Introduction to Electrochemical reactions

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Electrochemistry

- Create and or store electricity chemically.
- Use electricity to drive a reaction that normally would not run.
  - Plating metal onto a metal another metal is sometimes driven by electricity.

Terms

- Charge:
  - Coulomb
  - 1 mole of electrons posses 96500 coulombs of charge = 1 Faraday
- Voltage: Difference of charge
  - EMV: Electromotive force
  - $\mathcal{E}$
  - V
- Current: Amount of current flowing
  - I
  - Amps

Oxidation Reduction reactions

- An oxidation reduction reaction is where electrons are transferred from one atom to another.
- Therefore, the charges will be changing.

- Oxidation state: Apparent charge on atom.

Oxidation states

- If you can track the apparent charges on an atom then you can verify conclude a reaction is a redox reaction
- You will be given a list of rules to find the oxidation states.
- Apply rules to both sides of a reaction and look to see where charges change ☺

Rules for oxidation states

1. Oxygen = -2

   Exception: Peroxides = -1 (H-O-O-H)

2. Hydrogen = +1

   Exception = Hydrides = -1 (CaH_2)

1. Ionic charges = oxidation states
2. Elements = 0
3. Sum of the oxidation states = overall charge

Examples

-4

+4 -2 Important values are in RED

- CO_2

+2 -14

+1 +6 -2

- $K_2Cr_2O_7$

-8

+1 +7 -2

Try $KMnO_4$

Example equation

Combustion reaction -- Redox

$$\begin{array}{ccccccc} & +4 & & & -4 & & +2 \\ -4 & +1 & & 0 & +4\ -2 & & +1\ \ -2 \\ \multicolumn{2}{c}{CH_4} & + & O_2 \rightarrow & CO_2 & + & H_2O \end{array}$$

Double displacement – Not a redox

$$\begin{array}{ccccccc} +1\quad +5\ -6 & & +1\quad -1 & & +1\quad -1 & & +1\quad +5\ -2 \\ AgNO_3 & + & NaCl & \rightarrow & AgCl_{(s)} & + & NaNO_{3(aq)} \end{array}$$

Oxidation

<u>Old definition</u>

- Oxidation is and old term used to describe the process of a chemical gaining oxygen.

$$C + O_2 \rightarrow CO_2$$

Carbon is being oxidized.

- Still a good definition but is not complete.

Oxidation

New Definition

- A substance that loses electrons to another substance.
- Leo -- Lose electrons Oxidized

Oxidation state

$$C^0 + O^0 \longrightarrow C^{?}O_2$$

Oxidation state on C is +4

$$C^0 \longrightarrow C^{+4} + 4e-$$

Reduction

Old Definition

- Reduction is the old term used to describe the process of a chemical losing oxygen.

$$KMnO_4 \rightarrow Mn^{+2}$$

In this case the $KMnO_4$ is losing oxygen.

Reduction

New Definition

- Gain electrons from another substance
- GER – Gain Electrons Reduce

- $KMnO_4 \rightarrow Mn^{+2}$
- $K^{+1}Mn^{+7}O^{-2} \rightarrow Mn^{2+}$

So $Mn^{7+} + 5e^{-} \rightarrow Mn^{2+}$ This is reduction

Oxidizing/Reducing Agent
Reducing/Oxidizing Agent

These two sets of terms have the same meaning

Oxidizer –a chemical that loses electrons to another chemical

Reducing Agent – a chemical that causes another chemical to gain electrons

Reducer – a chemical that gains electrons from another chemical

Oxidizing Agent – a chemical that causes another chemical to lose electrons.

Oxidation vs. Reduction

- Oxidation can NOT occur without reduction.
- In order to lose an electron there must be something to accept it.
- Strong Oxidizers are weak reducers
  - In other words, if a substance wants to get ride of electrons really bad then it isn't going to want to take them. Or vice versa.

Single displacement -- Redox

Molecular equation (aqueous ions separate)

$AgNO_3(aq) + Cu(s) \longrightarrow Ag(s) + Cu(NO_3)_2(aq)$

Ionic equation (better representation of ions)

$Ag^+\ NO_3^- + Cu(s) \longrightarrow Ag(s) + Cu^{2+} + NO_3^-$

Net Ionic equation (eliminates spectator ions)

$Ag^+ + Cu^0(s) \longrightarrow Ag^0(s) + Cu^{2+}$

Spectator ions

Closer look

$Ag^{+} + Cu^{0}(s) \rightarrow Ag^{0}(s) + Cu^{2+}$

$Cu^{0}(s) \rightarrow Cu^{2+} + 2e^{-}$

$1e^{-} + Ag^{+} \rightarrow Ag^{0}(s)$

One electron will represent an oxidation and one will represent a reduction. Which is which????

