Unit 7: Reduction, Oxidation and Electrochemistry

Chapter 19: Electrochemistry

4.4: Oxidation-Reduction Reactions

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

Oxidation States (Oxidation Number): - a number that is arbitrary assigned to an atom in an element, molecule, and polyatomic ions to account for the number of electrons in ***redox*** reaction.

Rules for Assigning Oxidation Numbers:

1. **Natural Elements (include diatomic and polyatomics) have an Oxidation Number of 0.**

   Examples: $Na_{(s)}$, $O_{2\,(g)}$, $O_{3\,(g)}$, $H_{2\,(g)}$, $F_{2\,(g)}$, $P_{4\,(s)}$, and $Hg_{(l)}$ all have an oxidation number of 0.

2. **Single Atomic Ions have an Oxidation Number Equals to its Charge.**

   Example: K^+ has an oxidation number of +1.

3. **Oxygen in Binary Compound and Polyatomic Ions has an Oxidation Number of –2.**

   Examples: CO_2, CO, SO_3, SO_2, CO_3^{2-}, SO_4^{2-} and H_2O all have an oxidation number of –2 for oxygen.

   An exception occurs in peroxides (compound containing O_2^{2-}) where the oxygen has an oxidation number of –1.

4. **Hydrogen in Binary Compounds and Polyatomic Ions has an Oxidation Number of +1.**

   Examples: H_2O, HCl, HBr, CH_4, NH_4^+ and H_2S all has an oxidation number of + 1 for hydrogen.

5. **In Binary Compounds, the Atom that has the most attraction to electrons (HIGHER Electronegativity) is assigned the NEGATIVE Oxidation Number. This Negative Oxidation Number is the SAME as its Ionic Charge.**

   Examples:HF: F is more electronegative. Thus, F has an oxidation number of –1.
   NH_3: N is more electronegative. Thus, N has an oxidation number of –3.
   H_2S: S is more electronegative. Thus, S has an oxidation number of –2.

6. **The Sum of all Oxidation Numbers is 0 for all Electrically Neutral Compounds.**

   Examples:CO: Oxidation numbers: O = –2; **C = +2** [**(+2)** + (–2) = 0]
   SO_2: Oxidation numbers: O = –2; **S = +4** [**(+4)** + 2(–2) = 0]

7. **The Sum of all Oxidation Numbers is Equal to the Overall Charge for all Polyatomic Ions.**

   Examples:CO_3^{2-}: Oxidation numbers: O = –2; **C = +4** [**(+4)** + 3(–2) = –2]
   SO_4^{2-}: Oxidation numbers: O = –2; **S = +6** [**(+6)** + 4(–2) = –2]

Note: Same Atom from different chemical species might NOT have the Same Oxidation Number.
We write the charges of ionic species as *n*+ or *n*–. Oxidation numbers are written as +*n* or –*n*.

Example 1: Find the oxidation number for all atoms in each of the following elements or compounds:

a. NiO_2

Oxidation Numbers: O = −2
Ni: $n + 2(-2) = 0$ $\quad n = +4$

b. P_4O_{10}

Oxidation Numbers: O = −2
P: $4n + 10(-2) = 0$ $\quad n = +5$

c. N_2

Oxidation Numbers:
N_2 Diatomic Element $n = 0$

d. SF_4

Oxidation Numbers: F = −1
S: $n + 4(-1) = 0$ $\quad n = +4$

e. N_2H_4

Oxidation Numbers: H = +1
N: $2n + 4(+1) = 0$ $\quad n = -2$

f. Fe_3O_4

Oxidation Numbers: O = −2
Fe: $3n + 4(-2) = 0$ $\quad n = +\frac{8}{3}$

g. $KMnO_4$

Oxidation Numbers:
O = −2 K = +1
Mn: $(+1) + n + 4(-2) = 0$
$n = +7$

h. $Na_2C_2O_4$ or $Na_2OOCCOO$

Oxidation Numbers:
O = −2 Na = +1
C: $2(+1) + 2n + 4(-2) = 0$
$n = +3$

i. $XeOF_4$

Oxidation Numbers:
O = −2 F = −1
Xe: $n + (-2) + 4(-1) = 0$
$n = +6$

Example 2: Find the oxidation number for all atoms in each of the following polyatomic ions.

a. OCl^-

Oxidation Numbers: O = −2
Cl: $(-2) + n = -1$ $\quad n = +1$

b. ClO_2^-

Oxidation Numbers: O = −2
Cl: $n + 2(-2) = -1$ $\quad n = +3$

c. ClO_3^-

Oxidation Numbers: O = −2
Cl: $n + 3(-2) = -1$ $\quad n = +5$

d. ClO_4^-

Oxidation Numbers: O = −2
Cl: $n + 4(-2) = -1$ $\quad n = +7$

e. NO_2^-

Oxidation Numbers: O = −2
N: $n + 2(-2) = -1$ $\quad n = +3$

f. NO_3^-

Oxidation Numbers: O = −2
N: $n + 3(-2) = -1$ $\quad n = +5$

g. UO_2^{2+}

Oxidation Numbers: O = −2
U: $n + 2(-2) = +2$ $\quad n = +6$

h. $S_2O_3^{2-}$

Oxidation Numbers: O = −2
S: $2n + 3(-2) = -2$ $\quad n = +2$

i. $Cr_2O_7^{2-}$

Oxidation Numbers: O = −2
Cr: $2n + 7(-2) = -2$ $\quad n = +6$

Oxidation Reactions: - reactions that **LOSE Electrons** (**LEO** – "**L**osing **E**lectrons" – **O**xidation) or an **INCREASE (Oxidation)** in **Oxidation Number**.

- an **INCREASE in the number of Oxygen Atoms in the species** is a sign of oxidation reaction.
- a **DECREASE in the number of HYDROGEN atoms in the species** is a sign of oxidation reaction.

Examples:

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

0 to +3

(Lost 3 Electrons - Oxidation)
(Increased Oxidation Number - Oxidation)

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

+3 to +6

(Lost 6 Electrons – Oxidation)
(Increased Oxidation Number - Oxidation)

Reduction Reactions: - reactions that **GAIN Electrons** (**GER** – "**G**aining **E**lectrons" – **R**eduction) or a **DECRESE (Reduction)** in **Oxidation Number**.

Examples:

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

0 to −1 **(Reduced Oxidation Number - Reduction)**

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

+7 to +2 **(Reduced Oxidation Number - 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 or decreased in oxidation number).
- 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 or increased in oxidation number).
- in another words, **Oxidizing Species = Reducing Agent (LEO-RA)**

Example 2: Classify if the following reactions are redox reaction. For each of the redox reaction identified, label the reducing agent and oxidizing agent. Propose a reduction half-reaction and oxidation half-reaction.

a. $4\,Al_{(s)} + 3\,O_{2\,(g)} \rightarrow 2\,Al_2O_{3\,(s)}$

$4\,Al_{(s)} + 3\,O_{2\,(g)} \rightarrow 2\,Al_2O_{3\,(s)}$

Oxygen Oxidation #: **0 to −2** **(Reduction)**

Aluminium Oxidation #: **0 to +3** **(Oxidation)**

Oxidizing Agent = $O_{2\,(g)}$ **Reducing Agent = $Al_{(s)}$**

Oxidation Half-Reaction: $Al_{(s)} \rightarrow Al^{3+} + 3e^-$ **(Losing Electrons)**

Reduction Half-Reaction: $O_{2\,(g)} + 4e^- \rightarrow 2\,O^{2-}$ **(Gaining Electrons)**

b. $HCl_{(aq)} + NaF_{(aq)} \rightarrow HF_{(aq)} + NaCl_{(aq)}$

$HCl_{(aq)} + NaF_{(aq)} \rightarrow HF_{(aq)} + NaCl_{(aq)}$

Hydrogen Oxidation #: **+1 to +1** **(No Change)**

Chlorine Oxidation #: **−1 to −1** **(No Change)**

Sodium Oxidation #: **+1 to +1** **(No Change)**

Fluorine Oxidation #: **−1 to −1** **(No Change)**

(No Change in the Oxidation Number of any Atoms – NOT a Redox Reaction)

c. $Cr(NO_3)_{3\,(aq)} + Al_{(s)} \rightarrow Al(NO_3)_{3\,(aq)} + Cr_{(s)}$

An initial examination reveals that NO_3^- did not change in oxidation numbers

Complete Ionic Equation: $Cr^{3+}_{(aq)} + \mathbf{3\,NO_3^-{}_{(aq)}} + Al_{(s)} \rightarrow Al^{3+}_{(aq)} + \mathbf{3\,NO_3^-{}_{(aq)}} + Cr_{(s)}$

Net Ionic Equation: $Cr^{3+}_{(aq)} + Al_{(s)} \rightarrow Al^{3+}_{(aq)} + Cr_{(s)}$

Chromium Oxidation #: **+3 to 0** **(Reduction)**

Aluminium Oxidation #: **0 to +3** **(Oxidation)**

Oxidizing Agent = $Cr^{3+}_{(aq)}$ **Reducing Agent = $Al_{(s)}$**

Oxidation Half-Reaction: $Al_{(s)} \rightarrow Al^{3+} + 3e^-$ **(Losing Electrons)**

Reduction Half-Reaction: $Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$ **(Gaining Electrons)**

d. $CH_{4\,(g)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} + H_2O_{(g)}$

$CH_{4\,(g)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} + H_2O_{(g)}$

Oxygen Oxidation #: **0 to –2** **(Reduction)**

Carbon Oxidation #: **–4 to +4** **(Oxidation)**

Hydrogen Oxidation #: **+1 to +1** **(No Change)**

Oxidizing Agent = $O_{2\,(g)}$ **Reducing Agent = $CH_{4\,(g)}$**

Assignment

4.4 pg. 158–159 #36 to 41, 43 to 56

19.1: Redox Reactions

Balancing Oxidation-Reduction Reaction by Half-Reaction Method:

1. **Identify the atom that is undergoing a change in its oxidation number. Find out the change in oxidation number. Break up any Soluble Ionic Compound.**

2. **Balance the Oxidation Number by Adding Electrons to the side of the HIGHER Oxidation Number. The Number of Electrons Added is the Difference in the Oxidation Number.**

Examples: $Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)}$ **(Sn changes from +2 to +4. Hence, add 2 e⁻ to the right side.)**
$Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^-$ **(Charges and Elements are Balanced)**

$Fe^{3+}_{(aq)} \rightarrow Fe^{2+}_{(aq)}$ **(Fe changes from +3 to +2. Hence, add 1 e^- to the left side.)**
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$ **(Charges and Elements are Balanced)**

$Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)}$ **(Cl changes from 0 to +7. Hence, add 7 e^- to the product side.)**
$Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)} + 7e^-$ (Still need to Balance Hydrogen, Oxygen and the Charges)

3. **To balance the rest of the Half-Reaction (if necessary after step 2):**

    a. **Balance the Chemical Species Containing the Atom undergoing the Change in Oxidation Number. This is achieved by Multiplying the BOTH the Chemical Species and the Number of Electrons just added by the New Coefficient.**

Example: $Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)}$ (Cl changes from 0 to +7. Hence, add 7 e^- to the product side.)
$Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)} + 7e^-$ **(Multiply the $HClO_4$ and e^- by 2 to balance Cl_2.)**
$Cl_{2\,(g)} \rightarrow 2\,HClO_{4\,(aq)} + 14e^-$ (Still need to Balance Hydrogen, Oxygen and the Charges)

b. **Balance the Oxygen atom by adding $H_2O_{(l)}$ to the side that has less oxygen atom.**

Example: $Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)}$ (Cl changes from 0 to +7. Hence, add 7 e^- to the product side.)

$Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)} + 7e^-$ (Multiply the $HClO_4$ and e^- by 2 to balance Cl_2.)

$Cl_{2\,(g)} \rightarrow 2\ HClO_{4\,(aq)} + 14e^-$ **(Since there are no oxygen on the left and we have 8 oxygen atom to balance, 2 $HClO_4$, we need to add 8 H_2O to the reactant side.)**

$Cl_{2\,(g)} + 8\ H_2O_{(l)} \rightarrow 2\ HClO_{4\,(aq)} + 14e^-$ (Still need to Balance Hydrogen and the Charges)

c. **Balance the Hydrogen atom by adding $H^+_{(aq)}$ to the side that has less hydrogen atom.**

Example: $Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)}$ (Cl changes from 0 to +7. Hence, add 7 e^- to the product side.)

$Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)} + 7e^-$ (Multiply the $HClO_4$ and e^- by 2 to balance Cl_2.)

$Cl_{2\,(g)} \rightarrow 2\ HClO_{4\,(aq)} + 14e^-$ (Since there are no oxygen on the left and we have 8 oxygen atom to balance, 2 $HClO_4$, we need to add 8 H_2O to the reactant side.)

$Cl_{2\,(g)} + 8\ H_2O_{(l)} \rightarrow 2\ HClO_{4\,(aq)} + 14e^-$ **(We need 14 H^+ on the right to balance the 16 H of the left.)**

$Cl_{2\,(g)} + 8\ H_2O_{(l)} \rightarrow 2\ HClO_{4\,(aq)} + 14\ H^+_{(aq)} + 14e^-$ **(In ACIDIC Environment: Charges and Elements are Balanced)**

d. **In Basic Environment, Add the Same Number of OH^- as H^+ to BOTH Sides. Combine H^+ and OH^- that are on the Same Side into H_2O. Simplify the H_2O on Both Sides.**

Example: $Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)}$ (Cl changes from 0 to +7. Hence, add 7 e^- to the product side.)

$Cl_{2\,(g)} \rightarrow HClO_{4\,(aq)} + 7e^-$ (Multiply the $HClO_4$ and e^- by 2 to balance Cl_2.)

