ELECTROCHEMISTRY

I. Introduction: What is Electrochemistry?

Demo: *A Cu wire is placed in a solution of $Zn(NO_3)_2$.*
A light bulb is placed into the solution.

$$\overset{0}{Cu_{(s)}} + \overset{+2}{Zn}(\overset{-2}{NO_3})_{2\,(aq)} \longrightarrow \overset{0}{Zn_{(s)}} + \overset{+2}{Cu}(\overset{-2}{NO_3})_{2\,(aq)}$$

1) What happens to copper as it goes from reactant to product?
* Cu became more positive (lost electrons).

2) What happened to zinc as it went from reactant to product? What do you think occurred in order for zinc ions to become solid zinc metal?
* Zn^{2+} became less positive (gained electrons), to become neutral

3) What happened to the intensity of the light bulb over time? Why do you think this occurred?
* Bulb's intensity will remain the same because the amount of ē being transferred is 2 : 2.

Electrochemistry: looks at the __movement__ of __ē__ in a given chemical rxn.
As the e^- are being transferred from one species to the next, these __ē__ are used as a source of electrical energy.

NOTE: When we think transfer of e^-, we think ionic solutions, but electrochemistry happens for **both** ionic and __covalent__ solutions.

Example: $4\,\overset{0}{Al}_{(s)} + 3\,\overset{0}{O}_{2(g)} \longrightarrow 2\,\overset{+3}{Al_2}\overset{-2}{O_3}{}_{(s)}$
ionic species

* Each Al: lost 3ē
* Each O: gained 2ē.

$2\,\overset{+4}{S}\overset{-4}{O_2}{}_{(s)} + \overset{0}{O}_{2(g)} \longrightarrow 2\,\underset{+6}{\overset{+2}{S}}\underset{-6}{\overset{-2}{O_3}}{}_{(g)}$
covalent species

* Each S: lost 2ē
* Each O: gained 2ē (The $O_{2(g)}$ is the oxygen that underwent reduction.

II. Electrochemical Reactions – Redox Reactions

- In any __electrochemical__ rxn. there is a transfer of e^- from one species to another species.

  a) Oxidation: the __loss__ of e^-

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

  b) Reduction: __gain__ of e^- (Reducing in positivity)

  Example: $Cu^{2+} + 2ē \longrightarrow Cu$

- For a redox rxn to occur, oxidation is always followed with reduction – **REDOX RXN.**

Example: $Fe + Cu^{2+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + Cu$

III. Oxidation Numbers:

- In order to understand which ion has been oxidized or reduced, we must be able to assign oxidation numbers to ions.

Oxidation Number: the true or apparent charge on an atom or ion.

Rules for Assigning Charge:

1) Ox. # for neutral elements equal zero.

2) Ox # for any elemental ion is its combining capacity. (Combining Capacity = Oxidation #)

3) Oxygen: (O^{2-}) – Ox # = 2^-
   EXCEPTION: (H_2O_2) - Ox # = -1
   -1 oxygen

4) Hydrogen: (H^+) – Ox # = 1^+
   EXCEPTION: metallic hydrides (NaH) – Ox # = -1
   -1 / hydrogen

5) When assigning ox. # for a molecule, the more electronegative ion is assigned the **negative charge.**

6) Families 1 & 2 have the same oxidation # as their combining capacity.

Example: a) Fe (neutral element) - Ox # = 0

b) Mg^{2+} (elemental ion) – Ox # = +2

c) Fe_2O_3 (compound): O: **3** x 2^- = -6
Fe: **2** x ? = +6 (Charge per Fe ion = 3^+)
+3

Net Charge on Compound = 0

d) NO_3^{-1}: O: **3** x 2^- = -6
N: 1 x ? = +5 (For ion to have net charge of 1^-, N must be 5^+)
+5

Net charge on ion = 1^-

e) H_2O_2: O: 2 x 1^- = -2
H: 2 x 1^+ = +2 } The exception where Oxygen's oxidation # is (-1).

Net charge: = 0

f) MgH_2: H: 2 x 1^- = -2
Mg: 1 x 2^+ = +2 } Exception where Hydrogen's oxidation # is (-1)

Net Charge: 0

IV. Balancing Redox Rxns:

- **Redox Rxn:** has both oxidation + reduction
  - **½ Rxn:** describes only one part of the redox rxn., either reduction part OR oxidation part.

A. Balancing Redox Reactions Using ½ Rxn. Method

Example: Balance the following elementary redox rxn.

$\underbrace{Cu^{2+}_{(aq)} + Al_{(s)}}_{+2} \longrightarrow \underbrace{Cu_{(s)} + Al^{3+}_{(aq)}}_{+3}$ (There is currently an unbalance in charge - We need to balance it).

