cell.

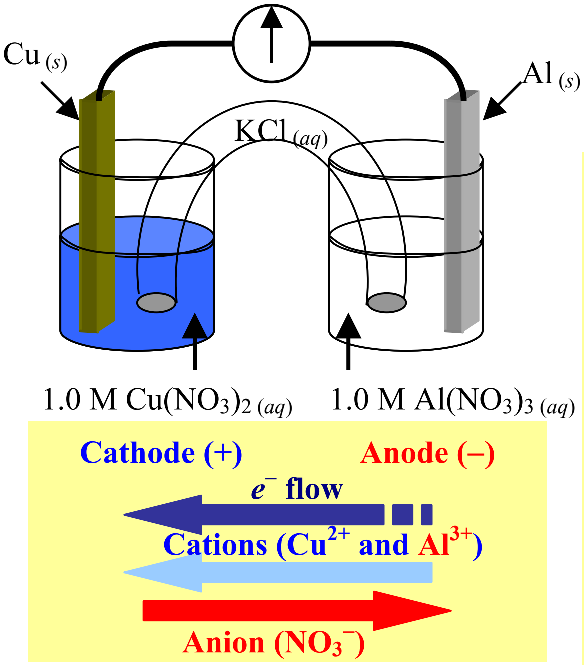
- single line, | , separates electrode and its electrolyte; double line, || , represents salt bridge, porous cup or porous disk.
- **ALWAYS write the Anode on the LEFT hand side.**

Line Notation and Standard Cell Potential of Galvanic Cells

Anode | Anode's Electrolyte || Cathode's Electrolyte | Cathode

$E°_{cell} = E°_{cathode} + E°_{anode}$ **($E°_{cell} > 0$ means Spontaneous Reaction)**

Example 1: For a galvanic cell using copper and aluminum electrodes as shown below, identify anode and cathode. Indicate movements of ions and electrons. Write the line notation and calculate the standard cell potential.



$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $E° = 0.34$ V

$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$ $E° = -1.66$ V

Since the half-reactions for $Cu_{(s)}$ is higher than $Al_{(s)}$, Cu^{2+} will be reduced ($Cu_{(s)}$ is the Cathode) and $Al_{(s)}$ will be oxidized (Anode – flipped half-reaction and voltage).

$$3\,(Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}) \qquad E° = 0.34 \text{ V}$$

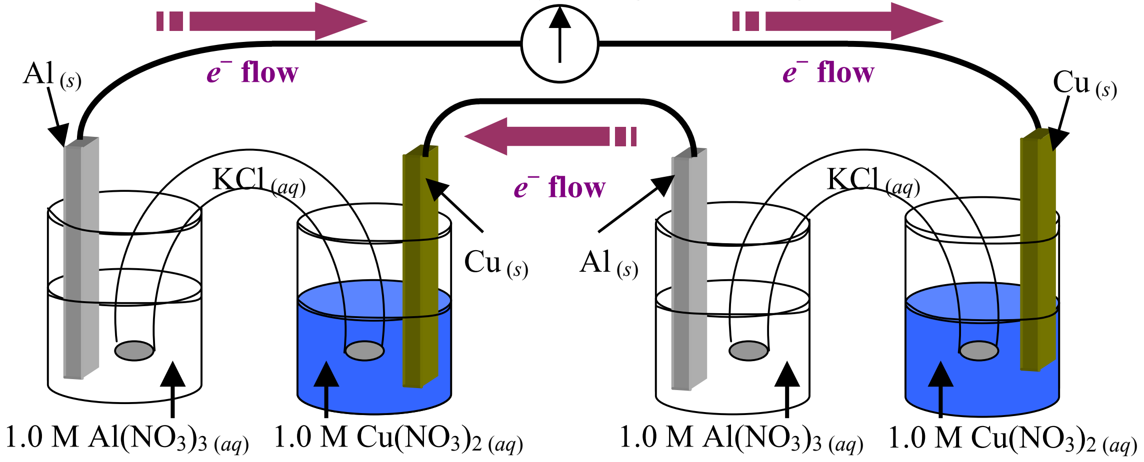
$$2\,(Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-) \qquad E° = +1.66 \text{ V}$$

$$3\,Cu^{2+}_{(aq)} + 2\,Al_{(s)} \rightarrow 2\,Al^{3+}_{(aq)} + 3\,Cu_{(s)} \qquad E°_{cell} = 2.00 \text{ V}$$

Note: We do NOT multiply $E°$.

Line Notation: $Al_{(s)} \mid Al^{3+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

Batteries: - portable galvanic cells that are commonly in **series** (cells that connect in a way such that the potential difference can be added to yield a greater voltage).



Anode (–) **Cathode (+)** **Anode (–)** **Cathode (+)**

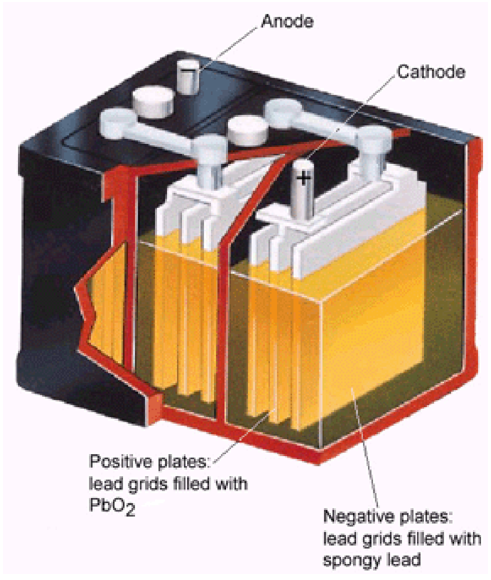
$$3\,(\mathrm{Cu^{2+}}_{(aq)} + 2e^- \rightarrow \mathrm{Cu}_{(s)}) \qquad E° = 0.34\ \mathrm{V}$$
$$2\,(\mathrm{Al}_{(s)} \rightarrow \mathrm{Al^{3+}}_{(aq)} + 3e^-) \qquad E° = +1.66\ \mathrm{V}$$
$$3\,\mathrm{Cu^{2+}}_{(aq)} + 2\,\mathrm{Al}_{(s)} \rightarrow 2\,\mathrm{Al^{3+}}_{(aq)} + 3\,\mathrm{Cu}_{(s)} \qquad E°_{cell} = 2.00\ \mathrm{V}$$

$$3\,(\mathrm{Cu^{2+}}_{(aq)} + 2e^- \rightarrow \mathrm{Cu}_{(s)}) \qquad E° = 0.34\ \mathrm{V}$$
$$2\,(\mathrm{Al}_{(s)} \rightarrow \mathrm{Al^{3+}}_{(aq)} + 3e^-) \qquad E° = +1.66\ \mathrm{V}$$
$$3\,\mathrm{Cu^{2+}}_{(aq)} + 2\,\mathrm{Al}_{(s)} \rightarrow 2\,\mathrm{Al^{3+}}_{(aq)} + 3\,\mathrm{Cu}_{(s)} \qquad E°_{cell} = 2.00\ \mathrm{V}$$

Total Voltage = 2.00 V + 2.00 V = 4.00 V

Different Types of Batteries:

1. **Lead-Acid Battery**: - a **rechargeable battery** commonly used in automobiles to start and maintain the sparks needed for the combustion of the gasoline engine.
   - consists of **Pb $_{(s)}$ as the anode** and **PbO$_2$ $_{(s)}$ as the cathode** in an **acidic (H$_2$SO$_4$ $_{(aq)}$) environment**. (Since solid lead is used, the lead-acid battery tends to be heavy. The **sulfuric acid** used in this type of battery is commonly known as **battery acid**.)
   - the battery is **in series with six identical galvanic cells** giving it 6 × 2V = **12 V** of potential difference.