$Cl_{2\,(g)} \rightarrow 2\ HClO_{4\,(aq)} + 14e^-$ (Since there are no oxygen on the left and we have 8 oxygen atom to balance, 2 $HClO_4$, we need to add 8 H_2O to the reactant side.)

$Cl_{2\,(g)} + 8\ H_2O_{(l)} \rightarrow 2\ HClO_{4\,(aq)} + 14e^-$

(We need 14 H^+ on the right to balance the 16 H of the left.)

$Cl_{2\,(g)} + 8\ H_2O_{(l)} \rightarrow 2\ HClO_{4\,(aq)} + 14\ H^+_{(aq)} + 14e^-$

(In BASIC Environment: Add 14 OH^- on Both Sides)

$Cl_{2\,(g)} + 8\ H_2O_{(l)} + 14\ OH^-_{(aq)} \rightarrow 2\ HClO_{4\,(aq)} + 14\ H^+_{(aq)} + 14\ OH^-_{(aq)} + 14e^-$

(Combine 14 H^+ and 14 OH^- on the right into 14 H_2O)

$Cl_{2\,(g)} + 8\ H_2O_{(l)} + 14\ OH^-_{(aq)} \rightarrow 2\ HClO_{4\,(aq)} + 14\ H_2O_{(l)} + 14e^-$

(Simplify the number of H_2O on either side.)

$Cl_{2\,(g)} + 14\ OH^-_{(aq)} \rightarrow 2\ HClO_{4\,(aq)} + 6\ H_2O_{(l)} + 14e^-$

(In BASIC Environment: Charges and Elements are Balanced)

4. **Always CHECK if the half-reaction is Balanced for All Elements and Charges.**
5. **Do Steps 1 to 4 again for the another atom that changes oxidation number.**
6. **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 equation in acidic environment. Identify the oxidizing agent and reduction agent.

a. $KMnO_{4\,(s)} + HBr_{\,(aq)} + Sn^{2+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + Sn^{4+}_{(aq)}$

$KMnO_{4\,(s)} + HBr_{\,(aq)} + Sn^{2+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + Sn^{4+}_{(aq)}$

Manganese Oxidation Number: +7 to +2 **(Reduction)**
Tin Oxidation Number: +2 to +4 **(Oxidation)**

Oxidation Half-Rxn: $Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^{-}$

Reduction Half-Rxn: $KMnO_{4\,(s)} + HBr_{\,(aq)} + 5e^{-} \rightarrow Mn^{2+}_{(aq)} + K^{+}_{(aq)} + Br^{-}_{(aq)}$ (Add $5e^{-}$, K^{+}, and Br^{-})
$KMnO_{4\,(s)} + HBr_{\,(aq)} + 5e^{-} \rightarrow Mn^{2+}_{(aq)} + K^{+}_{(aq)} + Br^{-}_{(aq)} + 4\,H_2O_{\,(l)}$
(Balance 4 O with 4 H_2O)
$KMnO_{4\,(s)} + 8\,HBr_{\,(aq)} + 5e^{-} \rightarrow Mn^{2+}_{(aq)} + K^{+}_{(aq)} + 8\,Br^{-}_{(aq)} + 4\,H_2O_{\,(l)}$
(Balance 8 H with 8 HBr and 8 Br^{-} - H^{+} is provided by HBr)

Combine Oxidation and Reaction Half-Reactions by Equating the Number of Electrons.

Ox Half-Rxn: $5\,(\,Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^{-}\,)$
Red Half-Rxn: $2\,(\,KMnO_{4\,(s)} + 8\,HBr_{\,(aq)} + 5e^{-} \rightarrow Mn^{2+}_{(aq)} + K^{+}_{(aq)} + 8\,Br^{-}_{(aq)} + 4\,H_2O_{\,(l)}\,)$
$2\,KMnO_{4\,(s)} + 16\,HBr_{\,(aq)} + 5\,Sn^{2+}_{(aq)} \rightarrow 5\,Sn^{4+}_{(aq)} + 2\,Mn^{2+}_{(aq)} + 2\,K^{+}_{(aq)} + 16\,Br^{-}_{(aq)} + 8\,H_2O_{\,(l)}$

Oxidizing Agent = $KMnO_{4\,(s)}$ **Reducing Agent =** $Sn^{2+}_{\,(aq)}$

b. $H_2SeO_{3\,(aq)} + H_2S_{\,(aq)} \rightarrow S_{\,(s)} + Se_{\,(s)}$

$H_2SeO_{3\,(aq)} + H_2S_{\,(aq)} \rightarrow S_{\,(s)} + Se_{\,(s)}$

Selenium Oxidation Number: +4 to 0 **(Reduction)**
Sulfur Oxidation Number: –2 to 0 **(Oxidation)**

Oxidation Half-Rxn: $H_2S_{\,(aq)} \rightarrow S_{\,(s)} + 2\,H^{+}_{(aq)} + 2e^{-}$ (Add $2e^{-}$ and 2 H^{+})

Reduction Half-Rxn: $H_2SeO_{3\,(aq)} + 4e^{-} \rightarrow Se_{\,(s)}$ (Add $4e^{-}$)
$H_2SeO_{3\,(aq)} + 4e^{-} \rightarrow Se_{\,(s)} + 3\,H_2O_{\,(l)}$ (Balance 3 O with 3 H_2O)
$H_2SeO_{3\,(aq)} + 4\,H^{+}_{(aq)} + 4e^{-} \rightarrow Se_{\,(s)} + 3\,H_2O_{\,(l)}$
(Balance 6 H with 4 H^{+} - There are already 2 H in H_2SeO_3)

Combine Oxidation and Reaction Half-Reactions by Equating the Number of Electrons.

Ox Half-Rxn: $2\,(\,H_2S_{\,(aq)} \rightarrow S_{\,(s)} + 2\,H^{+}_{(aq)} + 2e^{-}\,)$
Red Half-Rxn: $H_2SeO_{3\,(aq)} + 4\,H^{+}_{(aq)} + 4e^{-} \rightarrow Se_{\,(s)} + 3\,H_2O_{\,(l)}$
$H_2SeO_{3\,(aq)} + 2\,H_2S_{\,(aq)} \rightarrow 2\,S_{\,(s)} + Se_{\,(s)} + 3\,H_2O_{\,(l)}$ (4 H+ on either side cancel out)

Oxidizing Agent = $H_2SeO_{3\,(s)}$ **Reducing Agent =** $H_2S_{\,(aq)}$

Example 2: Balance the following equation in basic environment. Identify the oxidizing agent and reduction agent.

a. $NBr_{3\,(aq)} \rightarrow N_{2\,(g)} + Br^{-}_{(aq)} + HOBr_{(aq)}$

$NBr_{3\,(aq)} \rightarrow N_{2\,(g)} + Br^{-}_{(aq)} + HOBr_{(aq)}$

Nitrogen Oxidation Number: **+3 to 0** **(Reduction)**

Bromine Oxidation Number: **–1 to (–1) +1** **(Oxidation)**

Reduction Half-Rxn: $NBr_{3\,(aq)} + 3e^{-} \rightarrow N_{2\,(g)} + 3\,Br^{-}_{(aq)}$ (Add 3e^{-} and 3 Br^{-})

$2\,NBr_{3\,(aq)} + 6e^{-} \rightarrow N_{2\,(g)} + 6\,Br^{-}_{(aq)}$ (Multiply e^{-}, NBr_3 and Br^{-} by 2 to balance N_2)

Oxidation Half-Rxn: $Br^{-}_{(aq)} \rightarrow HOBr_{(aq)} + 2e^{-}$ (Add 2e^{-} - Have to separate Br^{-} from NBr_3. Otherwise, there is no way to balance N)

$Br^{-}_{(aq)} + H_2O_{(l)} \rightarrow HOBr_{(aq)} + 2e^{-}$ (Balance O with H_2O)

$Br^{-}_{(aq)} + H_2O_{(l)} + OH^{-}_{(aq)} \rightarrow HOBr_{(aq)} + H^{+}_{(aq)} + OH^{-}_{(aq)} + 2e^{-}$

(Balance H with H^{+}, but add equal OH^{-} to both sides – Basic Environment)

$Br^{-}_{(aq)} + H_2O_{(l)} + OH^{-}_{(aq)} \rightarrow HOBr_{(aq)} + H_2O_{(l)} + 2e^{-}$ (Simplify H_2O on both sides)

$Br^{-}_{(aq)} + OH^{-}_{(aq)} \rightarrow HOBr_{(aq)} + 2e^{-}$ (Check Balancing on Charges and Elements)

Combine Oxidation and Reaction Half-Reactions by Equating the Number of Electrons.

Red Half-Rxn: $2\,NBr_{3\,(aq)} + 6e^{-} \rightarrow N_{2\,(g)} + 6\,Br^{-}_{(aq)}$

Ox Half-Rxn: $3\,(\,Br^{-}_{(aq)} + OH^{-}_{(aq)} \rightarrow HOBr_{(aq)} + 2e^{-}\,)$

$2\,NBr_{3\,(aq)} + 3\,OH^{-}_{(aq)} \rightarrow N_{2\,(g)} + 3\,Br^{-}_{(aq)} + 3\,HOBr_{(aq)}$ (Simplify Br^{-} on both sides)

Oxidizing Agent and Reducing Agent = $NBr_{3\,(aq)}$

b. $Cl_{2\,(aq)} \rightarrow Cl^{-}_{(aq)} + ClO_3^{-}{}_{(aq)}$

$Cl_{2\,(aq)} \rightarrow Cl^{-}_{(aq)} + ClO_3^{-}{}_{(aq)}$

Chloride Oxidation Number: **0 to –1** **(Reduction)**

Chlorate Oxidation Number: **0 to +5** **(Oxidation)**

Oxidation Half-Rxn: $Cl_{2\,(g)} \rightarrow ClO_3^{-}{}_{(aq)} + 5e^{-}$ (Add 5e^{-})

$Cl_{2\,(g)} \rightarrow 2\,ClO_3^{-}{}_{(aq)} + 10e^{-}$ (Multiply e^{-} and ClO_3^{-} by 2 to balance Cl_2)

$Cl_{2\,(g)} + 6\,H_2O_{(l)} \rightarrow 2\,ClO_3^{-}{}_{(aq)} + 10e^{-}$ (Balance 6 O with 6 H_2O)

$Cl_{2\,(g)} + 6\,H_2O_{(l)} + 12\,OH^{-}_{(aq)} \rightarrow 2\,ClO_3^{-}{}_{(aq)} + 12\,H^{+}_{(aq)} + 12\,OH^{-}_{(aq)} + 10e^{-}$

(Balance H with H^{+}, but add equal OH^{-} to both sides – Basic Environment)

$Cl_{2\,(g)} + 6\,H_2O_{(l)} + 12\,OH^{-}_{(aq)} \rightarrow 2\,ClO_3^{-}{}_{(aq)} + 12\,H_2O_{(l)} + 10e^{-}$ (Simplify H_2O on both sides)

$Cl_{2\,(g)} + 12\,OH^{-}_{(aq)} \rightarrow 2\,ClO_3^{-}{}_{(aq)} + 6\,H_2O_{(l)} + 10e^{-}$ (Check Balancing)

Reduction Half-Rxn: $Cl_{2\,(g)} + e^{-} \rightarrow Cl^{-}_{(aq)}$ (Add 1e^{-})

$Cl_{2\,(g)} + 2e^{-} \rightarrow 2\,Cl^{-}_{(aq)}$ (Multiply e^{-} and Cl^{-} by 2 to balance Cl_2)

Combine Oxidation and Reaction Half-Reactions by Equating the Number of Electrons.

Ox Half-Rxn: $Cl_{2\,(g)} + 12\,OH^{-}_{(aq)} \rightarrow 2\,ClO_3^{-}{}_{(aq)} + 6\,H_2O_{(l)} + 10e^{-}$

Red Half-Rxn: $5\,(\,Cl_{2\,(g)} + 2e^{-} \rightarrow 2\,Cl^{-}_{(aq)}\,)$

$6\,Cl_{2\,(g)} + 12\,OH^{-}_{(aq)} \rightarrow 10\,Cl^{-}_{(aq)} + 2\,ClO_3^{-}{}_{(aq)} + 6\,H_2O_{(l)}$

Oxidizing Agent and Reducing Agent = $Cl_{2\,(g)}$

Predicting Observations of a Redox Reaction:

1. Look for **new solid** form or **gas** evolved.
2. Some of the **metal ions and polyatomic ions have different colours** (see table below).
3. There might be **pH changes** as [H^+] or [OH^-] increases or decreases as the redox reaction proceeds forward.