1) *Begin by writing the ½ rxns.*

* OX. ½: $Al_{(s)} \longrightarrow Al^{3+}_{(aq)}$

* RED. ½: $Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)}$

* These # represent the total amount needed of each type of atom.

2) *Balance the number of e⁻ by finding the LCM.*

* $[Al_{(s)} \longrightarrow Al^{3+}_{(aq)} + 3e^-] \times 2$

* $[Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}] \times 3$

* Because total amount of e^- lost = total amount gained!

LCM = 6

3) *Cancel out any similar species that appear on OPPOSITE sides of the two equations:*

$2Al \longrightarrow 2Al^{3+}_{(aq)} + \cancel{6e^-}$

$3Cu^{2+}_{(aq)} + \cancel{6e^-} \longrightarrow 3Cu_{(s)}$

Net Redox Equation: $\underbrace{3\ Cu^{2+} + 2\ Al}_{+6} \longrightarrow \underbrace{3\ Cu + 2\ Al^{3+}}_{+6}$ (Net charge on both sides is now equal/balanced).

NOTE: The net redox equation should NOT have any e^-.

$\boxed{\text{TOTAL } e^- \text{ LOST} = \text{TOTAL } e^- \text{ GAINED}}$

Some Terminology:

$$3\ Cu^{2+} + 2\ Al \longrightarrow 3\ Cu + 2\ Al^{3+}$$

- Cu^{2+}: was *reduced*. Therefore, it acts an **oxidizing agent.**

  * Substance that takes e^- from another species – thus oxidizing that species.

- Al: was oxidized. Therefore, it acts as a **reducing agent**

  * Substance that gives its e^- to another species. Thus, a reducing agent reduces another species.

NOTE: Most redox rxns. require either an acidic or basic environment in order to occur.

1) **Balancing ½ Reactions in Acidic Solutions:**

Example: Balance the ½ rxn: NO $\longrightarrow$ N_2O (in acidic solution)

a) Balance all the species EXCEPT H *or* O

$$2\,NO \longrightarrow N_2O$$

b) *Balance the OXYGEN by adding* H_2O *molecules – (Acceptable because the rxn. is occurring in an aqueous environment.)*

$$2NO \longrightarrow N_2O + H_2O$$

*c) Balance the HYDROGEN **last** by adding* H^+ *ions (Comes from the* acidic solⁿ.

$$2H^+ + 2NO \longrightarrow N_2O + H_2O$$

d) Add $\bar{e}$ *to balance the* charges.

$$\underbrace{2H^+ + 2NO}_{0} + 2\bar{e} \longrightarrow \underbrace{N_2O + H_2O}_{0} \quad \text{(Reduction ½)}$$

Exercise: Balance the ½ rxn.: $Cr_2O_7^{2-}$ $\longrightarrow$ Cr^{3+} in acid

$$6\bar{e} + \underbrace{14H^+_{(aq)} + Cr_2O^{-2}_{7\,(aq)}}_{+12} \longrightarrow \underbrace{2Cr^{3+}_{(aq)} + 7H_2O}_{+6}$$

$$14H^+_{(aq)} + Cr_2O^{-2}_{7(aq)} + 6\bar{e} \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

NOTE: Redox eqⁿs. will often only show the NIE, meaning only those species that undergo rxn.

2) **Balancing ½ Rxns. in Basic Solⁿs:**

Example: Balance the ½ rxn: Cl_2 $\longrightarrow$ ClO_3^- in basic solution

a) Balance all other atoms except H *and* O.

$$Cl_2 \longrightarrow 2ClO_3^-$$

b) Balance oxygen *atoms FIRST! using* H_2O:

$$6H_2O + Cl_2 \longrightarrow 2ClO_3^- + 12H^+$$

d) *Add the* same *# of* $\mathbf{OH^{-1}}$ *as* H^+ *to* both *sides of the reaction.*
Where there is both OH^- *and* H^+ *on the same side of the equation,* H_2O *is formed.*

$$12OH^- + 6H_2O_{(l)} + Cl_{2(g)} \longrightarrow 2ClO_3^- + \underbrace{12H^+ + 12OH^-}_{12H_2O}$$

e) *Subtract excess* H_2O *if they appear on* opposite *sides of the equation.*

$$\underbrace{Cl_2 + 12OH^-}_{-12} \longrightarrow \underbrace{2ClO_3^- + 6H_2O}_{-2}$$

f) *Add* $\bar{e}$ *to balance the charges.*

$$Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 6H_2O + 10\bar{e} \quad (\text{Oxidation } ½)$$

3) Balancing Redox Equations Using ½ Rxn. Method

Example: $Os + IO_3^- \longrightarrow OsO_4 + I_2$ (acid solution)