A typical lead-acid battery for automobiles (above) and its inner working (right)

Lead-Acid Battery Redox Reaction for One of the Six Identical Cells

(Reduction) $PbO_{2\,(s)} + HSO_4^{-}{}_{(aq)} + 3\,H^{+}{}_{(aq)} + 2e^{-} \rightarrow PbSO_{4\,(s)} + 2\,H_2O_{(l)}$ $E° = 1.69\text{ V}$ (Cathode)

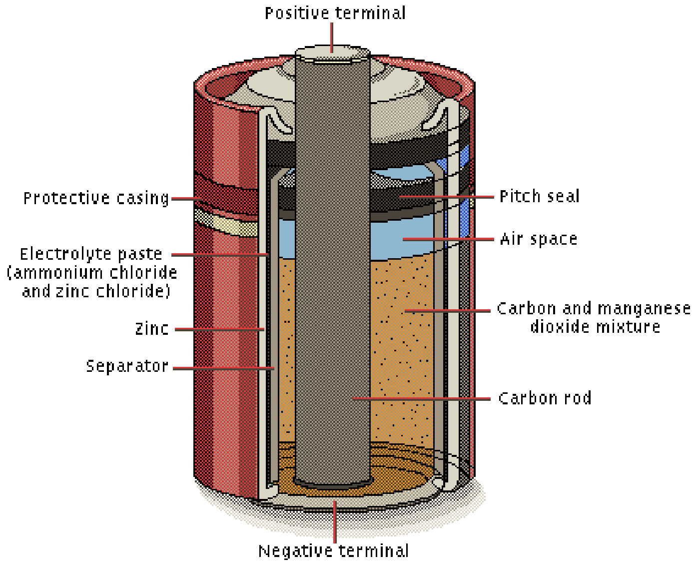
(Oxidation) $\underline{Pb_{(s)} + HSO_4^{-}{}_{(aq)} \rightarrow PbSO_{4\,(s)} + H^{+}{}_{(aq)} + 2e^{-}}$ $\underline{E° = +0.35\text{ V}}$ (Anode)

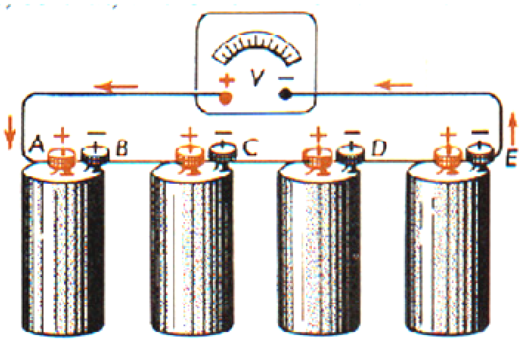
$$\mathbf{PbO_{2\,(s)} + Pb_{(s)} + 2\,HSO_4^{-}{}_{(aq)} + 2\,H^{+}{}_{(aq)} \rightarrow 2\,PbSO_{4\,(aq)} + 2\,H_2O_{(l)}} \qquad \underline{E°_{cell} = 2.04\text{ V}}$$

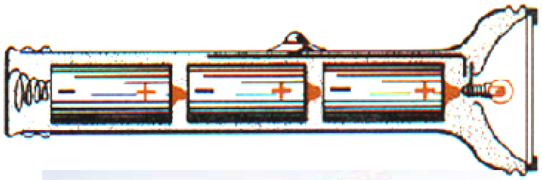
2. **Dry Cell**: - a **non-rechargeable battery** commonly used in electronic devices such as, radios, calculators, and electronic toys.

   a. **Zinc-Carbon Dry Cell**: - consists of **$Zn_{(s)}$ as the anode** and both **$MnO_{2\,(s)}$ (cathode with a carbon rod)** and the **acid ($NH_4Cl_{(s)}$)** are in a **dry paste** – hence the term **"dry"** cell.

   b. **Alkaline Dry Cell**: - in a **basic environment**, the NH_4Cl is replaced with NaOH or KOH, and zinc oxidized to $ZnO_{(s)}$ at the anode.
   - some dry cell battery is **in series with six identical Zn-C or alkaline dry cells**, giving it 6 × 1.5V = **9 V** of total potential difference.







A cutaway view of an acidic Zn-C dry cell (above). When dry cells are connected in series, their voltages can be added (top right). The inside of a 9 V battery reveals that there are six 1.5 V Zn-C dry cells connected in series (right).

Redox Reaction for an Acidic Zinc-Carbon Dry Cell Battery

(Reduction) $2\,MnO_{2\,(s)} + 2\,NH_4^{+}{}_{(aq)} + 2e^{-} \rightarrow Mn_2O_{3\,(s)} + 2\,NH_{3\,(aq)} + H_2O_{(l)}$ $E°_{cathode} = 0.78\text{ V}$

(Oxidation) $\underline{Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^{-}}$ $\underline{E°_{anode} = +0.76\text{ V}}$

$$\mathbf{2\,MnO_{2\,(s)} + Zn_{(s)} + 2\,NH_4^{+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + Mn_2O_{3\,(s)} + 2\,NH_{3\,(aq)} + H_2O_{(l)}} \qquad \underline{E°_{cell} = 1.54\text{ V}}$$

Redox Reaction for a Basic (Alkaline) Zinc-Carbon Dry Cell Battery

(Reduction) $2\,MnO_{2\,(s)} + H_2O_{(l)} + 2e^{-} \rightarrow Mn_2O_{3\,(s)} + 2\,OH^{-}{}_{(aq)}$ $E°_{cathode} = 0.78\text{ V}$

(Oxidation) $\underline{Zn_{(s)} + 2\,OH^{-}{}_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^{-}}$ $\underline{E°_{anode} = +0.76\text{ V}}$

$$\mathbf{2\,MnO_{2\,(s)} + Zn_{(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3\,(s)}} \qquad \underline{E°_{cell} = 1.54\text{ V}}$$

c. **Nickel Cadmium Battery**: - a dry cell with the same set up as alkaline dry cell but it can be **recharged** (a lot lighter than lead-acid batteries).

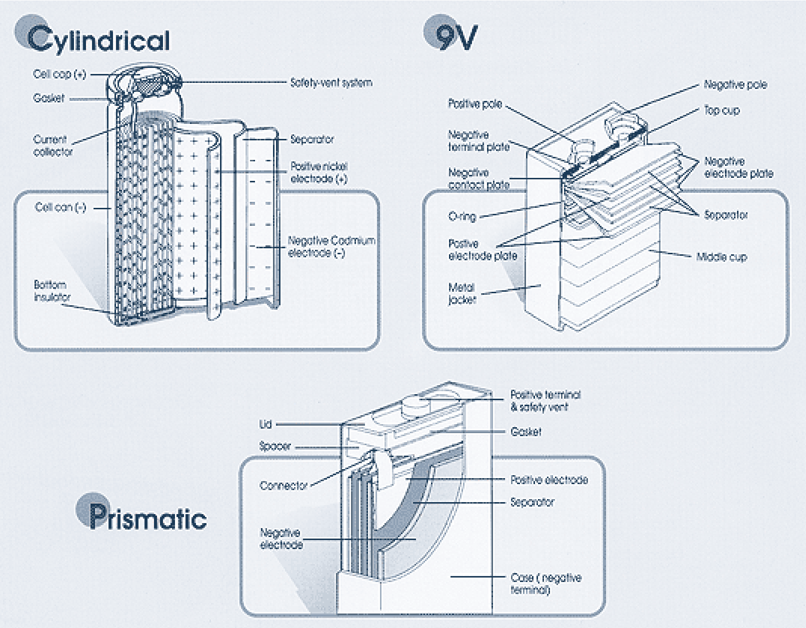
- it can developed a "*memory*" problem, so after each recharged cycled, the battery tends to have a shorter "life-span". This can be corrected by completely discharging the battery before recharging it fully for the next usage cycle.
- cadmium is an expensive metal, and cannot be disposed easily due to its toxicity. Special care must be taken to recycle Ni-Cd batteries.

Redox Reaction for a Ni-Cd Dry Cell Battery

(Reduction) $NiO_{2\,(s)} + 2\,H_2O_{(l)} + \mathbf{2e^-} \rightarrow Ni(OH)_{2\,(s)} + 2\,OH^-_{(aq)}$ $E^\circ_{cathode} = -0.49$ V

(Oxidation) $Cd_{(s)} + 2\,OH^-_{(aq)} \rightarrow Cd(OH)_{2\,(s)} + \mathbf{2e^-}$ $E^\circ_{anode} = +1.74$ V

$\mathbf{NiO_{2\,(s)} + Cd_{(s)} + 2\,H_2O_{(l)} \rightarrow Cd(OH)_{2\,(s)} + Ni(OH)_{2\,(s)}}$ $E^\circ_{cell} = 1.25$ V



Ni-Cd Rechargeable Batteries has E°_{cell} = 1.2 V (above). The cell constructions of various Ni-Cd batteries (left).

d. **Nickel Metal-Hydride Battery**: - a rechargeable dry cell that does not have a "memory" problem and can last 40 times longer than the Ni-Cd battery.

- the expensive and toxic cadmium is replaced by an inexpensive and environmentally friendly **metal-hydride** (a mixture of many metals alloys, including V, Ti, Zr, Ni, Cr, Co, and Fe).
- Ni-MH batteries are used in cellular phones, digital cameras, laptop computers, emergency backup lightings, power tools and even electric vehicles.
- its design is similar to that of the Ni-Cd battery and yields the same E°_{cell}.

Ni-MH batteries are a popular power source for portable electronic devices such as digital cameras.