Some General Ions Colours in Solution for Row 1 of the Transition Metals

Ionic Species		Solution Concentrations	
		1.0 M	**0.010 M**
Dichromate	$Cr_2O_7^{2-}$	orange	pale orange
Chromate	CrO_4^{2-}	yellow	pale yellow
Chromium (III)	Cr^{3+}	blue-green	green
Cobalt (III)	Co^{3+}	yellow	pale yellow
Hexa-cyano-cobalt (III)	$Co(CN)_6^{3-}$	yellow	pale yellow
Hexa-ammine-cobalt (III)	$Co(NH_3)_6^{3+}$	yellow	pale yellow
Cobalt (II)	Co^{2+}	red	pink
Copper (II)	Cu^{2+}	blue	pale blue
Copper (I)	Cu^+	blue-green	pale blue-green
Iron (III)	Fe^{3+}	reddish-brown	pink
Tri-thiocyano-iron (III)	$Fe(SCN)_3$	red	pink
Hexa-cyano-iron (III)	$Fe(CN)_6^{3-}$	red	pink
Iron (II)	Fe^{2+}	lime green	colourless
Hexa-cyano-iron (II)	$Fe(CN)_6^{4-}$	yellow	pale yellow
Permanganate	MnO_4^-	deep purple	purple-pink
Manganese (IV)	Mn^{4+}	dark brown	reddish-brown
Manganese (II)	Mn^{2+}	pinkish-red	colourless
Nickel (II)	Ni^{2+}	green	pale green
Hexa-ammine-nickel (II)	$Ni(NH_3)_6^{2+}$	blue	pale blue
Vanadium (V)	V^{5+}	yellow	pale yellow
Vanadium (IV)	V^{4+}	blue	pale blue
Vanadium (III)	V^{3+}	blue-green	pale blue-green
Vanadium (II)	V^{2+}	violet	light purple

Some Common Oxidizing and Reducing Agents

Oxidizing Agents

$MnO_4^- \rightarrow Mn^{2+}$ (acid / neutral); MnO_2 (basic)
$Cr_2O_7^{2-} \rightarrow Cr^{3+}$
$OOCCOO^{2-} \rightarrow CO_2$
Halogen Elements → Halide ions
$H_2O_2 \rightarrow H_2O$
$HNO_3 \rightarrow NO_2$ (concentrated); NO (dilute)
H_2SO_4 (concentrated) $\rightarrow SO_2$

Reducing Agents

Halide Ions → Elemental Halogens
Metal Elements → Metal Ions
$SO_3^{2-} \rightarrow SO_4^{2-}$
$NO_2^- \rightarrow NO_3^-$
Elemental Halogen (Basic solutions) → Halate or Hypohalite Ions (ClO_3^- or ClO^-)
H_2O_2 (Basic solutions) $\rightarrow O_2$

Species that can be BOTH Oxidizing and Reducing Agents

$SO_3^{2-} \rightarrow SO_4^{2-}$ or S
$S \rightarrow SO_3^{2-}$ or S^{2-}
$NO_2^- \rightarrow NO_3^-$ or NH_3

4.8: Redox Titrations

Redox Titration: - a titration involving redox half reactions to determine the concentration of an ion.
- **does not need any indicator** as the analyte ion tends to have a colour of its own.

Stoichiometry of Redox Titration:

1. Balance the Redox Reaction using the Half-Reaction Method.
2. Find the moles of the given reagent (usually with the titrant where the concentration and volume added are known).
3. Set up mole ratio and determine the number of moles of the analyte ion at equivalence point.
4. Calculate the concentration of the analyte ion.

Example 1: 10.0 mL of 0.0200 M acidified $KMnO_{4\,(aq)}$ is titrated with an unknown concentration of Sn^{2+} solution. The average volume of Sn^{2+} added was 32.42 mL. Use the answer of example **1a**. of section 19.1 as the equation for this redox reaction. Determine the concentration of Sn^{2+}. Comment on any qualitative observations.

Ox Half-Rxn: $5\,(\,Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^-\,)$

Red Half-Rxn: $2\,(\,KMnO_{4\,(aq)} + 8\,HBr_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + K^+_{(aq)} + 8\,Br^-_{(aq)} + 4\,H_2O_{(l)}\,)$

$$2\,KMnO_{4\,(aq)} + 16\,HBr_{(aq)} + 5\,Sn^{2+}_{(aq)} \rightarrow 5\,Sn^{4+}_{(aq)} + 2\,Mn^{2+}_{(aq)} + 2\,K^+_{(aq)} + 16\,Br^-_{(aq)} + 8\,H_2O_{(l)}$$

10.0 mL 32.42 mL
0.0200 mol/L ? mol/L

① $n_{KMnO_4} = CV = (0.0200\ \text{mol}/\cancel{\text{L}})\,(10.0\ \text{m}\cancel{\text{L}}) = 0.200\ \text{mmol}$

② $n_{Sn^{2+}} = 0.200\ \text{m}\cancel{\text{mol KMnO}_4} \times \dfrac{5\ \text{mol Sn}^{2+}}{2\ \cancel{\text{mol}}\ \cancel{\text{KMnO}_4}} = 0.500\ \text{mmol Sn}^{2+}$

③ $[Sn^{2+}] = \dfrac{n}{V} = \dfrac{0.5000\ \cancel{\text{m}}\text{mol}}{32.43\ \cancel{\text{m}}\text{L}} = 0.015417823\ \text{mol/L}$

$\boxed{[Sn^{2+}] = 0.0154\ \text{mol/L}}$

Qualitative Observations:

1. **MnO_4^- is purple pink colour at around 0.0200 M. As Sn^{2+} is added from the buret, MnO_4^- in the flask will turn into Mn^{2+}, which is colourless at low concentration.**
2. **The acidified Sn^{2+} solution initially had a low pH but the pH will increase as $HBr_{(aq)}$ is consumed in the titration.**

Assignment
19.1 pg. 855 #1 and 2
4.8 pg. 160–161 #89 to 98

19.2: Galvanic Cells

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.
- involve **Spontaneous Redox Reaction** and a **Positive Cell Potential** (see section 19.3)

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**.

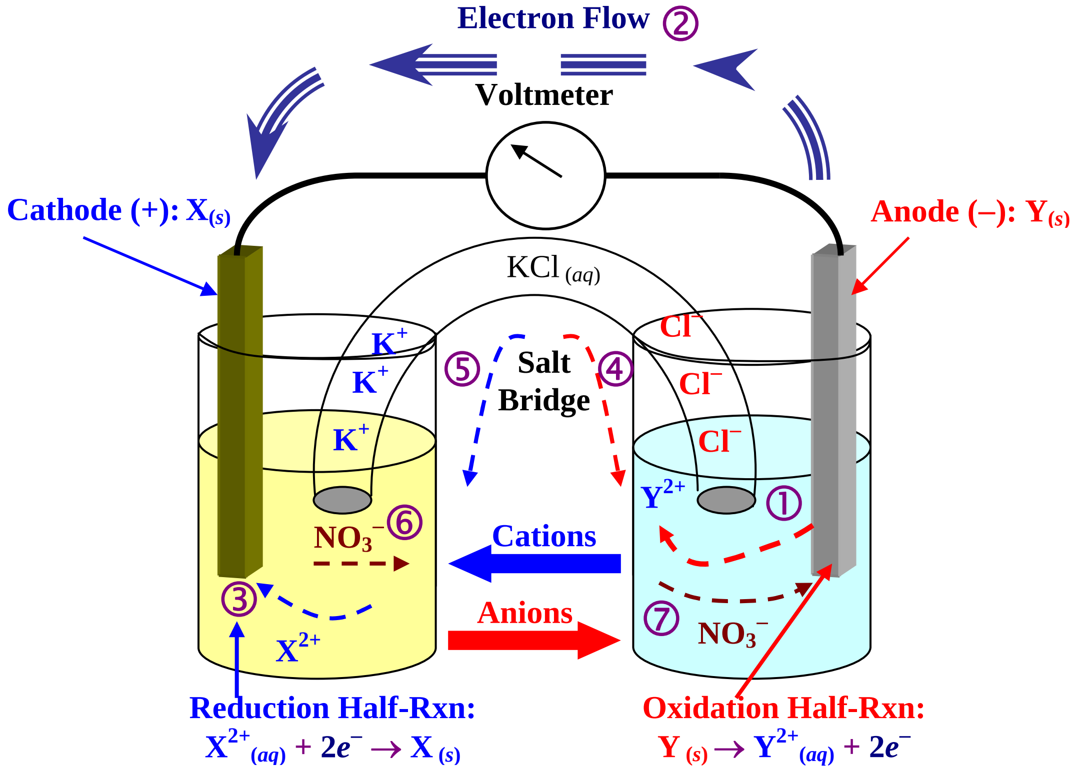
Volts (**V**): - the amount of **work (energy) in J per charge (*q*) coulomb (unit symbol: *C*) of electrons** transferred between two potentials (anode and cathode).
- commonly refer to as **potential difference**.

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.

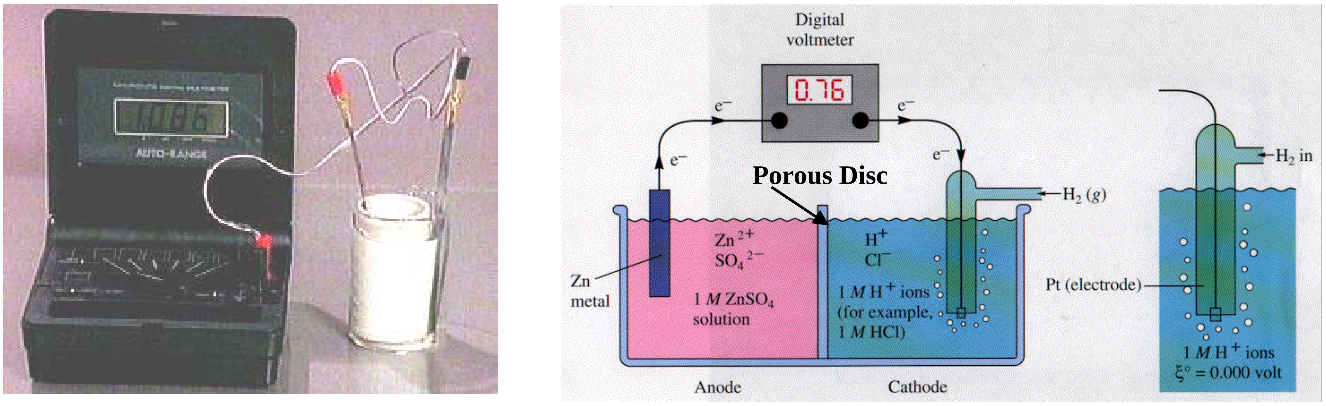
③ Electrons arrived at the Cathode combining with X^{2+} to form $X_{(s)}$.

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).

19.3: Standard Reduction Potentials

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).

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

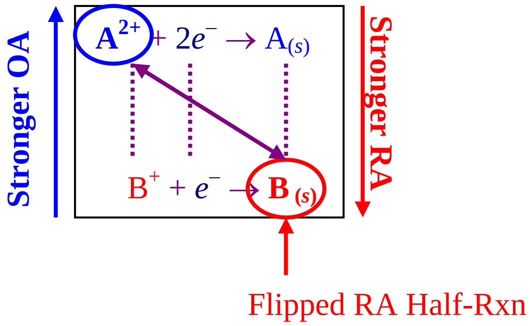
Standard Reduction Potential: - the electric potentials of reduction half-reactions as compared with hydrogen under standard condition (25°C and 1.0 mol/L of electrolytes or 1.0 atm of gaseous element (*see Table on the next page*).

- 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**. (This makes sense, as we know $F_{2\,(g)}$ is the most electronegative, and thereby is the strongest oxidizing agent – likes to gain electrons.)
- conversely, the **weakest reducing agent is listed on the right and increasing in strengths as one moves down the table**. (This also makes sense, 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 $Cr_2O_7^{2-}$.

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.

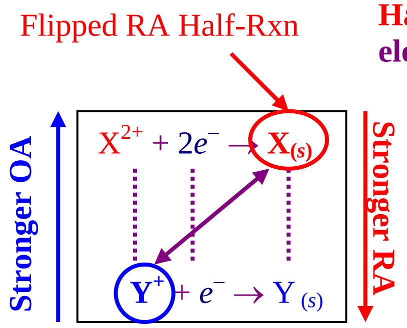
2. **Spontaneous Reaction**: - redox reactions that **will proceed forward** where chemical energy converts to electrical energy (galvanic cells).
- the **Oxidizing Agent (OA) on the LEFT is HIGHER than the Reducing Agent (RA) on the RIGHT**.
- **FLIP the Reducing Agent – Oxidation Half-Reaction (LOWER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



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

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

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 (electrolytic cell – see section 19.8)
- 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**.



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

$$2\,(Y^+ + e^- \rightarrow Y_{(s)}) \qquad \text{(Reduction)}$$
$$\underline{X_{(s)} \rightarrow X^{2+} + 2e^-} \qquad \text{(Oxidation)}$$
$$\underset{\text{OA}}{2\,Y^+} + \underset{\text{RA}}{X_{(s)}} \rightarrow \textbf{Non-Spontaneous}$$

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$F_2(g) + 2e^-$	→	$2F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$Au^{3+} + 3e^-$	→	$Au(s)$	1.50
$Cl_2(g) + 2e^-$	→	$2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^-$	→	$2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	→	$2Br^-$	1.07
$2Hg^{2+} + 2e^-$	→	Hg_2^{2+}	0.92
$Hg^{2+} + 2e^-$	→	$Hg(l)$	0.85
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Hg_2^{2+} + 2e^-$	→	$2Hg(l)$	0.79
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$I_2(s) + 2e^-$	→	$2I^-$	0.53
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	→	$Cu(s)$	0.34
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Sn^{4+} + 2e^-$	→	Sn^{2+}	0.15
$S(s) + 2H^+ + 2e^-$	→	$H_2S(g)$	0.14
$2H^+ + 2e^-$	→	$H_2(g)$	0.00
$Pb^{2+} + 2e^-$	→	$Pb(s)$	−0.13
$Sn^{2+} + 2e^-$	→	$Sn(s)$	−0.14
$Ni^{2+} + 2e^-$	→	$Ni(s)$	−0.25
$Co^{2+} + 2e^-$	→	$Co(s)$	−0.28
$Cd^{2+} + 2e^-$	→	$Cd(s)$	−0.40
$Cr^{3+} + e^-$	→	Cr^{2+}	−0.41
$Fe^{2+} + 2e^-$	→	$Fe(s)$	−0.44
$Cr^{3+} + 3e^-$	→	$Cr(s)$	−0.74
$Zn^{2+} + 2e^-$	→	$Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	→	$H_2(g) + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$	→	$Mn(s)$	−1.18
$Al^{3+} + 3e^-$	→	$Al(s)$	−1.66
$Be^{2+} + 2e^-$	→	$Be(s)$	−1.70
$Mg^{2+} + 2e^-$	→	$Mg(s)$	−2.37
$Na^+ + e^-$	→	$Na(s)$	−2.71
$Ca^{2+} + 2e^-$	→	$Ca(s)$	−2.87
$Sr^{2+} + 2e^-$	→	$Sr(s)$	−2.89
$Ba^{2+} + 2e^-$	→	$Ba(s)$	−2.90
$Rb^+ + e^-$	→	$Rb(s)$	−2.92
$K^+ + e^-$	→	$K(s)$	−2.92
$Cs^+ + e^-$	→	$Cs(s)$	−2.92
$Li^+ + e^-$	→	$Li(s)$	−3.05

Example 1: Predict the whether the following reactions will react and write the complete redox reactions.