$Os \longrightarrow OsO_4$ | $IO_3^- \longrightarrow I_2$

$4H_2O + Os \longrightarrow OsO_4 + 8H^+ + 8\bar{e}$ | $2IO_3^- \longrightarrow I_2 + 6H_2O$

(Oxidation ½) | $10\bar{e} + 12H^+ + 2IO_3^- \longrightarrow I_2 + 6H_2O$

$\boxed{\text{LCM of } 8 \,\&\, 10 = 40}$

$$5\times(4H_2O + Os \longrightarrow OsO_4 + 8H^+ + 8\bar{e})$$
$$+\; 4\times(12H^+ + 2IO_3^- + 10\bar{e} \longrightarrow I_2 + 6H_2O)$$

Redox: $5Os + 8IO_3^- + 8H^+ \longrightarrow 5OsO_4 + 4I_2 + 4H_2O$

Example: $ClO_2^- \longrightarrow ClO_3^- + Cl^-$ (basic solution)

Disproportionation Rxn.: a redox rxn. in which the same compound undergoes both oxidation and reduction.

$ClO_2^- \rightarrow ClO_3^-$ | $ClO_2^- \rightarrow Cl^-$

$2OH^- + \cancel{H_2O} + ClO_2^- \rightarrow ClO_3^- + \underbrace{2H^+ + 2OH^-}_{\cancel{2H_2O}\ H_2O} + 2\bar{e}$ | $\underbrace{4OH^- + 4H^+}_{\cancel{4H_2O}\ 2H_2O} + ClO_2^- \rightarrow Cl^- + \cancel{2H_2O} + 4OH^- + 4\bar{e}$

$\boxed{\text{LCM of } 2 \,\&\, 4 = 4}$

$$2\times(2OH^- + ClO_2^- \longrightarrow ClO_3^- + H_2O + 2\bar{e})$$
$$1\times(2H_2O + ClO_2^- + 4\bar{e} \longrightarrow Cl^- + 4OH^-)$$

Redox: $3ClO_2^- \longrightarrow 2ClO_3^- + Cl^-$

B. Balancing Redox Reactions Using Oxidation Number Method

Example: $HClO_2 + I^{-1} \longrightarrow Cl_2 + HIO$ (acidic solution)

1) *Assign Ox. # to all atoms..*

$$\overset{+1}{H}\overset{+3}{Cl}\overset{-4}{O_2} + \overset{-1}{I^-} \longrightarrow \overset{0}{Cl_2} + \overset{+1}{H}\overset{+1}{I}\overset{-2}{O}$$

gained 3e

lost 2e

1) *Since total change in Ox # = 0 – The* total *amount of e⁻ being given off by the* reducing *agent must equal the total amount of e⁻ being taken in by the* oxidizing *agent.*

* Total amount of ē lost & gained must be 6. (LCM of 2 & 3)

$$HClO_2 + I^- \longrightarrow Cl_2 + HIO$$

gained 3ē x 2

lost 2ē x 3

2) *Balance the O and H as learned previously.*

$$\underbrace{3H^+ + 2HClO_2 + 3I^-}_{\text{Net Charge} = 0} \longrightarrow \underbrace{Cl_2 + 3HIO + H_2O}_{\text{Net Charge} = 0}$$

CHECK: (✓)

Exercise: $MnO_4^- + SO_3^{2-} \longrightarrow MnO_2 + SO_4^{2-}$ (basic solution)

Answer: $2\,MnO_4^- + 3\,SO_3^{2-} + H_2O \longrightarrow 2\,MnO_2 + 3\,SO_4^{2-} + 2OH^-$

$$\underbrace{2OH^- + 2H^+}_{2H_2O} + 2\overset{+7}{Mn}\overset{-8}{O_4^-} + 3\overset{+4}{S}\overset{-6}{O_3^{2-}} \longrightarrow 2\overset{+4}{Mn}\overset{-4}{O_2} + 3\overset{+6}{S}\overset{-8}{O_4^{-2}} + \cancel{H_2O} + 2OH^-$$

H_2O

gained 3ē x 2

lost 2ē x 3

Exercise: $U^{4+} + MnO_4^- \longrightarrow Mn^{2+} + UO_2^{2+}$ (acid solution)

Answer: $^{+2H_2O}\ 5\,U^{4+} + 2\,MnO_4^{-1} \longrightarrow 2\,Mn^{2+} + 5\,UO_2^{2+} + 4\,H^+$

$$2H_2O + 5\overset{+4}{U^{4+}} + 2\overset{+7}{Mn}\overset{-8}{O_4^-} \longrightarrow 2\overset{+2}{Mn^{2+}} + 5\overset{+6}{U}\overset{-4}{O_2^{+2}} + 4H^+$$

gained 5ē x2

lost 2ē x6

$$\overbrace{}^{\text{gained } 6\bar{e} \times 5}$$

Example: $\underset{0}{P_4} + \underset{+5\ -6}{IO_3^{-1}} \longrightarrow \overset{+5}{\underset{+2\ \ -8}{H_2PO_4^{-1}}} + \underset{-1}{I^{-1}}$ (basic solution)

$$\underbrace{}_{\text{lost } 5\bar{e} \times 6}$$

6

6 — represents the total # of P atoms needed.