Redox Reaction for a Ni-MH Dry Cell Battery

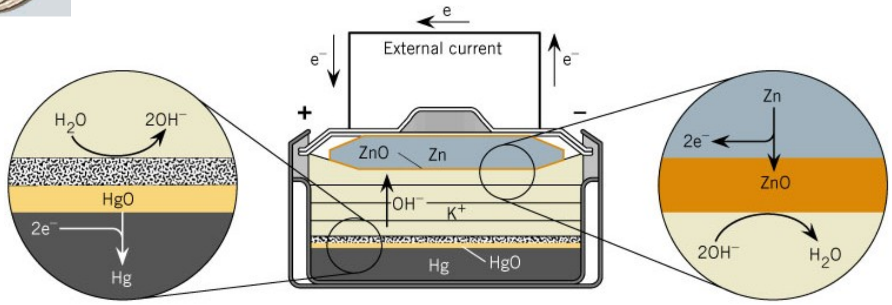
(Reduction) $NiOOH_{(s)} + H_2O_{(l)} + \mathbf{e^-} \rightarrow Ni(OH)_{2\,(s)} + OH^-_{(aq)}$ $E^\circ_{cathode} = -0.52$ V

(Oxidation) $MH_{(s)} + OH^-_{(aq)} \rightarrow M_{(s)} + H_2O_{(l)} + \mathbf{e^-}$ $E^\circ_{anode} = +0.73$ V

$\mathbf{NiOOH_{(s)} + MH_{(s)} \rightarrow M_{(s)} + Ni(OH)_{2\,(s)}}$ $E^\circ_{cell} = 1.25$ V

d. **Mercury Oxide Battery**: - a non-rechargeable dry cell due to its small size has found its uses in small electronic devices like watches.

- consists of **amalgamated zinc-mercury Zn(Hg)** $_{(s)}$ **as the anode** and both **HgO** $_{(s)}$ **(cathode)** and the **bases (KOH** $_{(s)}$ **and Zn(OH)** $_{2\,(s)}$**)** are in a **dry paste**.
- commonly known as the **button battery** due to its small size.



Redox Reaction for a Mecury Oxide Battery

(Reduction) $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2\,OH^-_{(aq)}$ $E^\circ_{cathode} = \ \ 0.10\text{ V}$

(Oxidation) $\underline{Zn(Hg)_{(s)} + 2\,OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + Hg_{(l)} + 2e^-}$ $\underline{E^\circ_{anode} = +1.25\text{ V}}$

$\mathbf{HgO_{(s)} + Zn(Hg)_{(s)} \rightarrow 2\,Hg_{(l)} + ZnO_{(s)}}$ $\underline{\mathbf{E^\circ_{cell} = \ \ 1.35\text{ V}}}$

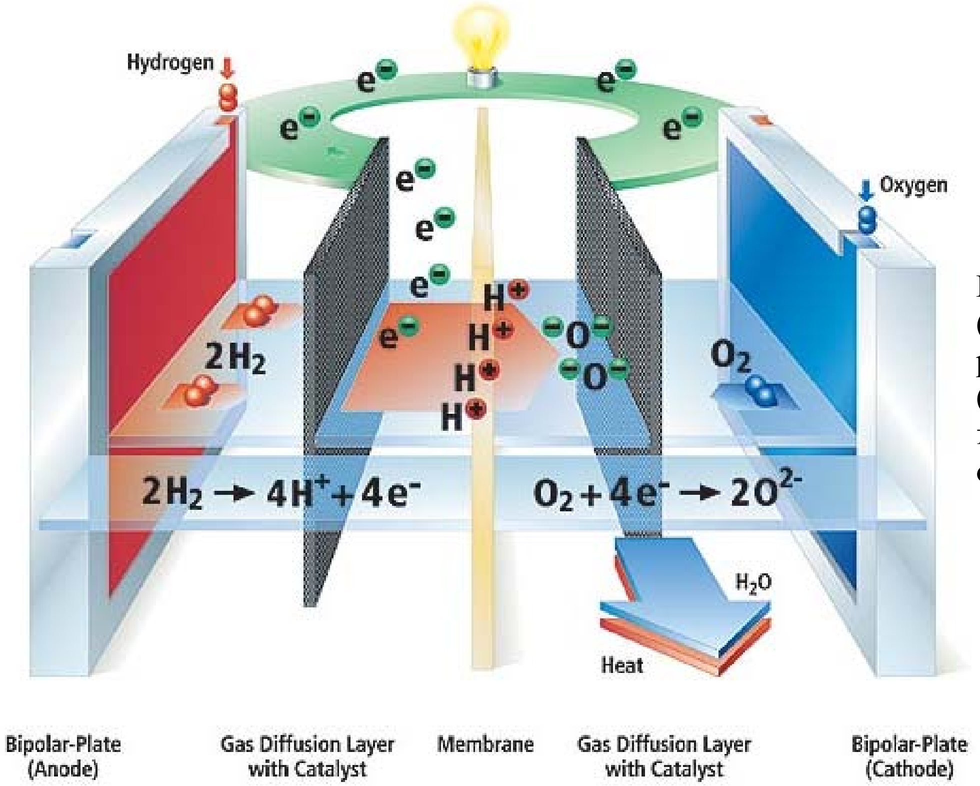
3. **Fuel Cell**: - a galvanic cell where there is a continuous supply of reactants.
   - the **hydrogen-oxygen fuel cell** produces water as a product and hence is an ideal power source for zero-emission vehicles

Redox Reaction for a Hydrogen Fuel Cell

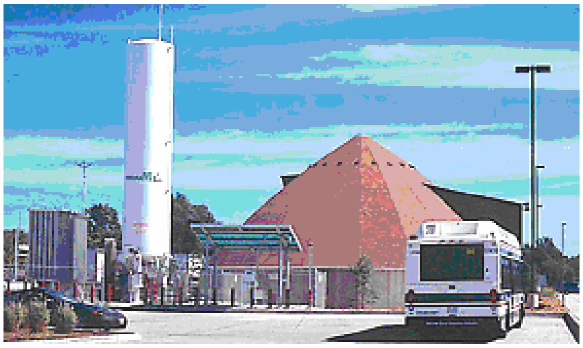
(Reduction) $O_{2\,(g)} + 2\,H_2O_{(l)} + 4e^- \rightarrow 4\,OH^-_{(aq)}$ $E^\circ_{cathode} = \ \ 0.40\text{ V}$

(Oxidation) $\underline{2\,(\,H_{2\,(g)} + 2\,OH^-_{(aq)} \rightarrow 2\,H_2O_{(l)} + 2e^-\,)}$ $\underline{E^\circ_{anode} = +0.83\text{ V}}$

$\mathbf{2\,H_{2\,(g)} + O_{2\,(g)} \rightarrow 2\,H_2O_{(l)}}$ $\underline{\mathbf{E^\circ_{cell} = \ \ 1.23\text{ V}}}$



Ford Hydrogen Fuel Cell Vehicle (FCV): The hydrogen tank (at 5000 psi) is stored inside the trunk (above). Under the hood with the fuel cell engine (below). Schematic of a Hydrogen Fuel Cell (left).



(Bottom left) The Hydrogen Fueling Station at the city of Chicago. Shown in the photo is Chicago's Fuel Cell Public Transit Vehicle. The solar panel, next to the hydrogen storage tank (vertical column), is used to supply power needed to decompose water into hydrogen and oxygen. Hence, from the production of hydrogen gas to its usage in the fuel cell vehicles, it is 100% environmentally friendly.

Electrolysis: - a power supply (external source of electricity) is used to cause a chemical change to occur.

Electrolytic Cells: - an apparatus that **Converts Electrical Energy *to* Chemical Energy**.
- it consists of **one or two containers of solutions** (electrolytes) and the electrodes (usually metals called anode and cathode), as well as a connection between these two containers (salt bridge, porous cup, or porous disk – if two containers are used), and a wire connecting the two electrodes along with a **power source**.

Anode: - the terminal where **oxidation** is taken place and commonly marked as the **Negative terminal**.