Closer look

$Ag^{+} + Cu^{0}(s) \rightarrow Ag^{0}(s) + Cu^{2+}$

$Cu^{0}(s) \rightarrow Cu^{2+} + 2e^{-}$ (oxidation)

$\underline{1e^{-} + Ag^{+} \rightarrow Ag^{0}(s)\ \ \text{(reduction)}}$

How would you balance this reaction?

Oxidation Reduction reactions Oxidizing agent/Reducing agent

$AgNO_3(aq) + Cu(s) \rightarrow Ag(s) + Cu(NO_3)_2(aq)$

$Cu^0(s) \rightarrow Cu^{2+} + 2e^-$ Oxidation

Reducing agent

$1e^- + Ag^+ \rightarrow Ag^0(s)$ Reduction

Oxidizing agent

Note: Includes entire starting chemical

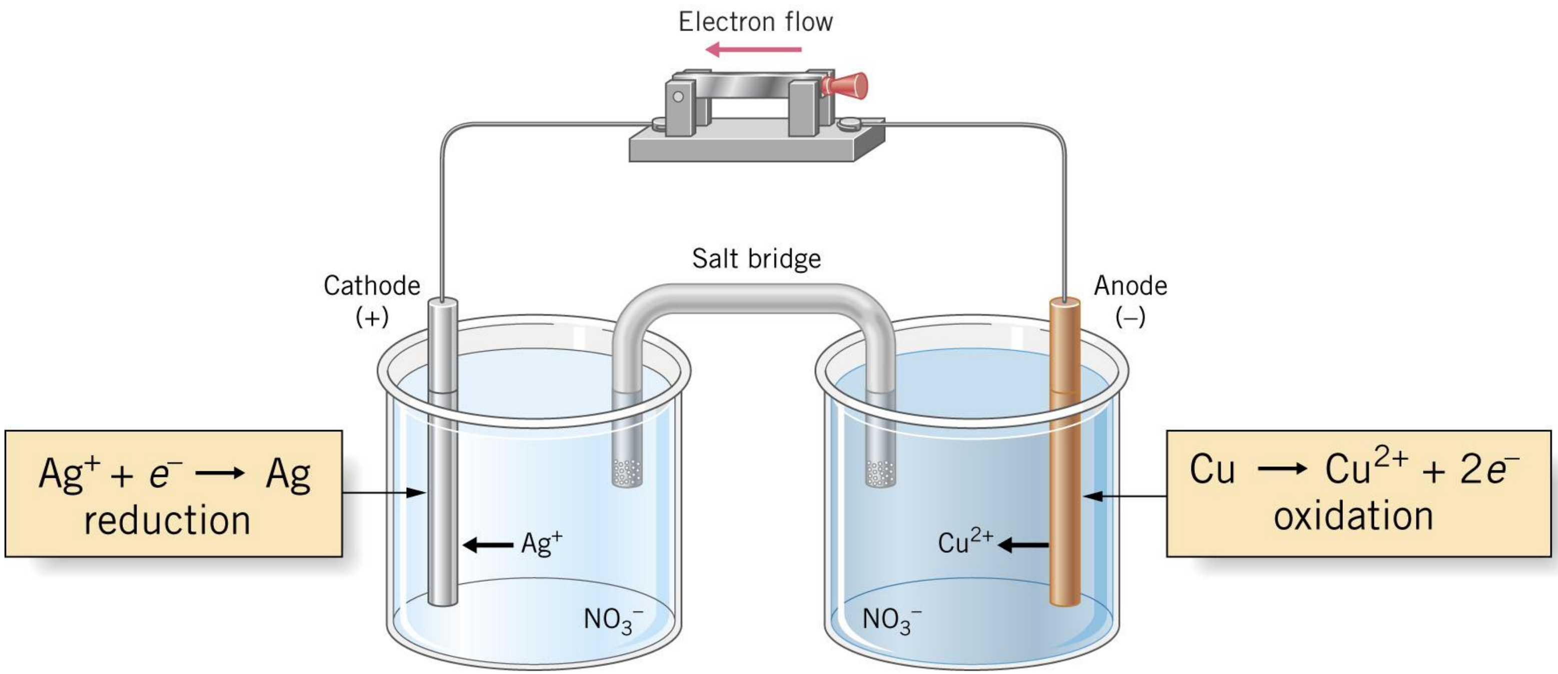
Oxidizing agent = $AgNO_3$

Voltage or EMF or $\mathcal{E}$

- Every redox reaction will have a reaction potential. This is the strength or force over which the electron is being moved.