You already have 4 P to begin with.

$$2\times\left[1\tfrac{1}{2}P_4 + 5IO_3^- \longrightarrow 6H_2PO_4^{-1} + 5I^-\right]$$

$$\overset{6H_2O}{\cancel{18H_2O}} + 3P_4 + 10IO_3^- \longrightarrow 12H_2PO_4^{-1} + 10I^- + \underbrace{12H^+ + 12OH^-}_{\cancel{12H_2O}}$$

$+ 12OH^-$

$$\overbrace{}^{\text{lost } 2\bar{e} \times 3}$$

Exercise: $\underset{0}{Zn} + \underset{+3\ -6}{As_2O_3} \longrightarrow \underset{-3\ +3}{AsH_3} + \underset{+2}{Zn^{2+}}$ (basic soln)

$$\underbrace{}_{\text{gained } 6\bar{e} \times 1}$$

* Always look @ oxidation # for one atom.

$$2\left(3Zn + \tfrac{1}{2}As_2O_3 \longrightarrow AsH_3 + 3Zn^{2+}\right)$$

$$\underbrace{12OH^- + 12H^+}_{9\ \cancel{12}H_2O} + 6Zn + As_2O_3 \longrightarrow 2AsH_3 + 6Zn^{2+} + \cancel{3H_2O} + 12OH^-$$

Example: $P_4 \longrightarrow H_2PO_2^- + PH_3$ (acid soln)

1) *Disproportionation Redox Rxn.* Rewrite the equation:

$$P_4 + P_4 \longrightarrow H_2PO_2^- + PH_3$$

2) All other steps follow the usual rules for assigning oxidation number and balancing.

Answer: $P_4 + 6\,H_2O \longrightarrow 3\,H_2PO_2^- + PH_3 + 3H^+$

$$\overbrace{}^{\text{lost } 1\bar{e} \times 3}$$

$$\underset{0}{P_4} + \underset{0}{P_4} \longrightarrow \underset{+2\ {}^{+1}\ -4}{H_2PO_2^-} + \underset{-3\ +3}{PH_3}$$

$$\underbrace{}_{\text{gained } 3\bar{e} \times 1}$$

$$\underbrace{\tfrac{3}{4}P_4 + \tfrac{1}{4}P_4}_{1P_4} \longrightarrow 3H_2PO_2^- + PH_3$$

$P_4 \longrightarrow 3H_2PO_2^- + PH_3$

$6H_2O + P_4 \longrightarrow 3H_2PO_2^- + PH_3$

$+ 3H^+$

V. Reduction Potential – Redox Reactions and Energy

- One of the most practical uses for electrochemical reactions is to harness the energy produced by the reaction in the form of electrons.

There are two types of redox reactions:

a) Spontaneous reactions- those that proceed without external energetic help. These reactions produce electricity.

b) Non-spontaneous reactions – Those that do **not** react spontaneously. These require energy in order to react.

A. Determining Whether a Reaction is Spontaneous:

- Redox rxns. which are spontaneous generate energy. This electricity is measured in volts.
- The greater the amount of voltage produced by a reaction, the more spontaneous that reaction is. (ie. The more (+) the E^0 is, the more spontaneous the reaction).

Standard Reduction Potential (E^0):

- All species are considered from the view point of its ability to be reduced.
- The reference species upon which all other species are compared to is the reduction of H^+ ion in solution.

$$\mathbf{2\,H^+_{(aq)} + e^- \leftrightarrow H_{2\,(g)} \quad (E^0 = 0.00V)}$$

- Conditions of a *standard system*: (a) Each reacting specie is 1M in solution.
  (b) Temperature is 25°C
  (c) Pressure is 1atm

NOTE: The more willing a species is willing to be reduced against H_2 gas, (the stronger it is as an Oxidizing agent), the more (+) the E^0.

Example: $F_{2\,(g)} + 2e^- \leftrightarrow 2F^-_{(aq)} \quad (E^0 = +2.87V)$

vs.