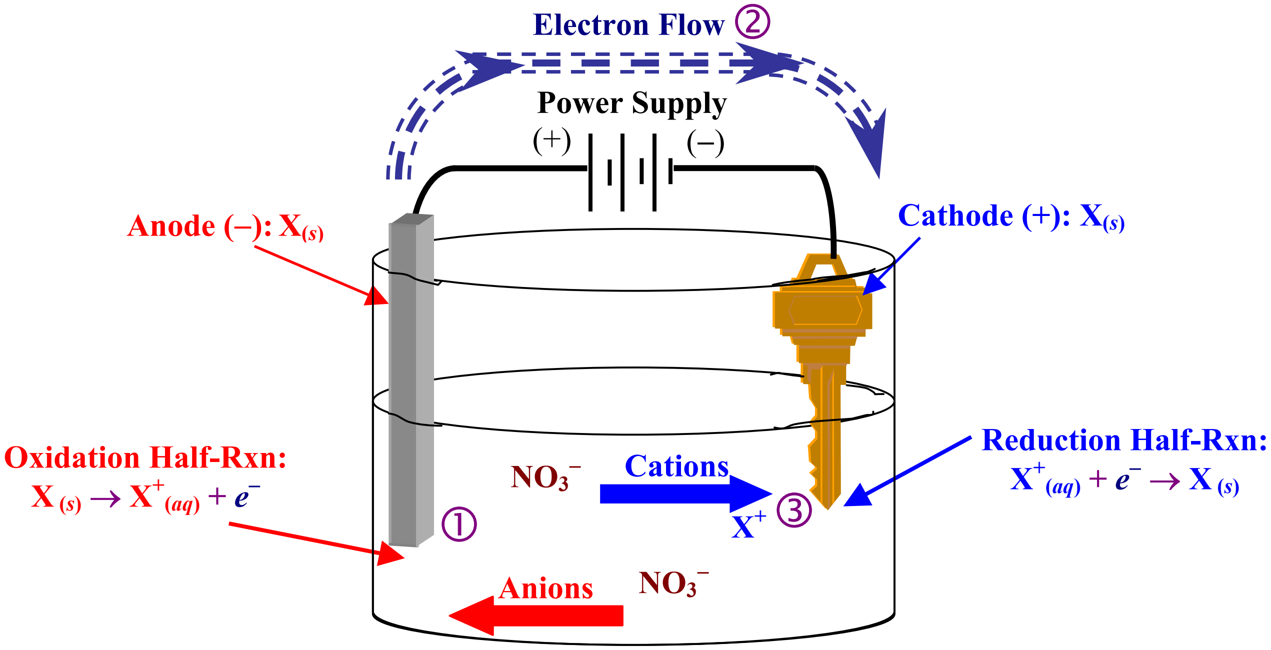
Cathode: - the terminal where **reduction** is taken place and commonly marked as the **Positive terminal**.

Cell Potential (E_{cell}): - for **electrolytic cells, the cell potential is Negative (Non-Spontaneous).**
- the **E°_{cell} of an electrolytic cell is the minimum voltage** needed to start and maintain the chemical reaction. $(E^\circ_{cell} = E^\circ_{cathode} + E^\circ_{anode})$

Electrolytic Cells

1. **Electrons move *from* Anode (–) *to* Cathode (+).**
2. **Cations move *towards* the Cathode.**
3. **Anions move *towards* the Anode.**

Anode (–): (LEOA–RA: Losing Electrons Oxidation Anode – Reducing Agent)
Cathode (+): (GERC–OA: Gaining Electrons Reduction Cathode – Oxidizing Agent)



Electrolytic Cell of a Single Solution Step by Step

① X^+ leaves $X_{(s)}$ at the Anode because the power supply "pumps" the electrons from $X_{(s)}$. At the same time, the bottom of the anode becomes more positive. This is corrected by the anions (like NO_3^-) migrating towards the cathode.

② Electrons produced at the Anode (−) move to Cathode (+).

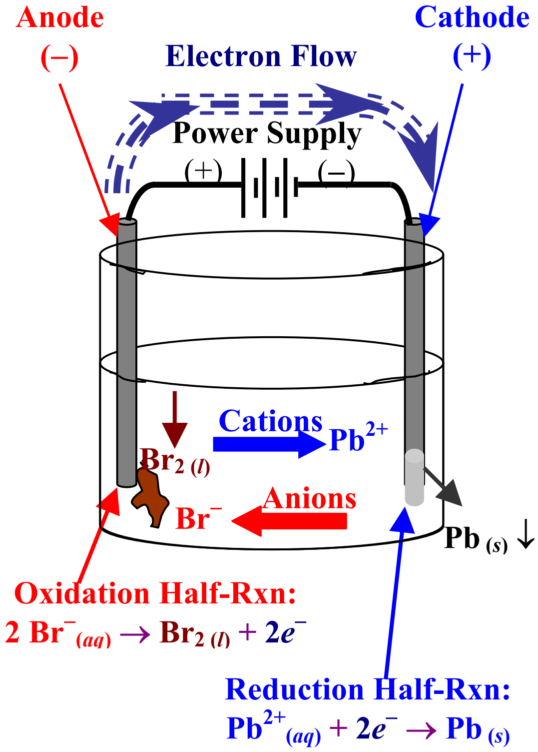
③ X^+ migrates towards the Cathode (+) to produce $X_{(s)}$ in order to complete the reduction half reaction. This can also be explained that X^+ migrate towards the cathode because electrons are moving into the bottom of the cathode making that region more negative.

Determining the Redox Reaction for Electrolytic Cell

1. **List ALL ions in the solution as well as water.**
2. **Identify the strongest oxidizing and reducing reagents.**
3. **Balance each of the reduction and oxidation half reactions.**
4. **Add both half reactions to form a complete redox reaction.**
5. **Calculate the $E°_{cell}$ of the overall reaction.**

Example 2: Determine the redox net-ionic reaction and the $E°_{cell}$ for the following solutions when two inert electrodes (carbon) are connected with an operating power supply. Draw and label a diagram for the set up. Suggest any possible observations for these electrolytic cells.

a. $PbBr_{2\,(aq)}$



	SOA		OA
Major Species:	Pb^{2+},	Br^-,	H_2O
		SRA	RA

$$O_{2\,(g)} + 4\,H^+_{(aq)} + 4e^- \rightarrow 2\,H_2O_{(l)} \qquad E° = 1.23\text{ V}$$
$$Br_{2\,(l)} + 2e^- \rightarrow Br^-_{(aq)} \qquad E° = 1.07\text{ V}$$
$$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)} \qquad E° = -0.13\text{ V}$$
$$2\,H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2\,OH^-_{(aq)} \qquad E° = -0.83\text{ V}$$

We can see that this is a Non-Spontaneous Rxn because the half-reactions for $Br^-_{(aq)}$ is higher than $Pb^{2+}_{(aq)}$. Pb^{2+} will be reduced (Cathode) and Br^- will be oxidized (Anode – half-rxn needs to flip).

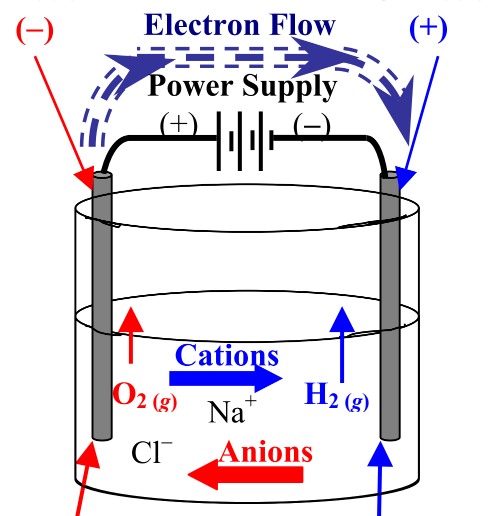
$$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)} \qquad E° = -0.13\text{ V}$$
$$\underline{2\,Br^-_{(aq)} \rightarrow Br_{2\,(l)} + 2e^- \qquad E° = -1.07\text{ V}}$$
$$Pb^{2+}_{(aq)} + 2\,Br^-_{(aq)} \rightarrow Br_{2\,(l)} + Pb_{(s)} \qquad E°_{cell} = -1.20\text{ V}$$

Minimum Voltage Needed = 1.20 V

Possible Observations:

1. **$Pb_{(s)}$ will be plated on the cathode.**
2. **$Br_{2\,(l)}$ (brown liquid) can be found near the anode.**

b. NaCl $_{(aq)}$



Oxidation Half-Rxn:
$2\,H_2O_{(l)} \rightarrow O_{2\,(g)} + 4\,H^+_{(aq)} + 4e^-$

Reduction Half-Rxn:
$2\,H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2\,OH^-_{(aq)}$

Possible Observations:

1. $H_{2\,(g)}$ bubbles out at the cathode.
2. $O_{2\,(g)}$ bubbles out of the anode.