Chapter 21: Electrochemistry

- Batteries serve as power sources for all types of gadgets
- The energy in a battery comes from a spontaneous redox reaction where the electron transfer is forced to take place through a wire
- The apparatus that provides electricity in this way is called a **galvanic** or **voltaic cell**



A galvanic cell. The cell consists of two half-cells where the oxidation and reduction half-reactions take place. The salt bridge is required for electrical neutrality. The overall *cell reaction* is:

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

- Cell reactions are obtained by adding the half-reactions
- Half-reactions are balanced using the **ion-electron method** (see Section 6.2)
- The electrodes are assigned the name **anode** or **cathode**
  - Reduction (electron gain) occurs at the cathode
    - Electrons appear as reactants in the half-reaction
  - Oxidation (electron loss) occurs at the anode
    - Electrons appear as products in the half-reaction

Determining Voltage or the potential of a chemical reaction

$\underline{Ag^{+} + Cu^{0}(s) \rightarrow Ag^{0}(s) + Cu^{2+}}$

$Cu^{0}(s) \rightarrow Cu^{2+} + 2e^{-}$ $\qquad E_{Oxidation}$: ???

$1e^{-} + Ag^{+} \rightarrow Ag^{0}(s)$ $\qquad E_{reduction}$: ???

$$E_{Oxidation} + E_{reduction} = E_{overall}$$

- Each half reaction has a potential to gain or lose electrons. A very active atom can force an electron on to an another atom even if the other atom doesn't want it. It is a back and forth battle.

Determining overall Voltage

$\underline{Ag^{+} + Cu^{0}(s) \rightarrow Ag^{0}(s) + Cu^{2+}}$

$Cu^{0}(s) \rightarrow Cu^{2+} + 2e^{-}$ $E_{Oxidation}$: ???

$1e^{-} + Ag^{+} \rightarrow Ag^{0}(s)$ $E_{reduction}$: ???

$$E_{Oxidation} + E_{reduction} = E_{overall}$$

Adding oxidation and reduction potentials will give you the total Potential of the reaction

+ E is spontaneous

-ΔG, +E, K >1 all represent spontaneous reactions

*** Where do we get electro potentials?***

- There are two types of electrical conduction in a galvanic cell
    - Metallic conduction occurs when electrons move through the wires
    - Electrolytic conduction occurs through the liquid by movement of ions, *not* electrons
- The movement of ions through the salt bridge and in solution is required for charge neutrality
    - Cations move in the general direction of the cathode
    - Anions move in the general direction of the anode

Finding Oxidation/Reduction potentials

- Chart of reduction potentials
  - You have been given a list of only reduction potentials in you workbook.
- How do you determine an oxidation potential?
  - Find reverse reaction (reduction) flip the equation and the sign.
  - $Cu^{0} + 2e^{-} \longrightarrow Cu^{2+}$ E: -.36v
  - $Cu^{2+} \longrightarrow Cu^{0} + 2e^{-}$ E: +.36v

- The anode has **negative polarity** because the electrons left behind by the Cu^{2+} ions give it a slightly negative charge
- The cathode has **positive polarity** because of the Ag^{+} ions “joining” the electrode give it a slightly positive charge
- For convenience, a **standard cell notation** has been developed by chemists
    - Anode half-cell is specified on the left
    - Cathode half-cell is specified on the right
    - Phase boundaries are indicated using “|”
    - The salt bridge separates the anode and cathode and is indicated using “||”

$$Cu^0(s) \rightarrow Cu^{2+} + 2e^- \quad E_{Oxidation}: +.36$$

$$1e^- + Ag^+ \rightarrow Ag^0(s) \quad E_{reduction}: +.76$$

$$E_{Oxidation} + E_{reduction} = +1.1V$$

Standard Reduction Potentials at 25°C

Stronger

Reducer

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

Weaker oxidizing agent

Weaker reducing agent

Stronger

Oxidizer

- **Note: Voltage scale is relative.**

Determine the voltage for a reaction that contains Cu, Zn, Cu^{2+}, and Zn^{2+}

- $Cu^0 \rightarrow Cu^{2+} + 2e^-$
- $Zn^0 \rightarrow Zn^{2+} + 2e^-$

- $Cu^{2+} + 2e^- \rightarrow Cu^0$
- $Zn^{2+} + 2e^- \rightarrow Zn^0$

- Who has the potential to take from who?
- Cu^0 can't give e^- to Zn causing zinc to become Zn^{2-}
- Cu has to give e^- to Zn^{2+}