$K^+_{(aq)} + e^- \leftrightarrow K_{(s)} \quad (E^0 = -2.93V)$

Example: Will 1M nitric acid dissolve gold metal to form 1M Au^{3+} ions in solution?

$$H^+_{(aq)} + NO^-_{3\,(aq)} + Au_{(s)} \xrightarrow{?} Au^{3+}_{(aq)}$$

Example: Are the following reactions spontaneous?

(a) $Al^{3+}_{(aq)} + Mg_{(s)} \rightarrow Al_{(s)} + Mg^{2+}_{(aq)}$

* $Al^{3+}_{(aq)} + 3\bar{e} \rightleftharpoons Al_{(s)}$: $-1.66V$

\+ * $Mg_{(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2\bar{e}$: $+2.37V$

$E^0_{total} = +0.71V$ spontaneous

Because $Mg_{(s)}$ is being oxidized, it provides us w/ energy – (Opposite from what's on our Reduction Table).

(b) $Na^{+}_{(aq)} + Cu_{(s)} \rightarrow Cu^{1+}_{(aq)} + Na_{(s)}$

* $Na^{+}_{(aq)} + \bar{e} \rightleftharpoons Na_{(s)}$: $-2.71V$

\+ * $Cu_{(s)} \rightleftharpoons Cu^{+1}_{(aq)} + 1\bar{e}$: $-0.52V$

$E^0_{total} = -3.23V$

Not spontaneous.

REMEMBER: A strong oxidizing agent will always spontaneously react with a strong reducing agent. The opposite relationship, however, cannot occur.

The Activity/Reactivity Series: shows the extent to which metals wish to oxidize:

Li K Ca Na Mg Al Mn Zn Cr Fe Pb Cu Hg Ag Pt

Most willing to Oxidize ⟵⟶ **Least Willing to Oxidize**

B. Non-Standard Conditions:

Example: $2\,Al_{(s)} + 3\,Mn^{2+}_{(aq)} \rightarrow 2\,Al^{3+}_{(aq)} + 3\,Mn_{(s)}$ ($E^0 = 0.48V$)

Determine whether the E^0 will increase or decrease with the following changes:

(a) $[Al^{3+}] = 2.0M$ $[Mn^{2+}] = 1.0M$

* $Mn^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Mn_{(s)}$: $-1.19V$

* $Al_{(s)} \rightleftharpoons 2Al^{3+}_{(aq)} + 3\bar{e}$: $+1.66V$

↑[ ]

↳ This causes rxn. to shift left, thereby lowering the amount of $\bar{e}$ produced ∴ E will decrease.

(b) $[Al^{3+}] = 1.0M$ $[Mn^{2+}] = 3.00M$

↑[ ]

* $Mn^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Mn_{(s)}$ $-1.19V$

* $Al_{(s)} \rightleftharpoons Al^{3+}_{(aq)} + 3\bar{e}$: $+1.66V$

↑$[Mn^{2+}]$ will result in more Mn^{2+} being reduced, which will require more $\bar{e}$ to be liberated from $Al_{(s)}$ – This results in increased E being produced.

VI. Spontaneous Redox Reactions:

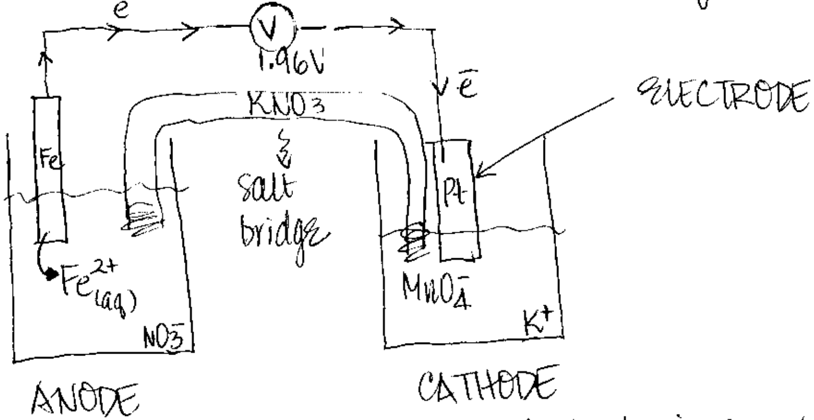
- Spontaneous reactions produce electrical energy to run objects.

Electrochemical Cells (Galvanic Cells or Voltaic Cells):

Ex. * $Fe \rightleftharpoons Fe^{2+}_{(aq)} + 2\bar{e}$: E° : 0.45V

* $MnO_4^- + 8H^+ + 5\bar{e} \rightleftharpoons Mn^{2+}_{(aq)} + 4H_2O$: E° : 1.51V

$\left.\begin{matrix} 0.45V \\ 1.51V \end{matrix}\right\} E^\circ_{total} = 1.96V$



Porous Disc/Salt Bridge: serves to absorb the ions in solution as oxidation or reduction takes place. The porous nature serves as the conduit to promote redox to occur.