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

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

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

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

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

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

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

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

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

Example 2: Four elements, A, B, C, and D, form diatomic molecules and negative ions. Arranged the elements in order from most reactive to least reactive if the following observations are made

$$\begin{array}{l} A_2 + 2\,C^- \rightarrow 2\,A^- + C_2 \\ B_2 + 2\,D^- \rightarrow \text{No Reaction} \\ C_2 + 2\,D^- \rightarrow 2\,C^- + D_2 \end{array}$$

The diatomic elements undergo reduction to become anions. For example, $A_2 + 2e^- \rightarrow 2\,A^-$. Thus, the elements are oxidizing agents.

	Strength of Oxidizing Agents
$\underline{A_2} + 2\,C^- \rightarrow 2\,A^- + \underline{C_2}$	$A_2 > C_2$
$\underline{B_2} + 2\,D^- \rightarrow$ **No Reaction**	$B_2 < D_2$
$\underline{C_2} + 2\,D^- \rightarrow 2\,C^- + \underline{D_2}$	$C_2 > D_2$

Putting all the inequalities together, we have $A_2 > C_2 > D_2 > B_2$

Example 3: As part of a laboratory procedure, a student recorded observations after placing strips of metal into aqueous solutions according to the following combinations. The results are recorded using "✓" representing a reaction and "✗" representing no reaction. Organize the oxidizing agents from the strongest to the weakest.

Metals / Ions	$A^{2+}_{(aq)}$	$B^{2+}_{(aq)}$	$C^{2+}_{(aq)}$	$D^{2+}_{(aq)}$
$A_{(s)}$	-----	✓	✗	✓
$B_{(s)}$	✗	-----	✗	✗
$C_{(s)}$	✓	✓	-----	✓
$D_{(s)}$	✗	✓	✗	-----

The Oxidizing Agent are the ions because they Reduced (Gained Electrons) to produce their metal elements. For example, $A^{2+} + 2e^- \rightarrow A_{(s)}$.

The Strongest Oxidizing Agent is the ion that is MOST Reactive (look at the above table vertically). Thus, in order of decreasing strength (reactivity):

$$B^{2+} > D^{2+} > A^{2+} > C^{2+}$$

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)

$Fe^{3+} \rightarrow Fe^{2+} \rightarrow Fe_{(s)}$	$Cr^{3+} \rightarrow Cr^{2+} \rightarrow Cr_{(s)}$	$Sn^{4+} \rightarrow Sn^{2+} \rightarrow Sn_{(s)}$
$Fe^{3+} + e^- \rightarrow \underline{\mathbf{Fe^{2+}}}$ $E° = +0.77$ V $\underline{\mathbf{Fe^{2+}}} + 2e^- \rightarrow Fe_{(s)}$ $E° = -0.44$ V	$Cr^{3+} + e^- \rightarrow \underline{\mathbf{Cr^{2+}}}$ $E° = -0.41$ V $\underline{\mathbf{Cr^{2+}}} + 2e^- \rightarrow Cr_{(s)}$ $E° = -0.91$ V	$Sn^{4+} + 2e^- \rightarrow \underline{\mathbf{Sn^{2+}}}$ $E° = +0.15$ V $\underline{\mathbf{Sn^{2+}}} + 2e^- \rightarrow Sn_{(s)}$ $E° = -0.14$ V

$H_2O_{(l)}$ as an Oxidizing Agent (Left Side of the Table)	$H_2O_{(l)}$ as an Reducing Agent (Right Side of the Table)
$\underline{\mathbf{2\ H_2O_{(l)}}} + 2e^- \rightarrow H_{2\,(g)} + 2\ OH^-$ $E° = -0.83$ V	$O_{2\,(g)} + 4\ H^+ + 4e^- \rightarrow \underline{\mathbf{2\ H_2O_{(l)}}}$ $E° = +1.23$ V

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.

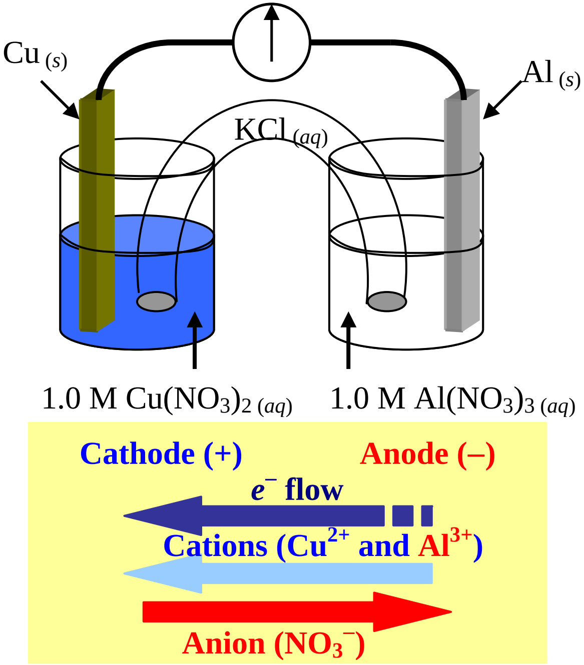
- single line, | , separates electrode and its electrolyte; double line, || , represents salt bridge, porous cup or porous disk.
- **ALWAYS write the Anode on the LEFT hand side.**

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 4: 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 $Al_{(s)}$, $\underline{Cu^{2+}}$ will be reduced ($Cu_{(s)}$ is the Cathode) and **$\underline{Al_{(s)}}$ will be oxidized (Anode – flipped half-reaction and voltage)**.

$$
\begin{array}{ll}
3\ (\ Cu^{2+}_{(aq)} + \mathbf{2e^-} \rightarrow Cu_{(s)}\ ) & E° = 0.34\text{ V} \\
\underline{2\ (\ Al_{(s)} \rightarrow Al^{3+}_{(aq)} + \mathbf{3e^-}\ )} & \underline{E° = +1.66\text{ V}} \\
\mathbf{3\ Cu^{2+}_{(aq)} + 2\ Al_{(s)} \rightarrow 2\ Al^{3+}_{(aq)} + 3\ Cu_{(s)}} & \underline{\mathbf{E°_{cell} = 2.00\text{ V}}}
\end{array}
$$

Note: We do NOT multiply $E°$.

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

19.4: Spontaneity of Redox Reactions

Faraday Constant (*F*): - the amount of charge (coulomb) in one mole of electrons. **($F = 96{,}500$ C/mol e^-)**

Free Energy and Cell Potential: - we can relate $E°_{\text{cell}}$ with $\Delta G°$ in order to predict spontaneity.

$E°_{\text{cell}} = -\dfrac{w}{q}$ ($E°_{\text{cell}}$ as emf is defined as the ability to do work ($-w$) per charge.)

$w = -qE°_{\text{cell}}$ (Manipulate Equation)

$\Delta G° = -qE°_{\text{cell}}$ ($\Delta G° = w_{\max} = w$ Free Energy is maximum useful work obtained, assuming 100% efficiency of the cell.)

$\Delta G° = -nFE°_{\text{cell}}$ ($F = \dfrac{q}{n_{e^-}}$ or $q = n_{electrons}F$)

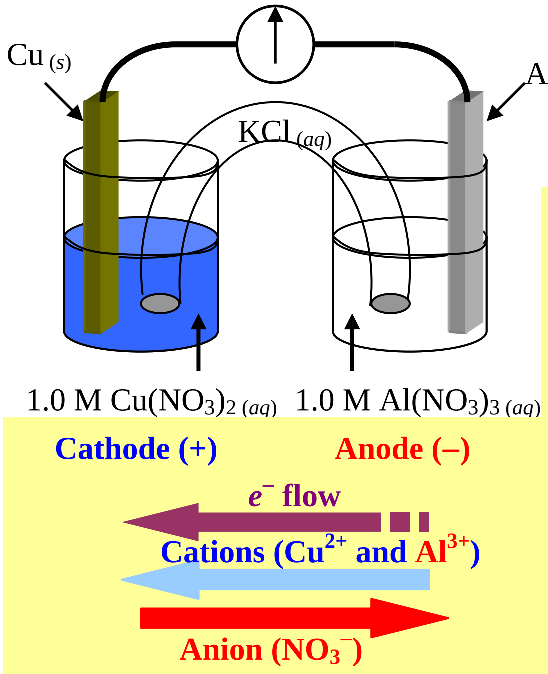
Free Energy and Cell Potential

$$\Delta G° = -nFE°_{\text{cell}}$$

$\Delta G°$ = Standard Free Energy (J)
n = moles of electrons transferred
F = Faraday Constant (9.65×10^4 C/mol e^-)
$E°_{\text{cell}}$ = Standard Cell Potential (V)

$E°_{\text{cell}} > 0$ means $\Delta G° < 0$ (Spontaneous Reaction)
$E°_{\text{cell}} < 0$ means $\Delta G° > 0$ (Non-Spontaneous Reaction)

Example 1: Using the aluminum-copper galvanic cell in example 4 of section 17.2, determine the $\Delta G°$ of under standard conditions and verify the reaction is spontaneous.



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

$\Delta G° = ?$
$n = 6$ moles of e^- ($3 \times 2e^-$ or $2 \times 3e^-$)
$F = 9.65 \times 10^4$ C/mol e^-
$E°_{\text{cell}} = 2.00$ V

$\Delta G° = -nFE°_{\text{cell}} = -$ (6 mol)(9.65×10^4 C/mol e^-)(2.00 V)
$\Delta G° = -1{,}158{,}000$ J

$$\boxed{\Delta G° = -1.16 \times 10^3 \text{ kJ}}$$

Since $\Delta G° < 0$ and its magnitude is quite large, we would expect this galvanic cell to be very spontaneous.

Assignment

19.2 & 19.3 pg. 855–856 #3 to 6. 11 to 18
19.4 pg. 856 #19, 21 to 26

19.5: The Effect of Concentration on Cell Emf

Equilibrium Quotient and Cell Potential: - when the equilibrium quotient of the redox reaction, $Q > K$, the electrochemical cell has its $E_{\text{cell}} > 0$ (anode is lower than the oxidizing agent in the Standard Reduction Potential Table), **making it spontaneous**.

The Nernst Equation: - an equation to **calculate cell potential (E_{cell}) at other conditions BESIDES 1.0 M and 25°C** with the **equilibrium quotient**.

$$\Delta G = \Delta G^\circ + RT \ln Q$$ (Free Energy Equation in terms of Temperature and Equilibrium)

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q$$ (Replace ΔG with $-nFE_{\text{cell}}$ and ΔG° with $-nFE^\circ_{\text{cell}}$)

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$ (Divide each term on both sides by $-nF$)

The Nernst Equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \quad \text{or} \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{mol} \bullet \text{V}}{n} \log Q \quad \text{(at 25°C)}$$

E_{cell} = Cell Potential (V) at Other Conditions

E°_{cell} = Standard Cell Potential (V) at 1.0 M and 25°C

n = moles of *electrons* transferred per redox reaction

R = Gas Constant [8.31 (V • C) / (mol • K)]

T = Temperature in Kelvin

F = Faraday Constant (9.65×10^4 C/mol)

$$Q = \frac{[B^{a+}]^b}{[A^{b+}]^a} = \frac{[\text{Anode Electrolyte}]^b}{[\text{Cathode Electrolyte}]^a} = \text{Equilibrium Quotient for } aA^{b+} + bB_{(s)} \rightarrow bB^{a+} + aA_{(s)}$$

Using the Nernst Equation to Explain Operation of a Galvanic Cell:

1. **One way to Increase the E_{cell} from E°_{cell} is to setup the galvanic cell such that $[B^{a+}] < [A^{b+}]$ ([Anode Electrolyte] < [Cathode Electrolyte]), $E_{\text{cell}} > E^\circ_{\text{cell}}$ (E_{cell} is elevated from E°_{cell}).**

2. **Initially, when the electrochemical reaction operates under standard condition, $E_{\text{cell}} = E^\circ_{\text{cell}}$. This is because $Q = 1$ ($\ln Q$ or $\log Q = 0$) and [Anode Electrolyte] = [Cathode Electrolyte] = 1.0 M.**

3. **As the electrochemical cell operates (battery is discharging), the concentration of ions will change (E_{cell} decreases from E°_{cell}). $[B^{a+}] > [A^{b+}]$ ([Anode Electrolyte] > [Cathode Electrolyte]), $E_{\text{cell}} < E^\circ_{\text{cell}}$.**

4. Eventually, when **$Q = K$, $E_{\text{cell}} = 0$**. Then, the **flow of electrons will stop** **(battery is completely discharged). (Therefore K of redox reaction is usually very large to begin with. Equilibrium Position is favouring the product side).**