Determine the voltage for a reaction that contains Cu, Zn, Cu^{2+}, and Zn^{2+}

- Option 1
- $Cu^0 \rightarrow Cu^{2+} + 2e^-$ E = -.34
- $Zn^{2+} + 2e^- \rightarrow Zn^0$ E = -.76

  E = -1.1V
- Option 2
- $Cu^{2+} + 2e^- \rightarrow Cu^0$ E = +.34
- $Zn^0 \rightarrow Zn^{2+} + 2e^-$ E = +.76

  E = +1.1V

Spontaneous

Galvanic Cell Notation

- $Cu^{2+} + 2e^- \longrightarrow Cu^0$ E = +.34
- $Zn^0 \longrightarrow Zn^{2+} + 2e^-$ E = +.76

E = +1.1V

$$\boxed{Cu^{2+}|Cu^o||Zn|Zn^{2+}}$$

- The cell diagram for the copper-silver galvanic cell is

$$\underset{\text{(anode)}}{Cu(s)|Cu^{2+}(aq)}||\underset{\text{(cathode)}}{Ag^{+}(aq)|Ag(s)}$$

- Galvanic cells can push electrons through a wire
- The magnitude of this ability is expressed as a **potential**
- The maximum potential a given cell can generate is called the **cell potential**, E_{cell}

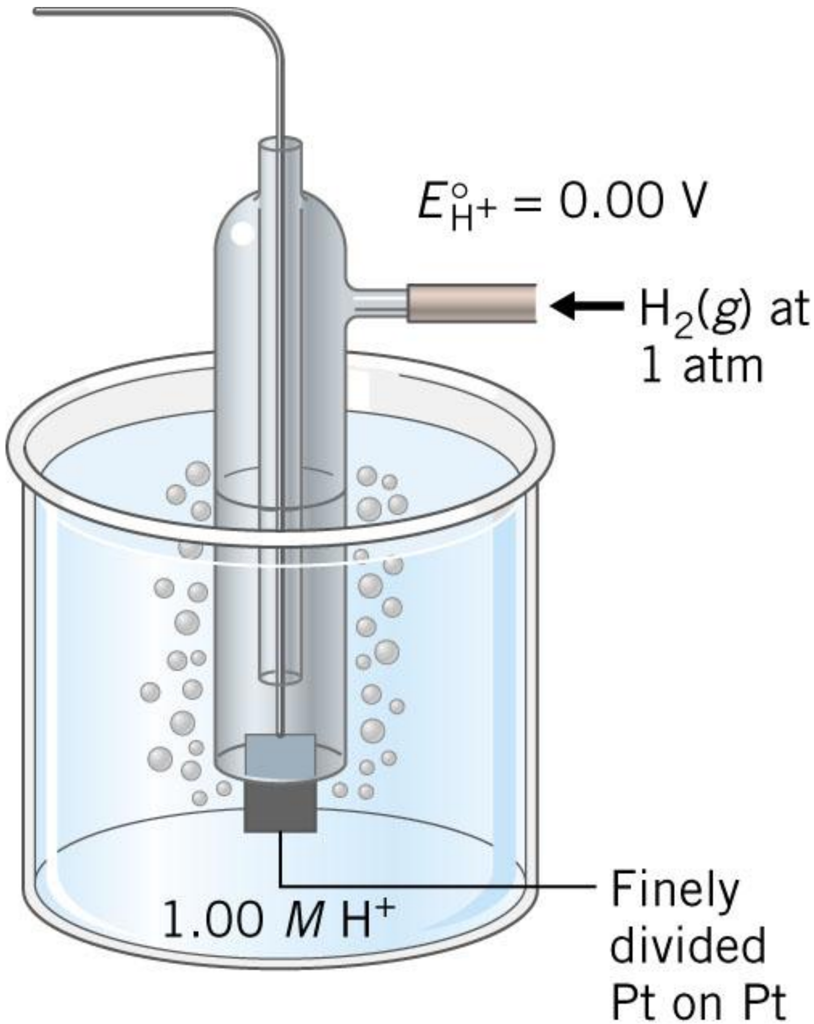
- The cell potential depends on the temperature and composition
- The **standard cell potential**, E^{o}_{cell}, is the cell potential measured at 298 K (25^{o}C) with all ion concentration 1.00 *M*
- Standard cell potentials are rarely more than a few volts
  - E^{o}_{cell} for the copper-silver galvanic cell is 0.46 V
  - E^{o}_{cell} for a single cell in a car battery is about 2 V