Electrode: site for ions to reduce onto. The electrode may or may not be reactive.

Anode: site of oxidation.
e^- travels **A**way from anode.

Cathode: site of reduction.

* Mass of $Fe_{(s)}$ solid decreases over time.

* Excess Fe^{2+} are balanced out in charge by the NO_3^- from the salt bridge.

* Pt electrode is inert ; its only job is to hold ē for $MnO_4^-{}_{(aq)}$ to reduce onto.

$$2MnO_4^- + 5Fe + 16H^+ \rightarrow 5Fe^{2+} + 2Mn^{2+} + 8H_2O$$

Line Notation:

- Short hand notation for any electrochemical reaction:

salt bridge

$$Fe \mid Fe^{2+} \parallel MnO_4^-, Mn^{2+} \mid Pt$$

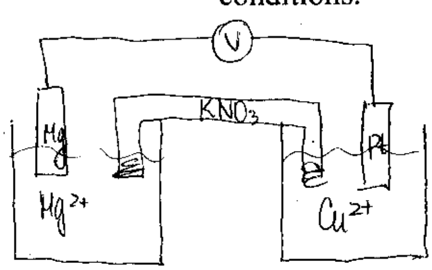
phase boundary

Example: Draw an electrochemical cell for the redox reaction between Mg and Cu^{2+} under standard conditions.

$Mg_{(s)} \rightleftharpoons Mg^{2+} + 2\bar{e}$: E° : 2.37V

$Cu^{2+} + 2\bar{e} \rightleftharpoons Cu_{(s)}$: E° : 0.34V

$\left.\begin{matrix} 2.37V \\ 0.34V \end{matrix}\right\} E^\circ_{total} = 2.71V$



A. Applications of Electrochemical Cells:

1) The Breathalyzer:

$$3\,C_2H_5OH + 2\,Cr_2O_7^{2-} + 16\,H^+ \longrightarrow 3\,CH_3COOH + 4\,Cr^{3+} + 11\,H_2O$$

orange-yellow → *dark green*

- Blood vessels lie closely to the alveoli in the lungs.
- Exchange of alcohol vapours from the blood vessels to the lungs is easily accomplished.
- The higher the content of alcohol, the greener the breathalyzer instrument shows!

2) Car Batteries:

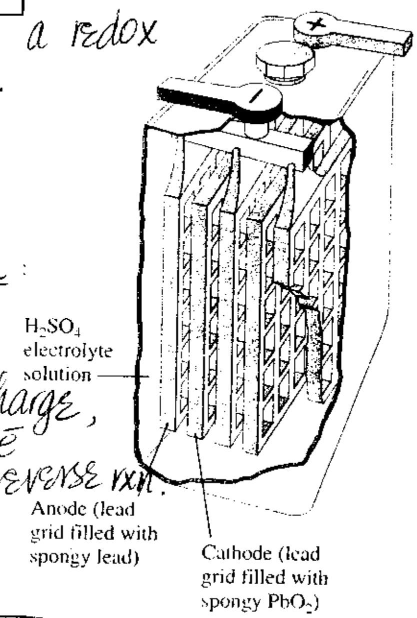
Anode: $Pb_{(s)} + HSO_4^- \longrightarrow PbSO_{4\,(s)} + H^+ + 2e$

Cathode: $PbO_{2\,(s)} + HSO_4^- + 3H^+ + 2e \longrightarrow PbSO_{4\,(s)} + 2\,H_2O$

Overall: $Pb_{(s)} + PbO_2 + 2H^+ + 2HSO_4^- \longrightarrow 2\,PbSO_4 + 2H_2O$

- Above rxn. occurs when battery is discharging – undergoing a redox rxn. Spontaneously reacting to produce electrical energy.
- As rxn. proceeds, the solid $PbSO_4$ product starts to accumulate onto the 2 electrodes (Pb and PbO_2).
- To recharge the battery, an electrical source is applied to the battery, forcing e back onto the solid $PbSO_4$, thus forcing the rxn. in reverse.
- The battery still eventually dies because the $PbSO_4$ flakes off over time, falling into the acidic solution.

ALTERNATOR: generator that generates charge, providing $\bar{e}$ for the reverse rxn.