Calculating *K* of a Redox Reaction:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q \qquad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n}\log Q \quad \text{(at 25°C)} \quad \text{(Nernst Equation)}$$

$$0 = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln K \qquad 0 = E^\circ_{\text{cell}} - \frac{0.0592}{n}\log K \quad \text{(at 25°C)} \quad \textbf{(For } Q = K,\ E_{\text{cell}} = 0\textbf{)}$$

$$\frac{RT}{nF}\ln K = E^\circ_{\text{cell}} \qquad \frac{0.0592}{n}\log K = E^\circ_{\text{cell}} \quad \text{(at 25°C)} \quad \text{(Rearrange equation)}$$

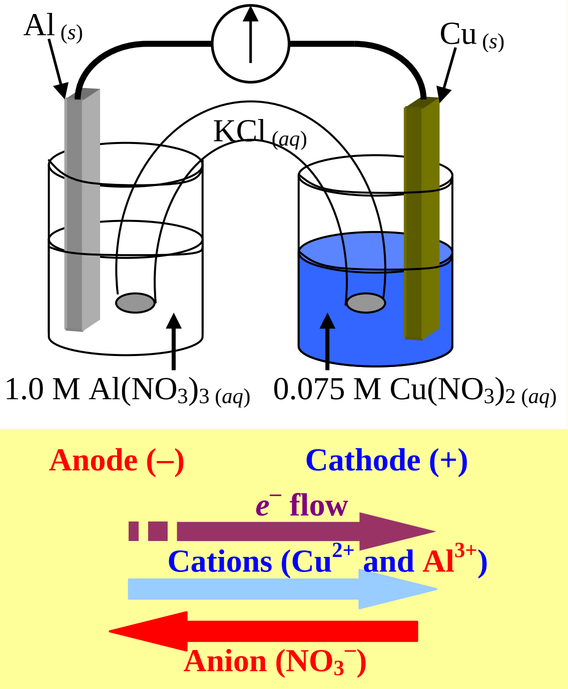
$$\ln K = \frac{nFE^\circ_{\text{cell}}}{RT} \qquad \log K = \frac{nE^\circ_{\text{cell}}}{0.0592} \quad \text{(at 25°C)} \quad \text{(Solve for } K\text{)}$$

Equilibrium Constant of Redox Equation

$$\ln K = \frac{nFE^\circ_{\text{cell}}}{RT} \quad \text{or} \quad \log K = \frac{nE^\circ_{\text{cell}}}{0.0592\ \text{mol} \bullet \text{V}} \quad \text{(at 25°C)}$$

Example 1: Using Example 4 of Section 19.3, the E°_{cell} for $\text{Al}_{(s)} \mid \text{Al}^{3+} \parallel \text{Cu}^{2+} \mid \text{Cu}_{(s)}$ is 2.00 V. Rewrite the net-ionic redox equation, and determine the E_{cell} of the following at 25°C. Include a diagram and label anode, cathode, electron flow, and ion migrations and their concentrations.

a. $\text{Al}_{(s)} \mid \text{Al}^{3+}\ (1.0\ \text{M}) \parallel \text{Cu}^{2+}\ (0.075\ \text{M}) \mid \text{Cu}_{(s)}$



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

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

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

$E_{\text{cell}} = ?$ $\qquad n = 6$ moles of e^- ($3 \times 2e^-$ or $2 \times 3e^-$)

$E^\circ_{\text{cell}} = 2.00$ V $\qquad T = 25$°C

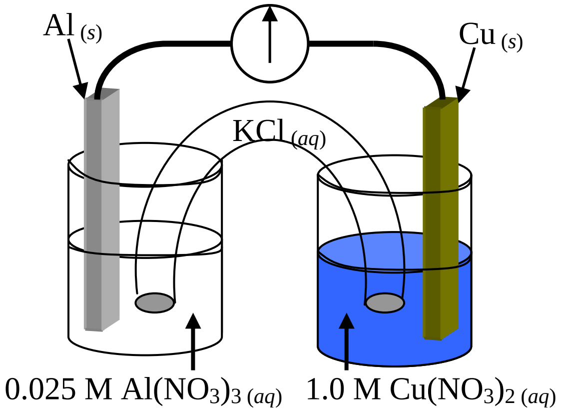
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{mol} \bullet \text{V}}{n}\log Q$$

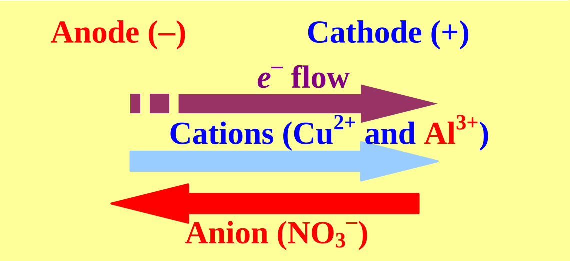
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{mol} \bullet \text{V}}{n}\log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3}$$

$$E_{\text{cell}} = (2.00\ \text{V}) - \frac{0.0592\ \cancel{\text{mol}} \bullet \text{V}}{(6\ \cancel{\text{mol}})}\log \frac{(1.0)^2}{(0.075)^3} \qquad \boxed{E_{\text{cell}} = 1.97\ \text{V}}$$

Since the [Al^{3+} = anode electrolyte] > [Cu^{2+} = cathode electrolyte], the E_{cell} is lowered from E°_{cell}.

b. $Al_{(s)} \mid Al^{3+}\ (0.025\ M) \parallel Cu^{2+}\ (1.0\ M) \mid Cu_{(s)}$





$$\begin{aligned} &3\,(\,Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}\,) && E^\circ = \ \ 0.34\ V \\ &2\,(\,Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-\,) && E^\circ = +1.66\ V \\ \hline &3\ Cu^{2+}_{(aq)} + 2\ Al_{(s)} \rightarrow 2\ Al^{3+}_{(aq)} + 3\ Cu_{(s)} && \underline{E^\circ_{cell} = \ \ 2.00\ V} \end{aligned}$$

$E_{cell} = ?$ $n = 6$ moles of e^- ($3 \times 2e^-$ or $2 \times 3e^-$)

$E^\circ_{cell} = 2.00\ V$ $T = 25°C$

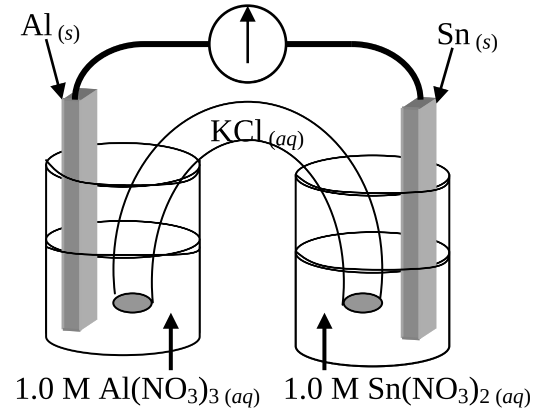
$$E_{cell} = E^\circ_{cell} - \frac{0.0592\ mol \bullet V}{n}\log Q$$

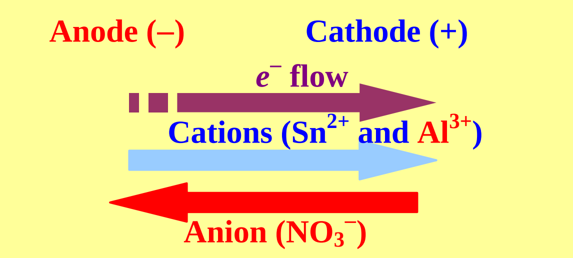
$$E_{cell} = E^\circ_{cell} - \frac{0.0592\ mol \bullet V}{n}\log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

$$E_{cell} = (2.00\ V) - \frac{0.0592\ \cancel{mol} \bullet V}{(6\ \cancel{mol})}\log \frac{(0.025)^2}{(1.0)^3} \qquad \boxed{E_{cell} = 2.03\ V}$$

Since the $[Al^{3+}$ = anode electrolyte$]$ < $[Cu^{2+}$ = cathode electrolyte$]$, the $\underline{E_{cell}}$ is elevated from $\underline{E^\circ_{cell}}$.

Example 2: Determine the equilibrium constant for the galvanic cell $Al_{(s)} \mid Al^{3+} \parallel Sn^{2+} \mid Sn_{(s)}$ at standard conditions. Include a diagram and label anode, cathode, electron flow, and ion migrations and their concentrations.





$$\begin{aligned} &3\,(\,Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}\,) && E^\circ = -0.14\ V \\ &2\,(\,Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-\,) && E^\circ = +1.66\ V \\ \hline &3\ Sn^{2+}_{(aq)} + 2\ Al_{(s)} \rightarrow 2\ Al^{3+}_{(aq)} + 3\ Sn_{(s)} && \underline{E^\circ_{cell} = \ \ 1.52\ V} \end{aligned}$$

$K = ?$ $n = 6$ moles of e^- ($3 \times 2e^-$ or $2 \times 3e^-$)

$E^\circ_{cell} = 1.52\ V$ $T = 25°C$

$$\log K = \frac{nE^\circ_{cell}}{0.0592\ mol \bullet V} = \frac{(6\ \cancel{mol})(1.52\ \cancel{V})}{0.0592\ \cancel{mol} \bullet \cancel{V}}$$

$$\log K = 154.0540541$$

$K = 10^{154.0540541}$ Too Large for Calculator to Handle

$K = (10^{0.0540541}) \times 10^{154}$

$$\boxed{K = 1.13 \times 10^{154}}$$

As we can see, the values of K for redox reactions are usually quite large.

Concentration Cells: - electrochemical cells where **both electrodes are of the same material** but the **concentration of the electrolytes are different**.
- under **standard condition, concentration cell has a E°_{cell} of 0** ($E^\circ_{\text{cathode}} = E^\circ_{\text{anode}}$).
- the half-cell that contains the **lower concentration electrolytes becomes the anode** (When [Anode Electrolyte] < [Cathode Electrolyte]), $E_{\text{cell}} > E^\circ_{\text{cell}}$ (E_{cell} is elevated from E°_{cell}).

Concentration Cells

$$E_{\text{cell, conc}} = \cancelto{0}{E^\circ_{\text{cell}}} - \frac{RT}{nF}\ln Q \quad \text{or} \quad E_{\text{cell, conc}} = \cancelto{0}{E^\circ_{\text{cell}}} - \frac{0.0592\ \text{mol} \bullet \text{V}}{n}\log Q$$

$$E_{\text{cell, conc}} = -\frac{RT}{nF}\ln Q \quad \text{or} \quad E_{\text{cell, conc}} = -\frac{0.0592\ \text{mol} \bullet \text{V}}{n}\log Q$$

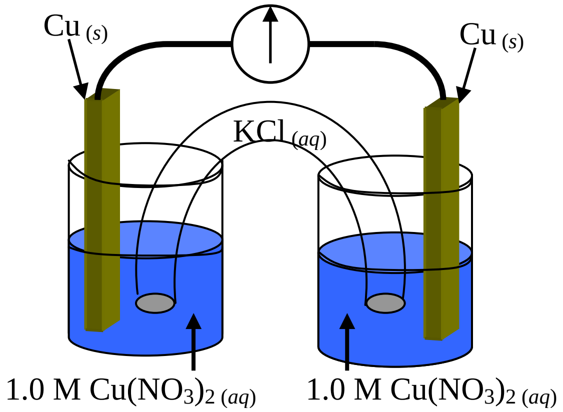
Q = Equilibrium Quotient for $a\text{A}^{b+}_{(\text{high conc})} + a\text{A}_{(s)} \rightarrow a\text{A}^{b+}_{(\text{low conc})} + a\text{A}_{(s)}$

$$Q = \frac{\left[\text{A}^{b+}_{(\text{low conc})}\right]^a}{\left[\text{A}^{b+}_{(\text{high conc})}\right]^a} = \frac{[\text{Anode Electrolyte}]}{[\text{Cathode Electrolyte}]}$$

Anode = Half-cell with Lower Concentration

Example 3: Calculate the E_{cell} of the following at 25°C. Draw a diagram and label the anode, cathode, and electron flow if applicable.