- The tendency for a species to gain electrons and be reduced is its **reduction potential**
- When measured at standard condition, it is called the **standard reduction potential**, E^o
- When two half-cells are are connected:
  - The one with the larger reduction potential will acquire electrons and undergo reduction
  - The half-cell with the lower reduction potential will give up electrons and undergo oxidation

- The difference in the two standard reduction potentials gives the standard cell potential

$$E^{\circ}_{cell} = \begin{pmatrix} \text{standard reduction} \\ \text{potential of the} \\ \text{substance reduced} \end{pmatrix} + \begin{pmatrix} \text{standard oxidation} \\ \text{potential of the} \\ \text{substance oxidized} \end{pmatrix}$$

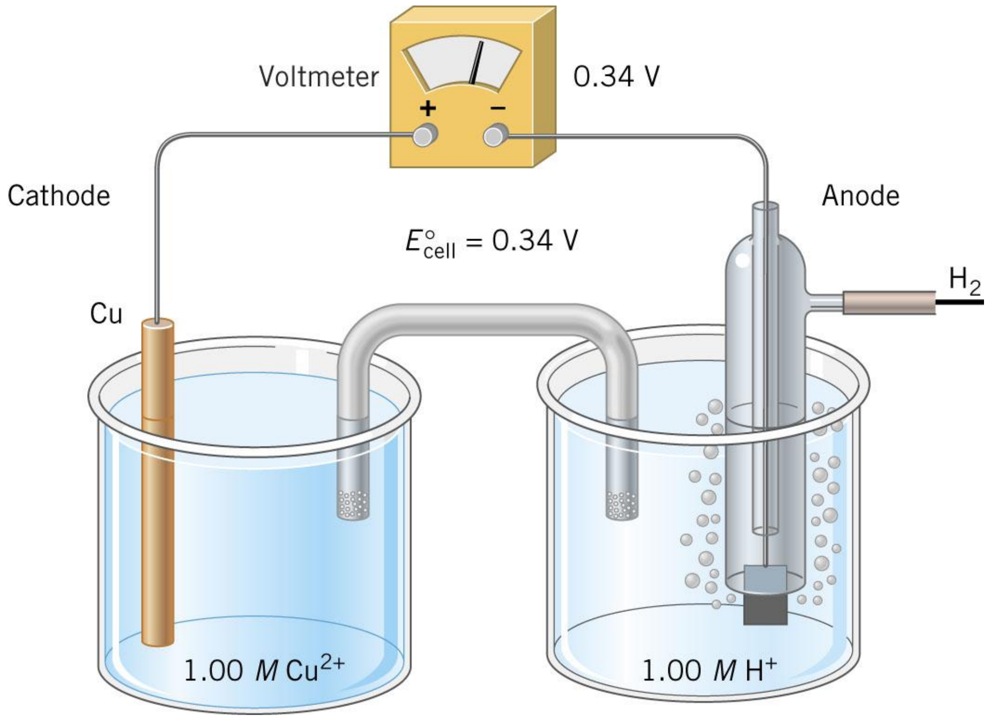
- It is not possible to measure the reduction potential of an isolated half-cell
- A reference electrode, called the **standard hydrogen electrode**, has been *assigned* the potential of exactly 0 V



Platinum is a common surface

The standard hydrogen electrode. Hydrogen gas at 1 atm is passed over finely divided platinum. The solution contains 1.00 *M* hydrogen ion. The reduction potential is exactly 0 V at 298 K (25^{o}C).

- Using a hydrogen half-cell, other reduction potentials can be measured



A galvanic cell comprised of copper and hydrogen half-cells. The reaction is $Cu^{2+}(aq)+H_2(g) \rightarrow Cu(s)+2H^+(aq)$

Cell notation:

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