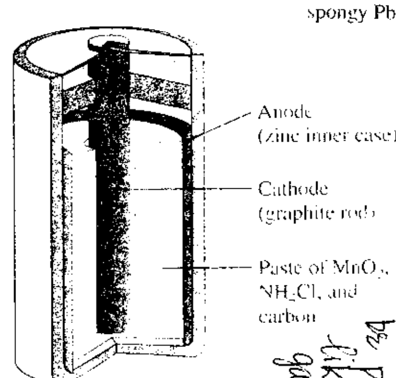


3) Alkaline Dry Cell (Duracel or Energizer):

Anode: $Zn_{(s)} + 2\,OH^- \longrightarrow ZnO_{(s)} + H_2O + 2\bar{e}$

Cathode: $2\,MnO_{2(s)} + H_2O + 2\bar{e} \longrightarrow Mn_2O_3 + 2OH^-$

- Electrolyte (~~catalyst~~) is basic – therefore, alkaline name.
- Zn is the liner on the battery wall.
- MnO_2 is a paste that fills the battery's shell –
- Electrode for the MnO_2 is a **Carbon Rod**
  (Electrode is inert purposely, so that it doesn't react with Zn. Carbon's job is to house reduced electrons)



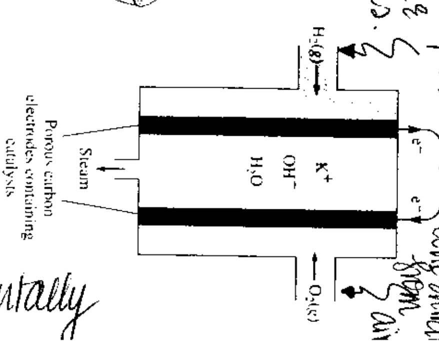
4) Fuel Cells:

Anode: $2\,H_{2\,(g)} + 4OH^- \longrightarrow 4\,H_2O + 4\bar{e}$

Cathode: $O_{2\,(g)} + 2\,H_2O + 4\bar{e} \longrightarrow 4\,OH^-$

Overall: $2\,H_{2\,(g)} + O_{2\,(g)} \longrightarrow 2\,H_2O_{(l)}$

* product is environmentally sound



* $H_2(g)$ can be pumped, like gas.

* can be consumed from air

- The unique feature of a fuel cell is that the reactants for the anode and cathode (or the "fuels" of the rxn.) are continuously replenished.
- The rxn. is efficient and produces environmentally friendly by-products.
- This is why it is a popular choice for "fueling" the cars of the future.

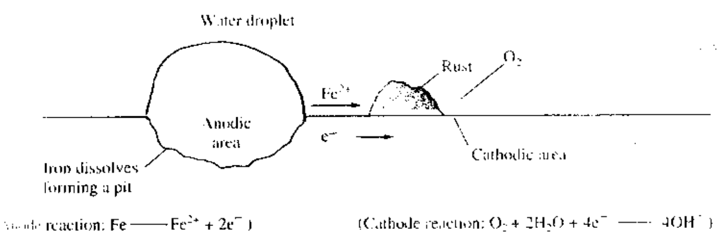
Redox in Nature: Corrosion

- Most metals do not exist in their natural states when found in nature. They exist as ores - The oxidized form of the metal.
- Almost all metals (except Au, Ag, Pt) are more oxidizable than O_2 and H_2O.

NOTE: "Rusting" only applies to Fe metal
Corrosion = oxidation of all metals.

Anode: $Fe \leftrightarrow Fe^{2+} + 2e$
Cathode: $O_2 + 2\,H_2O + 4e \leftrightarrow 4\,OH^-$

* Solid Fe will ionize in the presence of H_2O.
* The oxidized Fe^{2+} will provide $\bar{e}$ for the reduction of $O_{2(g)}$.
* The resulting reduction of O_2 to O^{-2} ; in H_2O creates $OH^-_{(aq)}$.
* The solid brown rust is $Fe(OH)_{2(s)}$.



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

Preventing Corrosion:

1) Galvanizing: process of coating a metal with a top coat of a more reactive metal. The more reactive metal will oxidize first, leaving an oxidized top coat that prevents further corrosion. (**Eg.** Zn coated iron or Zn coated steel).

2) Alloying: where more readily oxidized metals are mixed in with another metal. The mixture is meant to lower the reduction potential to near 0V.
(**Eg.** Stainless steel has Fe and C in its mixture).

3) Cathodic Protection: where a more oxidizable metal is "sacrificed" to be oxidized first, leaving the other metal protected.

* Galvanizing is a way of cathodically protecting a metal.

VII. Non-spontaneous Redox Reactions

- Reactions that require energy ___input___ in order to proceed.

Electrolytic Cells:

- **Electrolysis:** the process of supplying electrical energy to induce a redox rxn. to happen.
  Electro-potential is ___negative___.