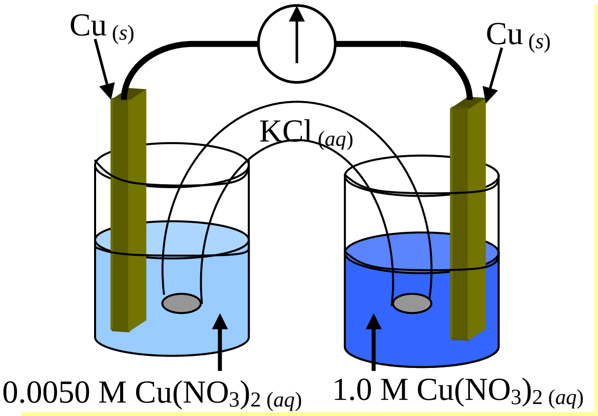
a. $\text{Cu}_{(s)}\ |\ \text{Cu}^{2+}\ (1.0\ \text{M})\ ||\ \text{Cu}^{2+}\ (1.0\ \text{M})\ |\ \text{Cu}_{(s)}$



$$\begin{array}{lr}
\text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)} & E^\circ = 0.34\ \text{V} \\
\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2e^- & E^\circ = -0.34\ \text{V} \\
\hline
\text{Cu}^{2+}_{(aq)} + \text{Cu}_{(s)} \rightarrow \text{No Reaction} & E^\circ_{\text{cell}} = 0.00\ \text{V}
\end{array}$$

When the two half-cells are Identical, there is no reaction and E°_{cell} = 0 V

b. $\text{Cu}_{(s)}\ |\ \text{Cu}^{2+}\ (0.0050\ \text{M})\ ||\ \text{Cu}^{2+}\ (1.0\ \text{M})\ |\ \text{Cu}_{(s)}$



Anode (–) **Cathode (+)**

e^- flow →

E_{cell} = ? n = 2 moles of e^- T = 25°C

$$E_{\text{cell, conc}} = -\frac{0.0592\ \text{mol} \bullet \text{V}}{n}\log Q$$

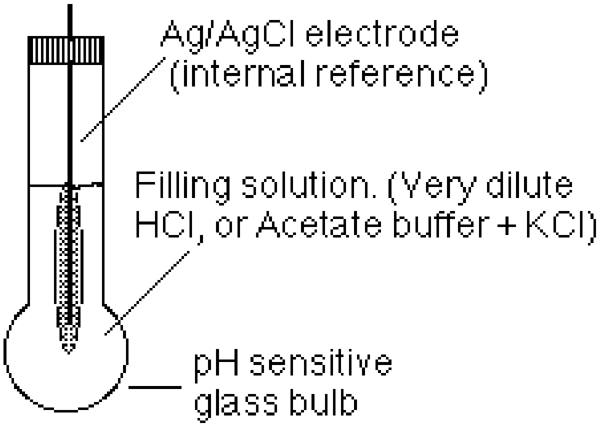
$$E_{\text{cell, conc}} = -\frac{0.0592\ \text{mol} \bullet \text{V}}{n}\log\frac{\left[\text{Cu}^{2+}_{\text{low conc}}\right]}{\left[\text{Cu}^{2+}_{\text{high conc}}\right]}$$

$$E_{\text{cell, conc}} = -\frac{0.0592\ \cancel{\text{mol}} \bullet \text{V}}{(2\ \cancel{\text{mol}})}\log\frac{(0.0050)}{(1.0)}$$

$$\boxed{E_{\text{cell, conc}} = 0.068\ \text{V}}$$

The bigger the difference between the concentrations of the electrolytes in the half-cells, the higher the $E_{\text{cell, conc}}$.

Ion-Selective Electrode: - a glass electrode with a tin-walled membrane containing a metal wire (coated with specialized crystal sensitive to certain ion concentration) enclosed within a reference solution.
- is used to measured selected ion concentration (most commonly H^+ for pH, but can be modified to measure concentrations of Cd^{2+}, Ca^{2+}, Cu^{2+}, K^+, Ag^+, Na^+, Br^-, Cl^-, CN^-, F^-, NO_3^- and S^{2-}).

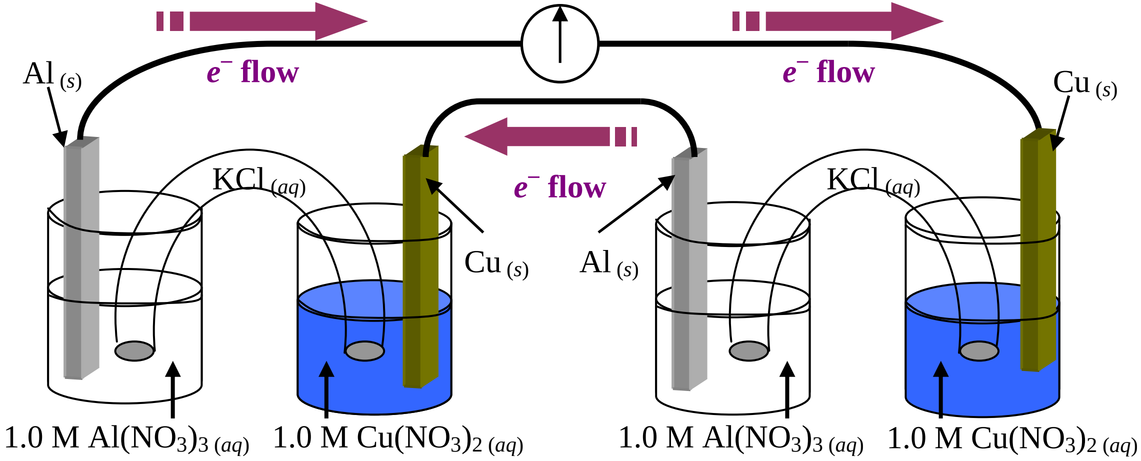


A typical pH Meter (above) and its inner working (right)

Assignment
19.5 pg. 856 #27 to 34

19.6: Batteries

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 (+)**

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

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

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

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

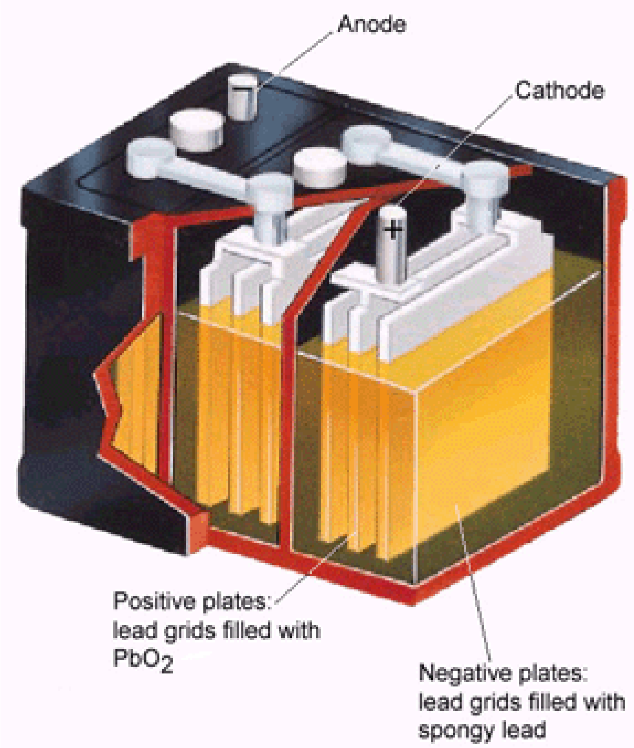
$2\,(\,Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-\,)$ $E° = +1.66$ V

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

Total Voltage = 2.00 V + 2.00 V = 4.00 V

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 ($H_2SO_{4\,(aq)}$) 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 total 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) $PbO_{2\,(s)} + HSO_4^{-}{}_{(aq)} + 3\,H^{+}{}_{(aq)} + 2e^{-} \rightarrow PbSO_{4\,(s)} + 2\,H_2O_{(l)}$ $E° = 1.69$ V (Cathode)

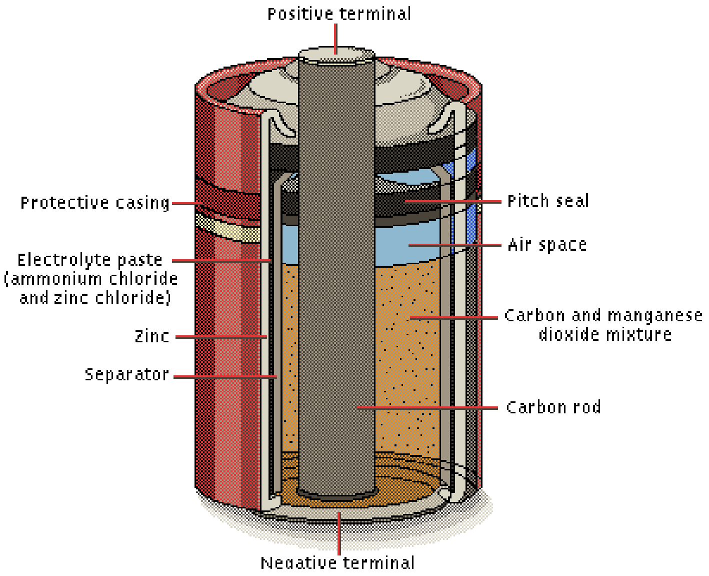
(Oxidation) $\underline{Pb_{(s)} + HSO_4^{-}{}_{(aq)} \rightarrow PbSO_{4\,(s)} + H^{+}{}_{(aq)} + 2e^{-}}$ $E° = +0.35$ V (Anode)

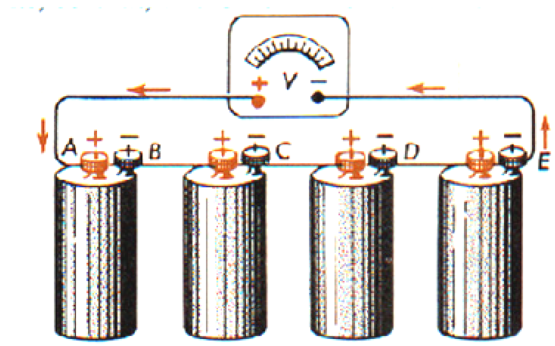
$\mathbf{PbO_{2\,(s)} + Pb_{(s)} + 2\,HSO_4^{-}{}_{(aq)} + 2\,H^{+}{}_{(aq)} \rightarrow 2\,PbSO_{4\,(s)} + 2\,H_2O_{(l)}}$ $\underline{E°_{cell} = \mathbf{2.04\ V}}$

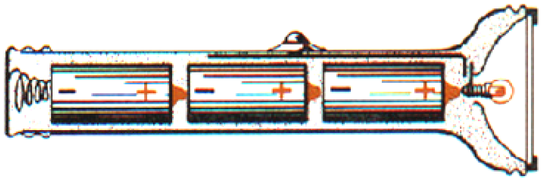
2. **Dry Cell**: - a **non-rechargeable battery** commonly used in electronic devices such as, radios, calculators, and electronic toys.

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

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

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

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

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

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

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

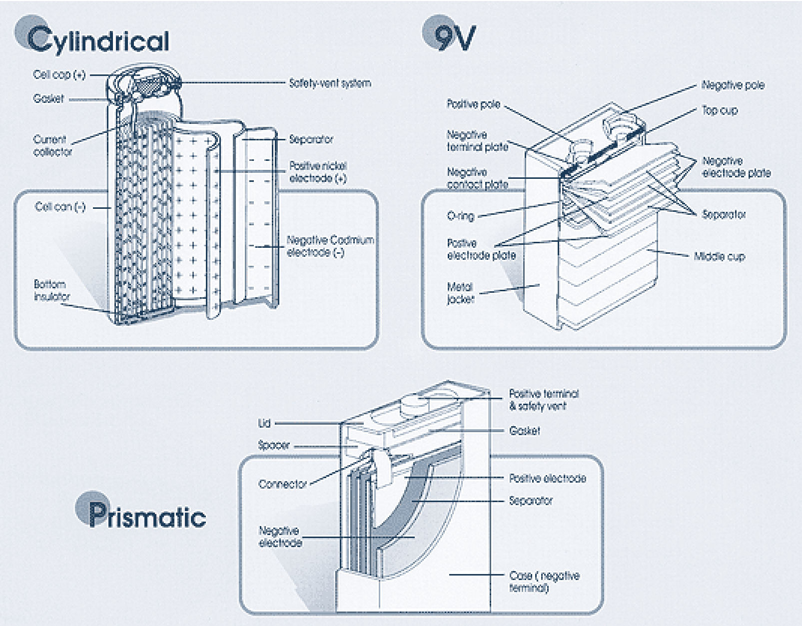
3. **Nickel Cadmium Battery**: - a dry cell with the same set up as alkaline dry cell but it can be **recharged** (a lot lighter than lead-acid batteries).
   - it can developed a "*memory*" problem, so after each recharged cycled, the battery tends to have a shorter "life-span". This can be corrected 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) $NiO_{2\ (s)} + 2\ H_2O_{(l)} + 2e^- \rightarrow Ni(OH)_{2\ (s)} + 2\ OH^-{}_{(aq)}$ $E°_{cathode} = -0.49$ V

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

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



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

4. **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.

Ni-MH batteries for portable electronic devices such as digital cameras.

- 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 $E°_{cell}$.

Redox Reaction for a Ni-MH Dry Cell Battery

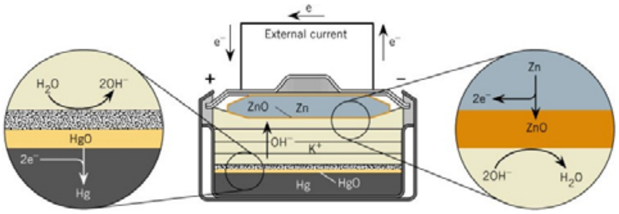
(Reduction) $NiOOH_{(s)} + H_2O_{(l)} + e^- \rightarrow Ni(OH)_{2\,(s)} + OH^-_{(aq)}$ $E°_{cathode} = –0.52$ V

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

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

5. **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.



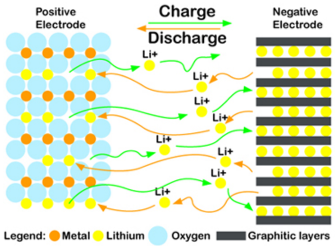
Redox Reaction for a Mecury Oxide Battery

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

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

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

6. **Lithium-Ion Battery**: - a rechargeable battery that can be recharged for hundreds of time.



- anode is made out of conducting carbon based material such as graphite.
- cathode is made of a transition metal oxide such as CoO_2, which ca hold Li^+ ion. Lithium is light (small molar mass) and has the greatest reducing strength, making it ideal for a rechargeable battery.
- the high reactivity of lithium means that a non-aqueous electrolyte such as an organic solvent with dissolved salt must be used.