	OA		SOA
Major Species:	Na^+,	Cl^-,	H_2O
		RA	SRA

$$
\begin{aligned}
Cl_{2\,(g)} + 2e^- &\rightarrow 2\,Cl^-_{(aq)} & E^\circ &= 1.36\text{ V}\\
O_{2\,(g)} + 4\,H^+_{(aq)} + 4e^- &\rightarrow \underline{2\,H_2O_{(l)}} & E^\circ &= 1.23\text{ V}\\
\underline{2\,H_2O_{(l)}} + 2e^- &\rightarrow H_{2\,(g)} + 2\,OH^-_{(aq)} & E^\circ &= -0.83\text{ V}\\
Na^+_{(aq)} + e^- &\rightarrow Na_{(s)} & E^\circ &= -2.71\text{ V}
\end{aligned}
$$

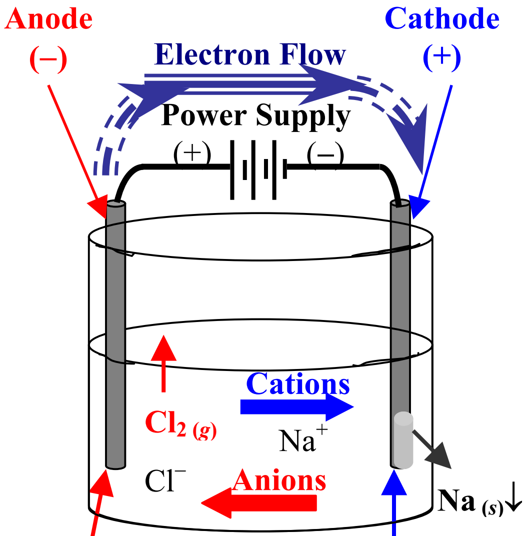
We can see that this is a Non-Spontaneous Rxn because the half-reactions for $H_2O_{(l)}$ as a reducing agent is higher than $H_2O_{(l)}$ as an oxidizing agent. $\underline{H_2O\text{ will be reduced at the Cathode}}$ and $\underline{H_2O\text{ will be oxidized at the Anode – half-rxn needs to flip}}$.

$$
\begin{aligned}
2\,(\,2\,H_2O_{(l)} + 2e^- &\rightarrow H_{2\,(g)} + 2\,OH^-_{(aq)}\,) & E^\circ &= -0.83\text{ V}\\
\underline{2\,H_2O_{(l)} &\rightarrow O_{2\,(g)} + 4\,H^+_{(aq)} + 4e^-} & \underline{E^\circ} &\underline{= -1.23\text{ V}}\\
2\,H_2O_{(l)} &\rightarrow O_{2\,(g)} + 2\,H_{2\,(g)} & \underline{E^\circ_{cell}} &\underline{= -2.06\text{ V}}
\end{aligned}
$$

Minimum Voltage Needed = 2.06 V

$\underline{NaCl_{(aq)}\text{ does not decompose into its elements}}$ but rather $\underline{\text{electrolysis of }H_2O\text{ is taking place}}$. This is because the Na^+ and Cl^- are weaker oxidizing and reducing agents compared to H_2O.

c. NaCl $_{(l)}$ (Molten NaCl)



Oxidation Half-Rxn:
$2\,Cl^-_{(l)} \rightarrow Cl_{2\,(g)} + 2e^-$

Reduction Half-Rxn:
$Na^+_{(l)} + e^- \rightarrow Na_{(s)}$

	SOA	SRA
Major Species:	$Na^+_{(l)}$,	$Cl^-_{(l)}$

$$
\begin{aligned}
Cl_{2\,(g)} + 2e^- &\rightarrow \underline{2\,Cl^-_{(l)}} & E^\circ &= 1.36\text{ V}\\
\underline{Na^+_{(l)}} + e^- &\rightarrow Na_{(s)} & E^\circ &= -2.71\text{ V}
\end{aligned}
$$

We can see that this is a Non-Spontaneous Rxn because the half-reactions for $Cl^-_{(l)}$ as a reducing agent is higher than $Na^+_{(l)}$ as an oxidizing agent. $\underline{Na^+\text{ will be reduced at the Cathode}}$ and $\underline{Cl^-\text{ will be oxidized at the Anode – half-rxn needs to flip}}$.

$$
\begin{aligned}
2\,(\,Na^+_{(l)} + e^- &\rightarrow Na_{(s)}\,) & E^\circ &= -2.71\text{ V}\\
\underline{2\,Cl^-_{(l)} &\rightarrow Cl_{2\,(g)} + 2e^-} & \underline{E^\circ} &\underline{= -1.36\text{ V}}\\
2\,Na^+_{(l)} + 2\,Cl^-_{(l)} &\rightarrow Cl_{2\,(g)} + 2\,Na_{(s)} & \underline{E^\circ_{cell}} &\underline{= -4.07\text{ V}}
\end{aligned}
$$

Minimum Voltage Needed = 4.07 V

$\underline{\text{Molten }NaCl_{(l)}\text{ decomposes into its elements}}$ in this case because there is no H_2O present.

Possible Observations:

1. $Na_{(s)}$ is plating out at the cathode.
2. $Cl_{2\,(g)}$ bubbles out of the anode.

Assignment

11.3 pg. 358 #9 to 13 and Worksheet: Electrochemistry

Worksheet: Electrochemistry

1. Balance the following redox reaction by first selecting the strongest oxidizing and reducing agents and writing the half-reactions. Determine whether the reaction is spontaneous or non-spontaneous. In cases of non-spontaneous reactions, do not write out the products.

a. A piece of tin metal is placed in a solution of iron (II) chloride.
b. Solid Iodine is placed in pure liquid hydrogen peroxide.
c. Copper (II) nitrate solution is added to a solution of chromium (II) bromide.
d. An acidified potassium permanganate solution is mixed with a solution of tin (II) bromide.
e. A piece of silver metal is a zinc sulfate solution.
f. A piece of cobalt metal is immersed in a hydrochloric acid.
g. A piece of gold jewellery was worn in a chlorinated swimming pool.

2. For the following line notations of galvanic cells,
i. draw a diagram using a salt bridge. **ii.** identify the anode and cathode.
iii. indicate movements of ions and electrons. **iv.** write a redox reaction and find the standard cell potential.

a. $Pb_{(s)}$ | (1 mol/L) $Pb(NO_3)_{2\,(aq)}$ || (1 mol/L) $AgNO_{3\,(aq)}$ | $Ag_{(s)}$
b. $Fe_{(s)}$ | (1 mol/L) $Fe(NO_3)_{2\,(aq)}$ || (1 mol/L) $Cu(NO_3)_{2\,(aq)}$ | $Cu_{(s)}$
c. $Mg_{(s)}$ | (1 mol/L) $MgBr_{2\,(aq)}$ || (1 mol/L) $SnBr_{2\,(aq)}$ | $Sn_{(s)}$
d. $Cr_{(s)}$ | (1 mol/L) $Cr(NO_3)_{2\,(aq)}$ || (1 mol/L) $Ni(NO_3)_{2\,(aq)}$ | $Ni_{(s)}$

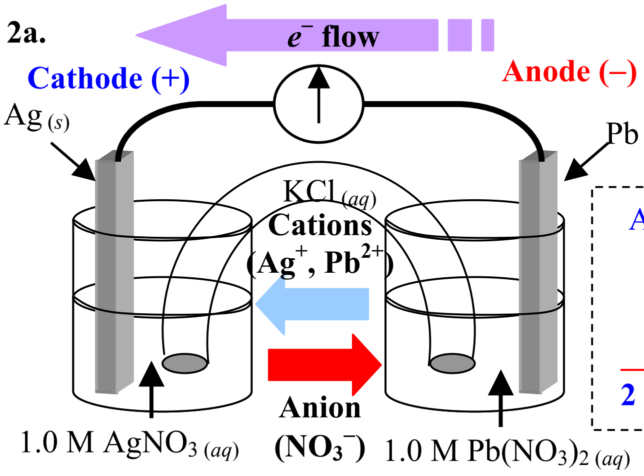
3. Determine the redox net-ionic reaction and the $E°_{\text{cell}}$ for the following solutions when two inert electrodes (carbon) are connected with an operating power supply. Draw and label a diagram for the set up. Suggest any possible observations for these electrolytic cells.

a. $ZnI_{2\,(aq)}$ **b.** $CoBr_{2\,(aq)}$ **c.** $NiCl_{2\,(aq)}$

Answers

1a. $Sn_{(s)} + Fe^{2+}_{(aq)} \rightarrow$ No Reaction (Non-spontaneous); $Fe^{2+}_{(aq)}$ – Oxidizing Agent; $Sn_{(s)}$ – Reducing Agent
b. $I_{2\,(s)} + H_2O_{2\,(l)} \rightarrow$ No Reaction (Non-spontaneous); $I_{2\,(s)}$ – Oxidizing Agent; $H_2O_{2\,(l)}$ – Reducing Agent
c. $Cu^{2+}_{(aq)} + 2\,Cr^{2+}_{(aq)} \rightarrow 2\,Cr^{3+}_{(aq)} + Cu_{(s)}$ (Spontaneous); $Cu^{2+}_{(aq)}$ – Oxidizing Agent; $Cr^{3+}_{(aq)}$ – Reducing Agent
d. $2\,MnO_4^{-}{}_{(aq)} + 16\,H^{+}_{(6aq)} + 5\,Sn^{2+}_{(aq)} \rightarrow 5\,Sn^{4+}_{(aq)} + 2\,Mn^{2+}_{(aq)} + 8\,H_2O_{(l)}$ (Spontaneous);
$MnO_4^{-}{}_{(aq)}$ – Oxidizing Agent; $Sn^{2+}_{(aq)}$ – Reducing Agent
e. $Ag_{(s)} + Zn^{2+}_{(aq)} \rightarrow$ No Reaction (Non-Spontaneous); $Zn^{2+}_{(aq)}$ – Oxidizing Agent; $Ag_{(s)}$ – Reducing Agent
f. $Co_{(s)} + 2\,H^{+}_{(aq)} \rightarrow H_{2\,(g)} + Co^{2+}_{(aq)}$ (Spontaneous); $H^{+}_{(aq)}$ – Oxidizing Agent; $Co_{(s)}$ – Reducing Agent
g. $Au_{(s)} + Cl_{2\,(g)} \rightarrow$ No Reaction (Non-Spontaneous); $Cl_{2\,(g)}$ – Oxidizing Agent; $Au_{(s)}$ – Reducing Agent