Example: $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$ $\quad E^{\circ}_{theoretical} =$

There are 3 types of electrolytic cells:

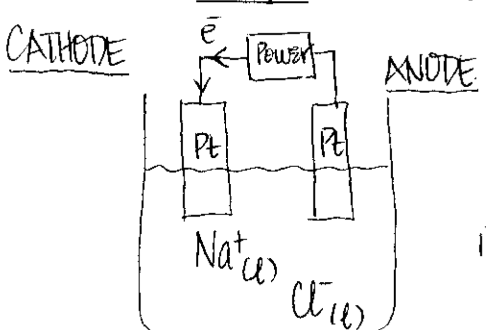
a) **Type 1:** ___molten___ (melted) salt.
Electrodes are ___inert___.

b) **Type 2:** ___Aqueous___ solution.
Electrodes are ___inert___.

c) **Type 3:** ___Aqueous___ solutions
Electrodes may be ___reactive___.

a) ***Type 1***:

Example: molten NaCl and platinum electrodes

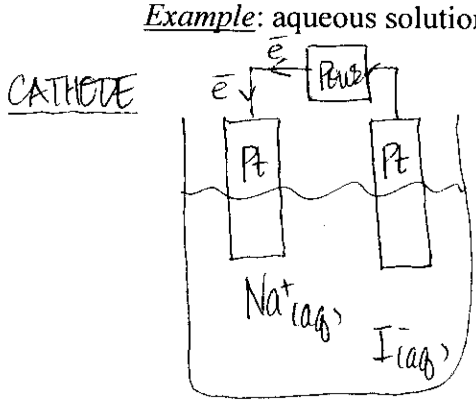


$$(\text{CATHODE}): Na^+_{(l)} + \bar{e} \rightleftharpoons Na_{(s)}$$
$$(\text{ANODE}): 2Cl^-_{(l)} \rightleftharpoons Cl_{2(g)} + 2\bar{e}$$
$\Big\}$ $E^{\circ}_{theoretical} = -$

1) No separation of reactants is required b/cause we are not harnessing the $\bar{e}$ as in a spontaneous rxn.
2) No salt bridge required because no circuit is needed. Also, no balancing of excess ions are required.

b) ***Type 2***:

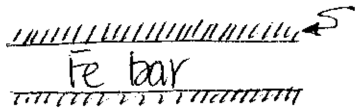
Example: aqueous solution of NaI. Electrode is platinum.



Possible Reactants: $Na^+_{(aq)}$, $I^-_{(aq)}$, $H_2O_{(l)}$

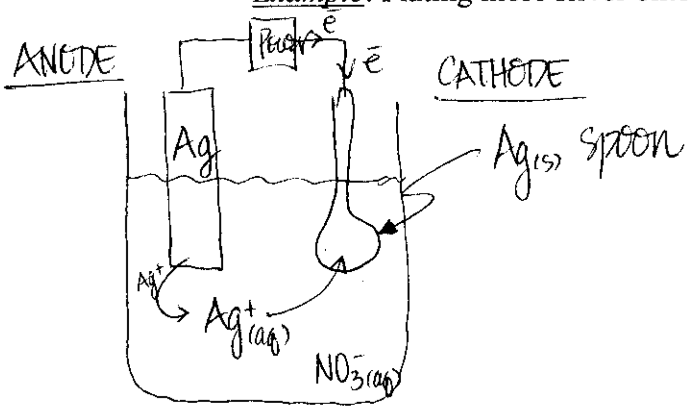
c) *Type 3*: Electroplating (Plating):

Method is used to force a metal to __reduce__ onto another surface.
This method is used extensively in __galvanizing__. (Also in jewelry plating).



* Galvanizing process where we wish to force Zn^{2+} to reduce onto $Fe_{(s)}$

Example: Plating more silver onto a tarnished silver spoon.



* Possible Reactants: $Ag^+_{(aq)}$, $Ag_{(s)}$, H_2O.

(ANODE): $Ag_{(s)} \rightleftharpoons Ag^+_{(aq)} + \bar{e}$

(CATHODE): $Ag^+_{(aq)} + \bar{e} \rightleftharpoons Ag_{(s)}$

$\Big\}\ E^\circ_{theoretical} = 0.0V$

Other examples include making "tin" cans, "chrome" mags/rims.

A. Factors Affecting Yield in an Electrolytic Process:

1) The amount of electrons or __charge__ *flowing through the system. The more charge or e^- running through, the more reduction can occur.*
Amount of charge is measured in __Coulombs__.

2) The charge on the ion. The more e^- needed for the redox reaction, the __longer__ *it will take for the reaction to be fully completed.*

Example: $Ag^+ + e^- \longleftrightarrow Ag_{(s)}$ **vs.** $+ 2e^- \longleftrightarrow$

* Reduction of F_2 will take longer to occur than Ag^+ because reduction of F_2 requires $2\bar{e}$.

3) Amount of __time__ *given for the electrolysis to occur.*