Redox Reaction for a Lithium-Ion Battery

(Reduction) $Li^+_{(aq)} + CoO_{2\,(s)} + e^- \rightarrow LiCoO_{2\,(s)}$ $E^\circ_{cathode} = 0.35$ V

(Oxidation) $Li_{(s)} \rightarrow Li^+_{(aq)} + e^-$ $E^\circ_{anode} = +3.05$ V

$\mathbf{CoO_{2\,(s)} + Li_{(s)} \rightarrow LiCoO_{2\,(s)}}$ $E^\circ_{cell} = 3.40$ V

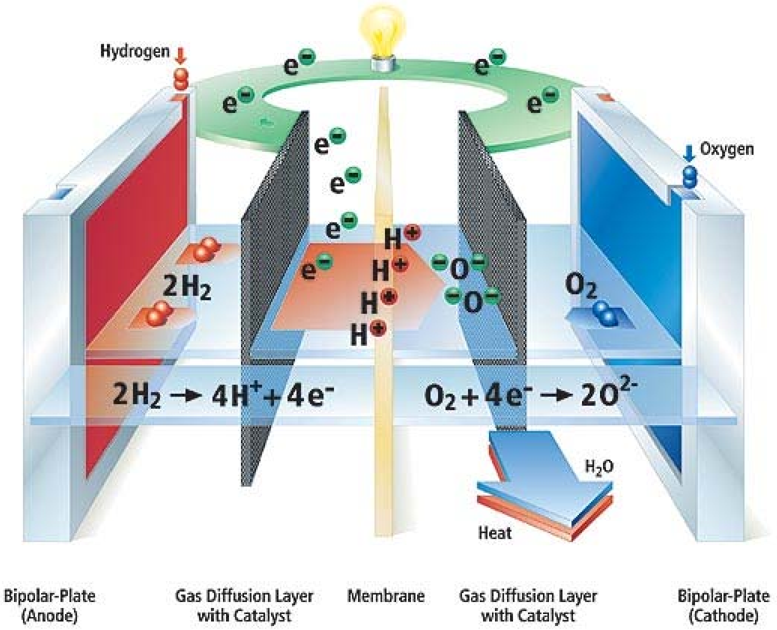
7. **Fuel Cell**: - a galvanic cell where there is a continuous supply of reactants.
   - the **hydrogen-oxygen fuel cell** produces water as a product and hence is an ideal power source for zero-emission vehicles

Redox Reaction for a Hydrogen Fuel Cell

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

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

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



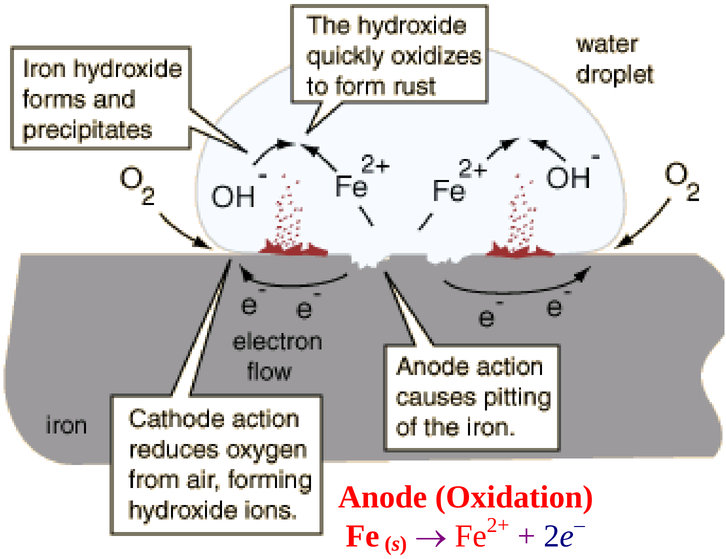
Schematic of a Hydrogen Fuel Cell (above).

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).

(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.

19.7: Corrosion

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)

$\mathbf{Fe}_{(s)} \rightarrow Fe^{2+} + 2e^-$

Cathode (Reduction)

$\mathbf{O_2} + \mathbf{2\ H_2O} + 4e^- \rightarrow 4\ OH^-$

(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.

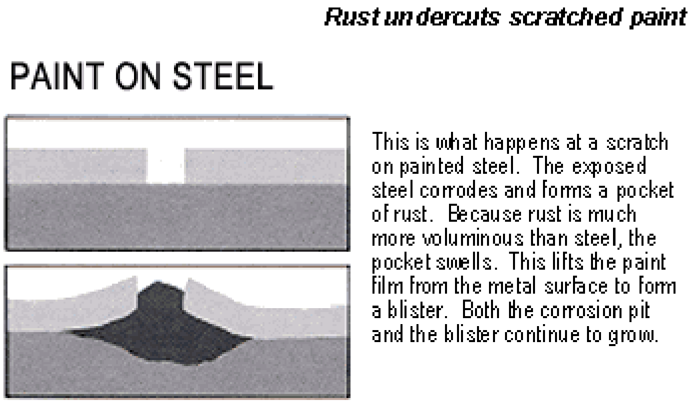
(Above) This view was taken with a scanning electron microscope (1200 ×) and shows the corroded surface of a piece of iron metal. The corrosion was artificially induced by subjecting the iron metal to an ionizing potential while being submerged in a sodium silicate solution. The iron dissolves from the 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:

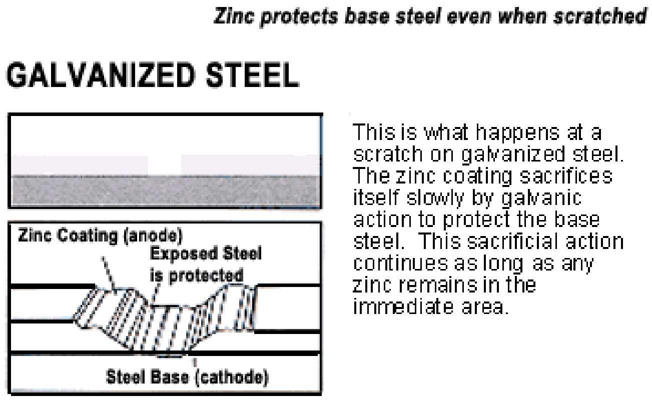
1. **Painting**: - putting a protective coating like paint on metals covers the metal surfaces so oxidation of the metal cannot take place.
   - if the paint coating is scratched, oxidation will occur on the metal. Any rust needs to be removed before a fresh coat of paint is put on.

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).



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.



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.

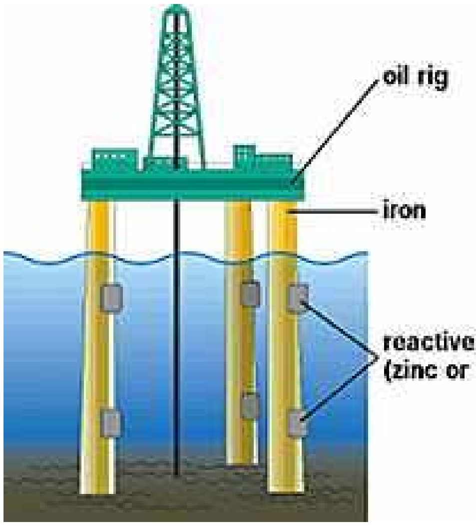
$O_2 + 2\,H_2O + 4e^- \rightarrow 4\,OH^-$ $E°_{reduction} = 0.40$ V
$Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$ $E°_{reduction} = -0.44$ V
$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$ **(SRA)** $E°_{reduction} = -0.76$ V

Zinc will be oxidized first (sacrificed) before iron.

$O_2 + 2\,H_2O + 4e^- \rightarrow 4\,OH^-$ $E°_{reduction} = 0.40$ V
$\underline{2\,(Zn_{(s)} \rightarrow Zn^{2+} + 2e^-)}$ **(SRA)** $\underline{E°_{oxidation} = +0.76 \text{ V}}$
$O_2 + 2\,H_2O + 2\,Zn_{(s)} \rightarrow 2\,Zn^{2+} + 4\,OH^-$ $E°_{cell} = 1.16$ V

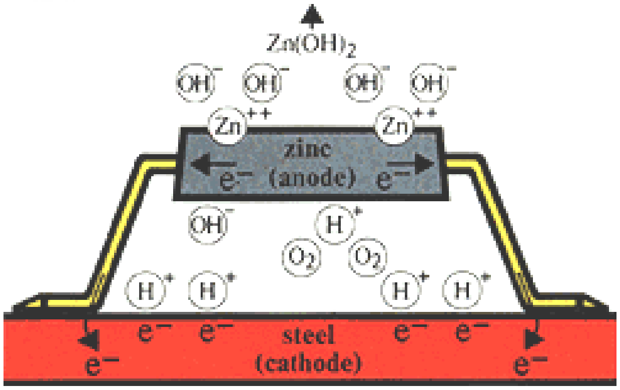
O_2-$Zn_{(s)}$ has a Higher Voltage than $E°_{cell}$ of O_2-$Fe_{(s)}$. Therefore, it is More Spontaneous.

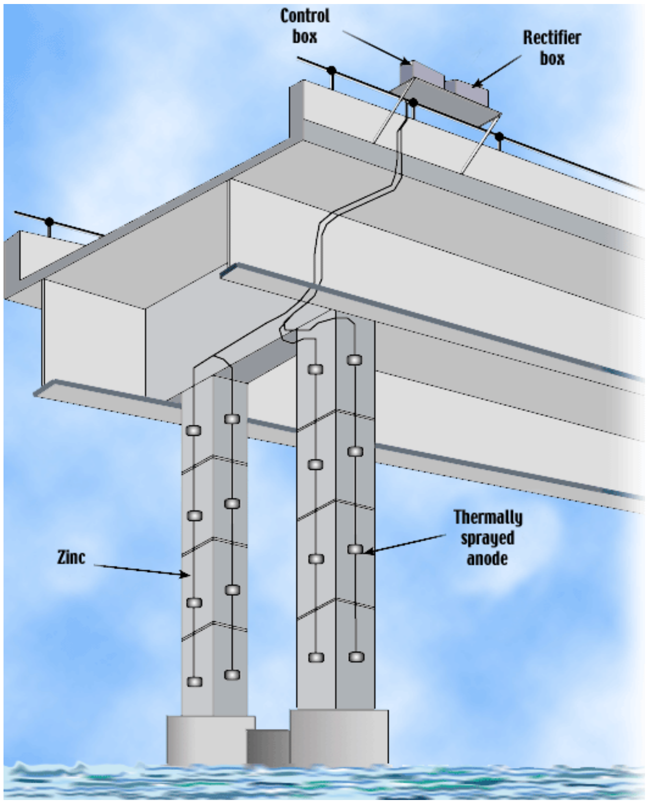
(Above and right) Deep-sea structures like offshore oil drilling platforms used sacrificial metals to protect the main structure from corrosion

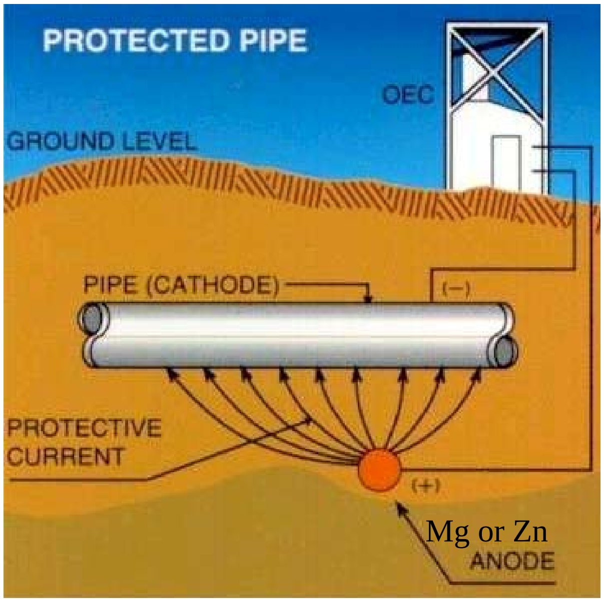


(Above) Zinc sacrificial metals.

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.

Assignment

19.6 pg. 856–857 #35, 36, 38
19.7 pg. 857 #39 to 42

19.8: Electrolysis

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 **Positive terminal**.

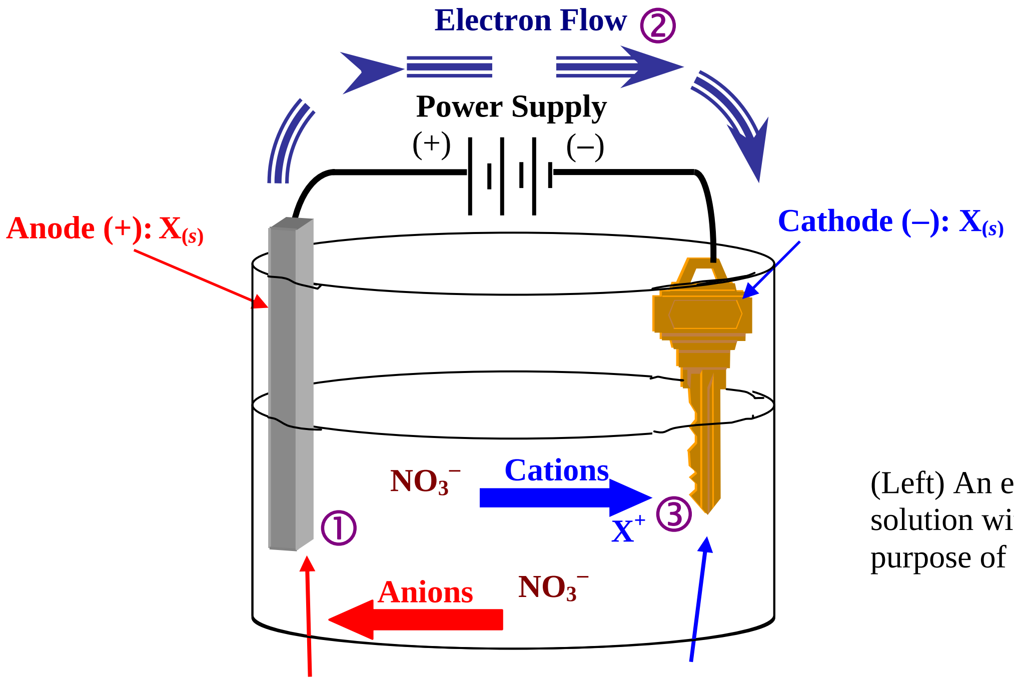
Cathode: - the terminal where **reduction** is taken place and commonly marked as the **Negative terminal**.