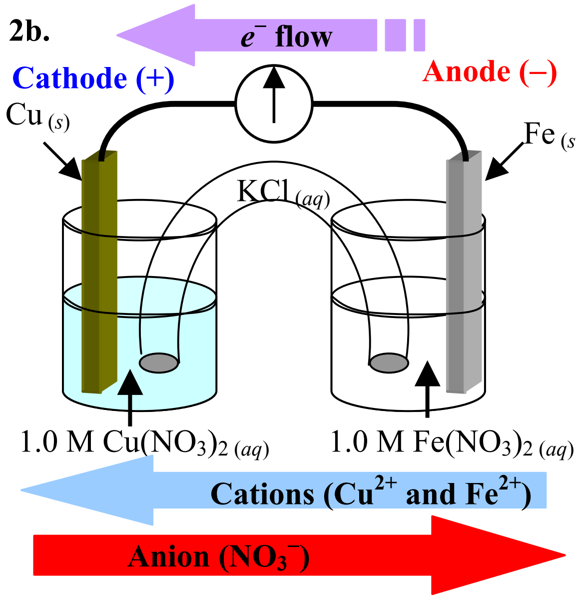
2a.



$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$ $E° = +0.80$ V
$Pb^{2+}_{(aq)} + 2e^{-} \rightarrow Pb_{(s)}$ $E° = -0.13$ V

$2\,(\,Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}\,)$ $E°_{\text{cathode}} = +0.80$ V
$\underline{Pb_{(s)} \rightarrow Pb^{2+}_{(aq)} + 2e^{-}}$ $\underline{E°_{\text{anode}} = +0.13\text{ V}}$
$\mathbf{2\,Ag^{+}_{(aq)} + Pb_{(s)} \rightarrow Pb^{2+}_{(aq)} + 2\,Ag_{(s)}}$ $\underline{\mathbf{E°_{\text{cell}} = +0.93\text{ V}}}$

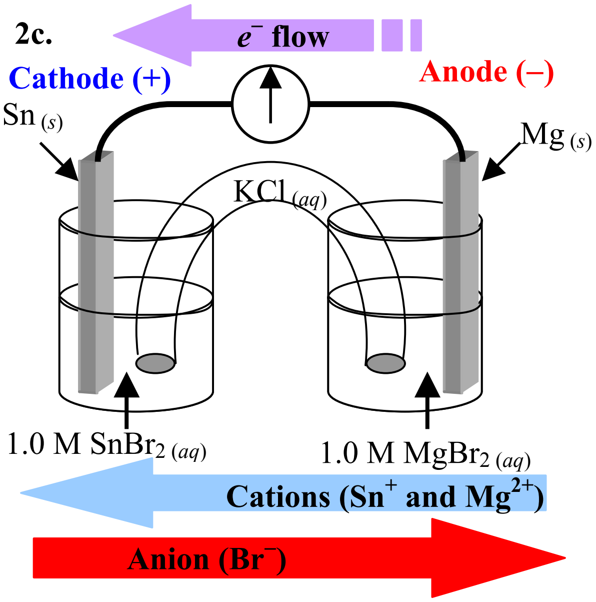
2b.



$$\begin{array}{ll}
Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)} & E° = +0.34\text{ V} \\
Fe^{2+}{}_{(aq)} + 2e^- \rightarrow Fe_{(s)} & E° = -0.45\text{ V}
\end{array}$$

$$\begin{array}{lr}
Cu^{2+}{}_{(aq)} + \mathbf{2e^-} \rightarrow Cu_{(s)} & E°_{\text{cathode}} = +0.34\text{ V} \\
\underline{Fe_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + \mathbf{2e^-}} & \underline{E°_{\text{anode}} = +0.45\text{ V}} \\
\mathbf{Cu^{2+}{}_{(aq)} + Fe_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + Cu_{(s)}} & \underline{\mathbf{E°_{\text{cell}} = +0.79\text{ V}}}
\end{array}$$

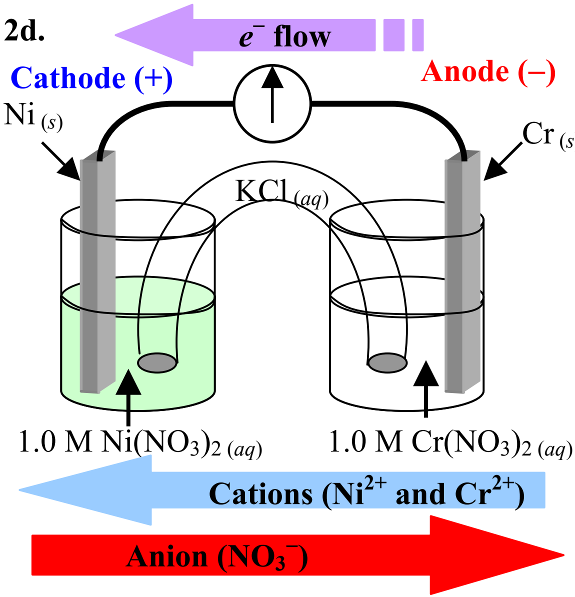
2c.



$$\begin{array}{ll}
Sn^{2+}{}_{(aq)} + 2e^- \rightarrow Sn_{(s)} & E° = -0.14\text{ V} \\
Mg^{2+}{}_{(aq)} + 2e^- \rightarrow Mg_{(s)} & E° = -2.37\text{ V}
\end{array}$$

$$\begin{array}{lr}
Sn^{2+}{}_{(aq)} + \mathbf{2e^-} \rightarrow Sn_{(s)} & E°_{\text{cathode}} = -0.14\text{ V} \\
\underline{Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + \mathbf{2e^-}} & \underline{E°_{\text{anode}} = +2.37\text{ V}} \\
\mathbf{Sn^{2+}{}_{(aq)} + Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + Sn_{(s)}} & \underline{\mathbf{E°_{\text{cell}} = +2.23\text{ V}}}
\end{array}$$

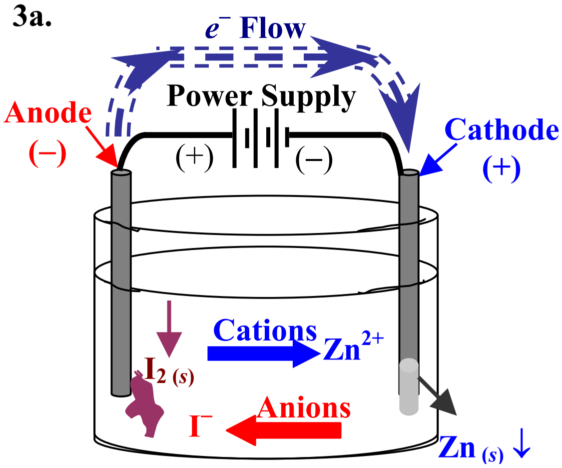
2d.



$$\begin{array}{ll}
Ni^{+}{}_{(aq)} + 2e^- \rightarrow Ni_{(s)} & E° = -0.26\text{ V} \\
Cr^{2+}{}_{(aq)} + 2e^- \rightarrow Cr_{(s)} & E° = -0.91\text{ V}
\end{array}$$

$$\begin{array}{lr}
Ni^{2+}{}_{(aq)} + \mathbf{2e^-} \rightarrow Ni_{(s)} & E°_{\text{cathode}} = -0.26\text{ V} \\
\underline{Cr_{(s)} \rightarrow Cr^{2+}{}_{(aq)} + \mathbf{2e^-}} & \underline{E°_{\text{anode}} = +0.91\text{ V}} \\
\mathbf{Ni^{2+}{}_{(aq)} + Cr_{(s)} \rightarrow Cr^{2+}{}_{(aq)} + Ni_{(s)}} & \underline{\mathbf{E°_{\text{cell}} = +0.65\text{ V}}}
\end{array}$$

3a.



$O_{2\,(g)} + 4\,H^+_{(aq)} + 4e^- \rightarrow 2\,\underline{H_2O}_{(l)}$ $E^\circ = +1.23\text{V}$

$I_{2\,(s)} + 2e^- \rightarrow 2\,\underline{I^-}_{(aq)}$ $E^\circ = +0.54\text{ V}$

$\underline{Zn^{2+}_{(aq)}} + 2e^- \rightarrow Zn_{(s)}$ $E^\circ = -0.76\text{ V}$

$2\,\underline{H_2O}_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2\,OH^-_{(aq)}$ $E^\circ = -0.83\text{V}$

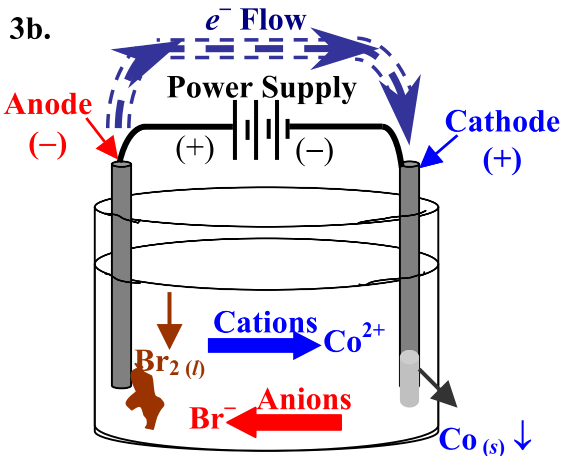
$Zn^{2+}_{(aq)} + \mathbf{2e^-} \rightarrow Zn_{(s)}$ $E^\circ_{\text{cathode}} = -0.76\text{ V}$

$\underline{2\,I^-_{(aq)} \rightarrow I_{2\,(s)} + \mathbf{2e^-}}$ $\underline{E^\circ_{\text{anode}} = -0.54\text{ V}}$

$\mathbf{Zn^{2+}_{(aq)} + 2\,I^-_{(aq)} \rightarrow I_{2\,(s)} + Zn_{(s)}}$ $\underline{\mathbf{E^\circ_{\text{cell}} = -1.30\text{ V}}}$

Minimum Voltage Needed = 1.30 V

3b.



$O_{2\,(g)} + 4\,H^+_{(aq)} + 4e^- \rightarrow 2\,\underline{H_2O}_{(l)}$ $E^\circ = +1.23\text{V}$

$Br_{2\,(l)} + 2e^- \rightarrow 2\,\underline{Br^-}_{(aq)}$ $E^\circ = +1.07\text{ V}$

$\underline{Co^{2+}_{(aq)}} + 2e^- \rightarrow Co_{(s)}$ $E^\circ = -0.28\text{ V}$

$2\,\underline{H_2O}_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2\,OH^-_{(aq)}$ $E^\circ = -0.83\text{V}$

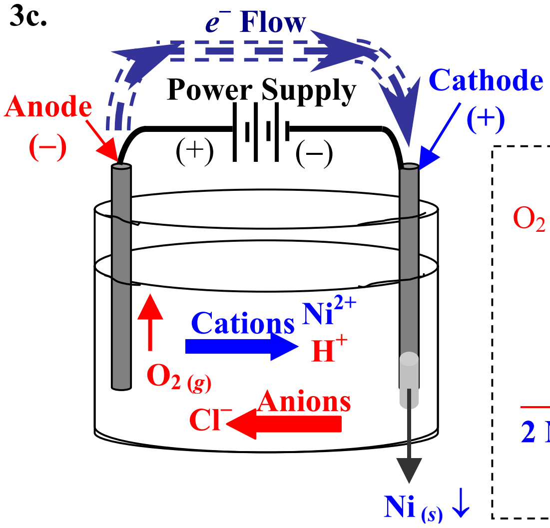
$Co^{2+}_{(aq)} + \mathbf{2e^-} \rightarrow Co_{(s)}$ $E^\circ_{\text{cathode}} = -0.28\text{ V}$

$\underline{Br^-_{(aq)} \rightarrow Br_{2\,(l)} + \mathbf{2e^-}}$ $\underline{E^\circ_{\text{anode}} = -1.07\text{ V}}$

$\mathbf{Co^{2+}_{(aq)} + 2\,Br^-_{(aq)} \rightarrow Br_{2\,(l)} + Co_{(s)}}$ $\underline{\mathbf{E^\circ_{\text{cell}} = -1.35\text{ V}}}$

Minimum Voltage Needed = 1.35 V

3c.



$Cl_{2\,(g)} + 2e^- \rightarrow 2\,\underline{Cl^-}_{(aq)}$ $E^\circ = +1.36\text{ V}$

$O_{2\,(g)} + 4\,H^+_{(aq)} + 4e^- \rightarrow 2\,\underline{\mathbf{H_2O}}_{(l)}$ $E^\circ = +1.23\text{V}$

$\underline{Ni^{2+}_{(aq)}} + 2e^- \rightarrow Ni_{(s)}$ $E^\circ = -0.26\text{ V}$

$2\,\underline{H_2O}_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2\,OH^-_{(aq)}$ $E^\circ = -0.83\text{V}$

$2\;(\,Ni^{2+}_{(aq)} + \mathbf{2e^-} \rightarrow Ni_{(s)}\,)$ $E^\circ_{\text{cathode}} = -0.26\text{ V}$

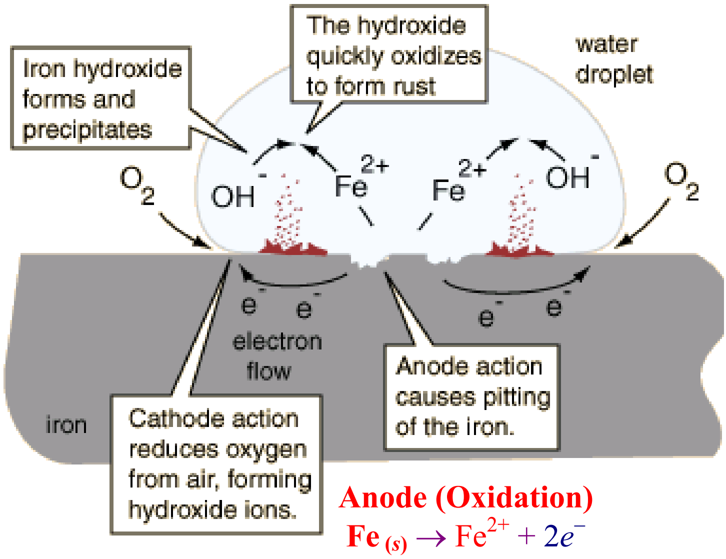
$\underline{H_2O_{(l)} \rightarrow O_{2\,(g)} + 4\,H^+_{(aq)} + \mathbf{4e^-}}$ $\underline{E^\circ_{\text{anode}} = -1.23\text{ V}}$

$\mathbf{2\,Ni^{2+}_{(aq)} + H_2O_{(l)} \rightarrow O_{2\,(l)} + 4\,H^+_{(aq)} + 2\,Ni_{(s)}}$ $\underline{\mathbf{E^\circ_{\text{cell}} = -1.49\text{ V}}}$

Minimum Voltage Needed = 1.49 V

11.4: Oxygen is Responsible for Corrosion and Combustion

Corrosion: - oxidation of metal into metal-oxides.
- from the Standard Reduction Potential Table, metals are generally strong reducing agent (bottom right side). Because metals tend to have low electronegativity, they lose electrons easily to found cations (oxidation).
- since solid gold is the weakest of all metal reducing agents, it lacks the ability to oxidize and hence gold is considered a precious metal where all currencies are based on.



Anode (Oxidation)
$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$

Cathode (Reduction)
$O_2 + 2\ H_2O + 4e^- \rightarrow 4\ OH^-$

(Above) The electrochemical corrosion of iron where oxygen (oxidizing agent – cathode) is reacting with iron (reducing agent – anode) to form rust. Electrochemical cell action driven by the energy of oxidation continues the corrosion process.

(Above) This view was taken with a scanning electron microscope (1200 ×) and shows the corroded surface of a piece of iron metal. The corrosion was artificially induced by subjecting the iron metal to an ionizing potential while being submerged in a sodium silicate solution. The iron dissolves from the surface as it oxidizes, forming a cavity (20 microns diameter). The oxidized iron mixes with the silicate solution and forms a glassy insoluble material that reforms in the cavity.

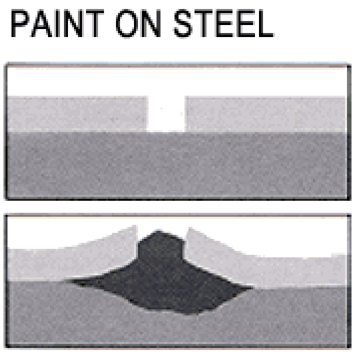
Ways to Prevent Corrosion:

1. **Painting**: - putting a protective coating like paint on metals covers the metal surfaces so oxidation of the metal cannot take place.
   - if the paint coating is scratched, oxidation will occur on the metal. Any rust needs to be removed before a fresh coat of paint is put on.