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. ($E°_{cell} = E°_{cathode} + E°_{anode}$)

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)–



Oxidation Half-Rxn:
$X_{(s)} \rightarrow X^+_{(aq)} + e^-$

Reduction Half-Rxn:
$X^+_{(aq)} + e^- \rightarrow X_{(s)}$

(Left) An electrolytic cell of a single solution with a power supply for the purpose of electroplating.

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 are forced to leave the Anode (+) and move to the Cathode (–).

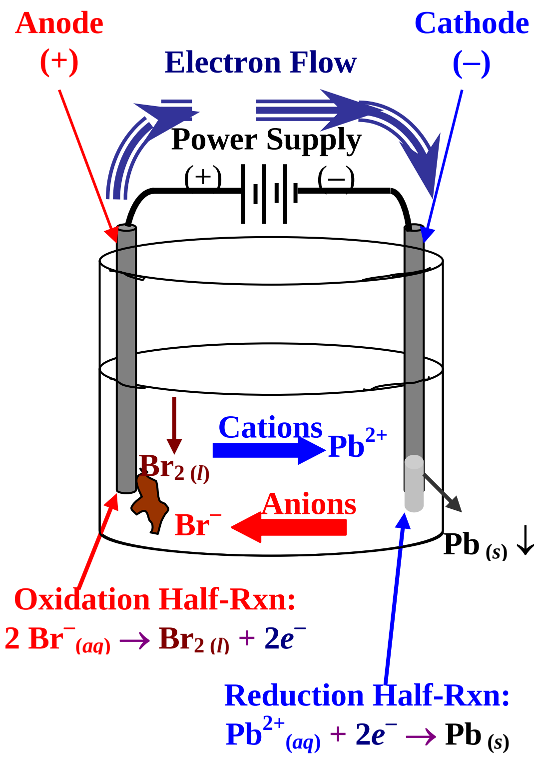
③ X^+ migrates towards the Cathode (–) to produce $X_{(s)}$ in order to complete the reduction half reaction. This can also be explained that X^+ migrate towards the cathode because electrons are moving into the bottom of the cathode making that region more negative.

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 1: 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. $PbBr_{2\,(aq)}$



Oxidation Half-Rxn:
$2\,Br^-_{(aq)} \rightarrow Br_{2\,(l)} + 2e^-$

Reduction Half-Rxn:
$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$

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

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

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

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

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

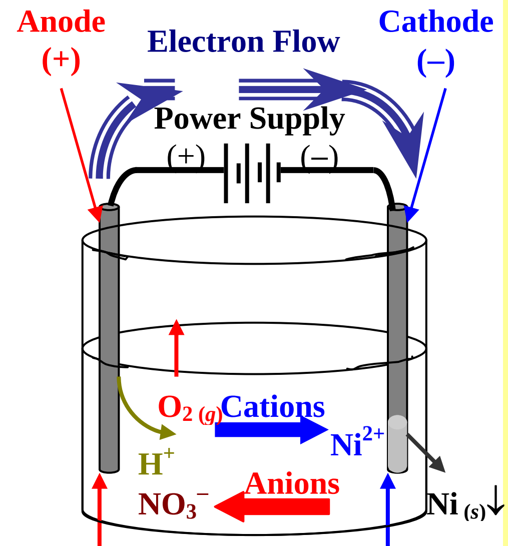
$$
\begin{array}{ll}
Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)} & E° = -0.13\text{ V} \\
2\,Br^-_{(aq)} \rightarrow Br_{2\,(l)} + 2e^- & E° = -1.07\text{ V} \\
\hline
Pb^{2+}_{(aq)} + 2\,Br^-_{(aq)} \rightarrow Br_{2\,(l)} + Pb_{(s)} & E°_{cell} = -1.20\text{ V}
\end{array}
$$

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. $Ni(NO_3)_{2\,(aq)}$



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

Reduction Half-Rxn:
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$

	SOA		OA
Major Species:	Ni^{2+},	NO_3^-,	H_2O
			SRA

$O_{2\,(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$ $E^\circ = 1.23$ V
$2NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow N_2O_{4\,(g)} + 2H_2O_{(l)}$ $E^\circ = 0.80$ V
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ $E^\circ = -0.26$ V
$2H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2OH^-_{(aq)}$ $E^\circ = -0.83$ V

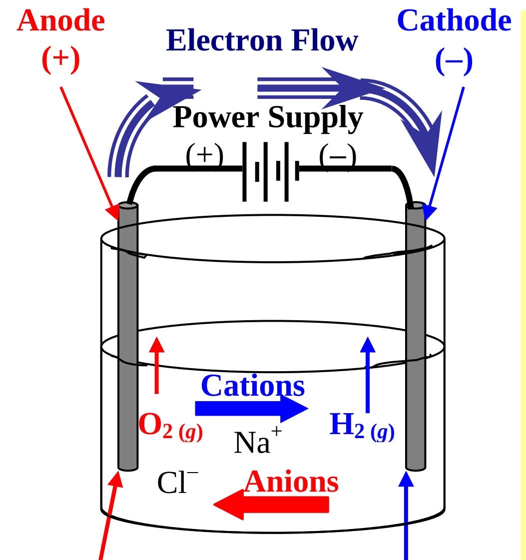
NO_3^- is neither an oxidizing agent because the solution has no H^+. We can see that this is a Non-Spontaneous Rxn because the half-reactions for $H_2O_{(l)}$ is higher than $Ni^{2+}_{(aq)}$. Ni^{2+} will be reduced (Cathode) and H_2O will be oxidized (Anode – half-rxn needs to flip).

$2\,(Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)})$ $E^\circ = -0.26$ V
$2H_2O_{(l)} \rightarrow O_{2\,(g)} + 4H^+_{(aq)} + 4e^-$ $E^\circ = -1.23$ V
$2Ni^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow O_{2\,(g)} + 2Ni_{(s)} + 4H^+_{(aq)}$ $E^\circ_{cell} = -1.49$ V

Minimum Voltage Needed = 1.49 V

Possible Observations:
1. **$Ni_{(s)}$ will be plated on the cathode.**
2. **$O_{2\,(g)}$ will be bubbling out of the anode.**
3. **pH of the solution will decrease as $[H^+]$ increases.**

c. $NaCl_{(aq)}$



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

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

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

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

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. H_2O will be reduced at the Cathode and H_2O will be oxidized at the Anode – half-rxn needs to flip.

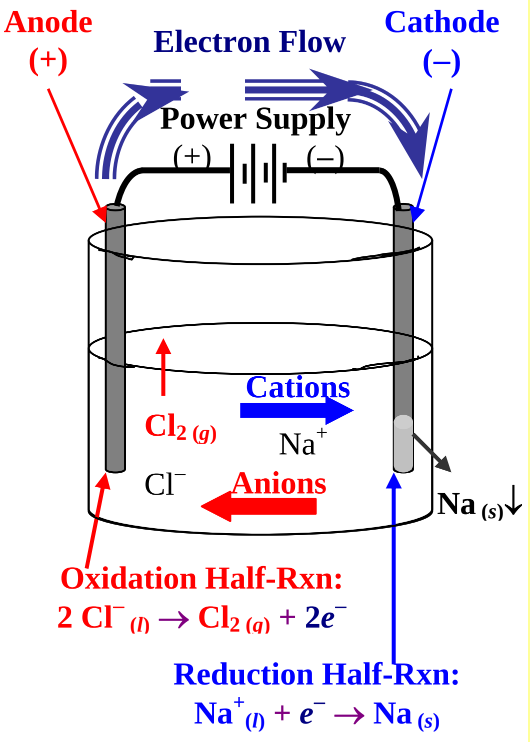
$2\,(2H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2OH^-_{(aq)})$ $E^\circ = -0.83$ V
$2H_2O_{(l)} \rightarrow O_{2\,(g)} + 4H^+_{(aq)} + 4e^-$ $E^\circ = -1.23$ V
$2H_2O_{(l)} \rightarrow O_{2\,(g)} + 2H_{2\,(g)}$ $E^\circ_{cell} = -2.06$ V

Minimum Voltage Needed = 2.06 V

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

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

d. $NaCl_{(l)}$ (Molten NaCl)



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

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

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. Na$^+$ will be reduced at the Cathode and Cl$^-$ will be oxidized at the Anode – half-rxn needs to flip.

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

Minimum Voltage Needed = 4.07 V

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

Moles of Electrons in Electroplating

$$n_{e^-} = \frac{It}{F}$$

n_{e^-} = moles of electrons in half-reaction

t = time (seconds)

I = Current (A or C/s)

$F = 9.65 \times 10^4$ C/mol

Example 2: If a 30.0 A of current flow through an electrolytic cell containing molten aluminum oxide for 1.00 hour. What mass of aluminum will be deposited at the cathode?

I = 30.0 A = 30.0 C/s

t = 1.00 hour = 60.0 min = 3600 s

$F = 9.65 \times 10^4$ C/mol

n_{e^-} = ?

M_{Al} = 26.98 g/mol

m_{Al} = ?

$$n_{e^-} = \frac{It}{F} = \frac{(30.0\,\cancel{C}/\cancel{s})(3600\,\cancel{s})}{(9.65\times10^4\,\cancel{C}/mol)} = 1.119170984\text{ mol}$$

$$\begin{array}{ccccc}
Al^{3+}_{(l)} & + & 3e^- & \rightarrow & Al_{(s)} \\
 & & 1.119170984\text{ mol} & & ?\text{ g}
\end{array}$$

$$n_{Al} = 1.119170984\,\cancel{mol\,e^-} \times \frac{1\text{ mol Al}}{3\,\cancel{mol}\,e^-} = 0.3730569948\text{ mol Al}$$

$$m_{Al} = (0.3730569948\,\cancel{mol}\text{ Al})(26.98\text{ g}/\cancel{mol}) \qquad \boxed{m_{Al} = 10.1\text{ g}}$$

Example 3: A student wishes to plate 11.74 g of $Ni_{(s)}$ onto a piece of metal using 2.00 mol/L solution of $NiBr_2$. How long should the student run a 0.500 A current in order to produce the desire mass of nickel?

$I = 0.500$ A = 0.500 C/s
$F = 9.65 \times 10^4$ C/mol
$m_{Ni} = 11.74$ g
$M_{Ni} = 58.69$ g/mol

$n_{e^-} = ?$
$t = ?$

$\mathbf{Ni^{2+}_{(aq)}}$	+	$\mathbf{2e^-}$	$\rightarrow$	$\mathbf{Ni_{(s)}}$
		? mol		11.74 g 58.69 g/mol

$$n_{Ni} = \frac{11.74\ \cancel{g}\ \text{Ni}}{58.69\ \cancel{g}/\text{mol}} = 0.2000340774 \text{ mol Ni}$$

$$n_{e^-} = 0.2000340774\ \cancel{\text{mol Ni}} \times \frac{2 \text{ mol } e^-}{1\ \cancel{\text{mol Ni}}} = 0.4000681547 \text{ mol } e^-$$

$$n_{e^-} = \frac{It}{F} \qquad t = \frac{n_{e^-}F}{I} = \frac{(0.4000681547\ \cancel{\text{mol}})(9.65 \times 10^4\ \cancel{\text{C}}/\cancel{\text{mol}})}{(0.500\ \cancel{\text{C}}/\text{s})}$$

$$t = 77213.15386\ \cancel{\text{s}} \times \frac{1 \text{ hr}}{3600\ \cancel{\text{s}}} \qquad \boxed{t = 21.4 \text{ hours}}$$

Example 4: A certain electrolytic cell produced 39.00 g of Cl_2 from molten NaCl. The time it took for this process was 80.0 minutes. What was the average current ran during this time?

$m_{Cl_2} = 39.0$ g
$M_{Cl_2} = 70.906$ g/mol
$t = 80.0$ min = 4800 s
$F = 9.65 \times 10^4$ C/mol

$n_{e^-} = ?$
$I = ?$

$\mathbf{2\ Cl^-_{(l)}}$	$\rightarrow$	$\mathbf{Cl_{2\,(g)}}$	+	$\mathbf{2e^-}$
		39.0 g 70.906 g/mol		? mol

$$n_{Cl_2} = \frac{39.0\ \cancel{g}\ \text{Cl}_2}{70.906\ \cancel{g}/\text{mol}} = 0.5500239754 \text{ mol Cl}_2$$

$$n_{e^-} = 0.5500239754\ \cancel{\text{mol Cl}_2} \times \frac{2 \text{ mol } e^-}{1\ \cancel{\text{mol Cl}_2}} = 1.100047951 \text{ mol } e^-$$

$$n_{e^-} = \frac{It}{F} \qquad I = \frac{n_{e^-}F}{t} = \frac{(1.100047951\ \cancel{\text{mol}})(9.65 \times 10^4\ \text{C}/\cancel{\text{mol}})}{(4800\ \text{s})} \qquad \boxed{I = 22.1 \text{ A}}$$

Assignment

19.8 pg. 856–858 #37, 43 to 60