2. **Alloys**: - by mixing metals in various percentages to form an alloy, the reduction potential increases.
   - stainless steel is composed of iron and carbon, which has a higher reduction potential than iron metal. Therefore, stainless steels do not rust.
   - **Surface Alloy**: - when alloy is coated of the metal surface by bombardment of alloy metals in gaseous ions form (alloying plasma – ion gas that consists of alloys to be coated). This makes a cheaper alternative than making the entire material out of alloy.

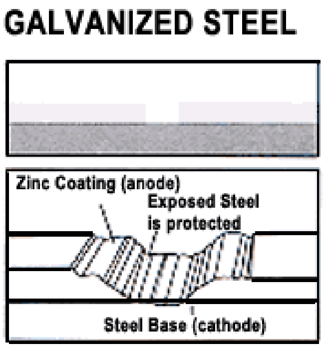
3. **Galvanization**: - the plating of a metal with a lower reduction potential (higher oxidizing potential – stronger reducing agents like zinc or magnesium) on to the metal intended for protection.
   - the oxygen will likely react with the stronger reducing agent metal, leaving the other metal unreacted.
   - the metal with the lower reduction potential is in effect protecting the other metal, hence we call this the galvanizing metal **sacrificial metal**.
   - galvanized metal last longer than zinc and does not need reapplication because it is "self-healing" when scratched (see below).

Rust undercuts scratched paint



This is what happens at a scratch on painted steel. The exposed steel corrodes and forms a pocket of rust. Because rust is much more voluminous than steel, the pocket swells. This lifts the paint film from the metal surface to form a blister. Both the corrosion pit and the blister continue to grow.

Zinc protects base steel even when scratched



This is what happens at a scratch on galvanized steel. The zinc coating sacrifices itself slowly by galvanic action to protect the base steel. This sacrificial action continues as long as any zinc remains in the immediate area.

Example: Zinc is often used to galvanize iron metal.

$\mathbf{O_2} + \mathbf{2\,H_2O} + 4e^- \rightarrow 4\,\text{OH}^-$ $\qquad E^\circ_{\text{reduction}} = 0.40\text{ V}$

$\text{Fe}^{2+} + 2e^- \rightarrow \mathbf{Fe}_{(s)}$ $\qquad E^\circ_{\text{reduction}} = -0.44\text{ V}$

$\text{Zn}^{2+} + 2e^- \rightarrow \mathbf{Zn}_{(s)}$ **(SRA)** $\qquad E^\circ_{\text{reduction}} = -0.76\text{ V}$

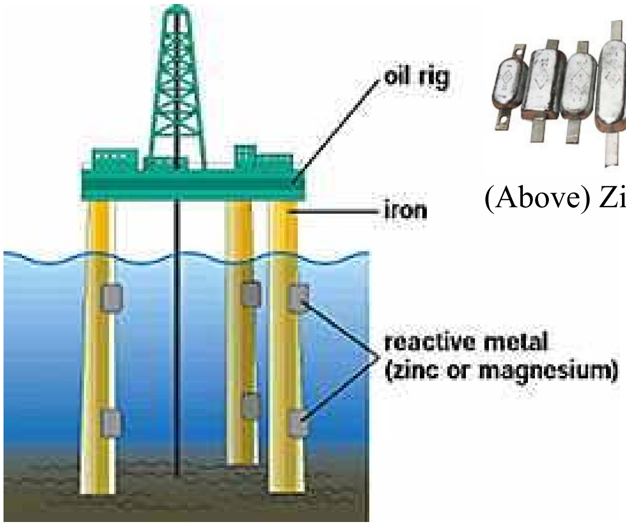
Zinc will be oxidized first (sacrificed) before iron.

$\mathbf{O_2} + \mathbf{2\,H_2O} + 4e^- \rightarrow 4\,\text{OH}^-$ $\qquad E^\circ_{\text{reduction}} = 0.40\text{ V}$

$\underline{\mathbf{2}\,(\mathbf{Zn}_{(s)} \rightarrow \text{Zn}^{2+} + 2e^-)}$ **(SRA)** $\qquad \underline{E^\circ_{\text{oxidation}} = +0.76\text{ V}}$

$\mathbf{O_2} + \mathbf{2\,H_2O} + \mathbf{2\,Zn}_{(s)} \rightarrow 2\,\text{Zn}^{2+} + 4\,\text{OH}^-$ $\qquad \mathbf{E^\circ_{\text{cell}} = 1.16\text{ V}}$

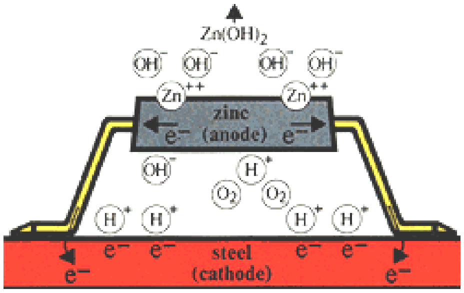
O_2-$Zn_{(s)}$ has a <u>Higher Voltage</u> than E°_{cell} of O_2-$Fe_{(s)}$. Therefore, it is <u>More Spontaneous.</u>

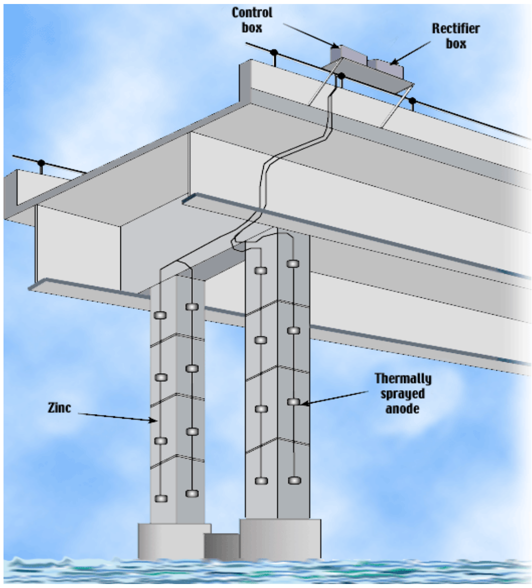


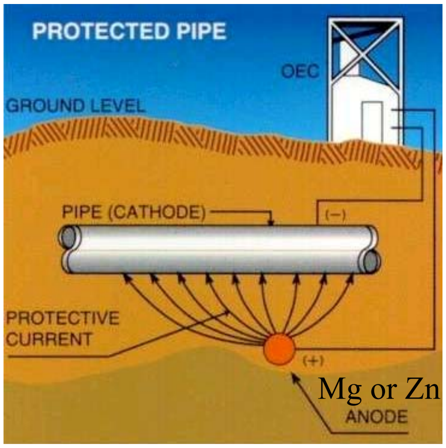
(Above) Zinc sacrificial metals.

(Above and right) Deep-sea structures like offshore oil drilling platforms used sacrificial metals to protect the main structure from corrosion

4. **Cathodic Protection**: - it is similar to galvanization, in an electrolytic environment (sea water and underground water), the sacrificial metal – the most active metal (anode) will oxidize first. Electrons flow to the protected less reactive metal (cathode). When the anode supplies current, it will gradually dissolve into ions in the electrolyte, and at the same time produce electrons, which the cathode will receive through the metallic connection with the anode. The result is that the cathode will be negatively polarised and hence be protected against corrosion.
   - unlike galvanization, we do not need to "coat" the protected metal. However, the anode metal has to be replaced over time.
   - find its usage for any metal placed underground (gas pipes and gas tanks) and structures or marine transport over the seas and oceans (like bridges, offshore oil rigs and ships).







The basic principle behind cathodic protection (top left). Sacrificial metals are placed on columns of the sea-bridge (above) and underground with a metal pipe (left). All are connected by wires to facilitate the process of cathodic protection.

Combustion: - a redox reaction involving the **adding of oxygen to a non-metal** (also refer to as ***"burning"*** to **produce non-metal oxide**).

- in all cases of combustion, the **non-metal material is oxidized and acting as a reducing agent** (because it becomes a non-metal oxide); while the **oxygen is reduced and acting as an oxidizing agent**.

Examples: some combustions reactions with non-metals elements or compounds.

(Hydrocarbons)	$C_6H_{12}O_{6\,(s)} + 6\,O_{2\,(g)} \rightarrow 6\,CO_{2\,(g)} + 6\,H_2O_{(g)}$	(C is oxidized and O is reduced)
(Sulfur)	$S_{8\,(s)} + 8\,O_{2\,(g)} \rightarrow 8\,SO_{2\,(g)}$	(S is oxidized and O is reduced)
(Nitrogen)	$N_{2\,(g)} + 2\,O_{2\,(g)} \rightarrow 2\,NO_{2\,(g)}$	(N is oxidized and O is reduced)

Assignment

11.4 pg. 358 #14 to 18

Hands-On Activity: Splitting Water (pg. 353)

Chapter 11 Review: pg. 358 #1 to 11 (Key Terms and Matching Definitions)
pg. 359–360 (Exercises) #1 to 25