Oxidation-Reduction Reactions

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Electron transfer reactions

- Electrons transferred from one substance to another
- Originally only combustion of fuels or reactions of metal with oxygen
- Important class of chemical reactions that occur in all areas of chemistry & biology
- Also called **redox reactions**

Oxidation-Reduction Reactions

Involves 2 processes:

Oxidation = Loss of Electrons (LEO)

$Na \longrightarrow Na^+ + e^-$ Oxidation Half-Reaction

Reduction = Gain of electrons (GER)

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ Reduction Half-Reaction

Net reaction:

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

- Oxidation & reduction **always** occur together
- Can't have one without the other

Oxidation Reduction Reaction

Oxidizing Agent

- Substance that accepts **e^-'s**
  - Accepts **e^-'s** from another substance
  - Substance that is reduced
  - $Cl_2 + 2e^- \longrightarrow 2Cl^-$

Reducing Agent

- Substance that donates e^-'s
  - Releases **e^-'s** to another substance
  - Substance that is oxidized
  - $Na \longrightarrow Na^+ + e^-$

Guidelines For Redox Reactions

- Oxidation & reduction always occur simultaneously
- Total number of electrons lost by one substance = total number of electrons gained by second substance
- For a redox reaction to occur, something must accept electrons that are lost by another substance

Hierarchy of Rules for Assigning Oxidation Numbers

1. Oxidation numbers must add up to charge on molecule, formula unit or ion.
2. Atoms of free elements have oxidation numbers of zero.
3. Metals in Groups 1A, 2A, and Al have +1, +2, and +3 oxidation numbers, respectively.
4. H & F in compounds have +1 & –1 oxidation numbers, respectively.
5. Oxygen has –2 oxidation number.
6. Group 7A elements have –1 oxidation number.

Hierarchy of Rules for Assigning Oxidation Numbers

7. Group 6A elements have –2 oxidation number.
8. Group 5A elements have –3 oxidation number.
9. When there is a conflict between 2 of these rules or ambiguity in assigning an oxidation number, apply rule with lower oxidation number & ignore conflicting rule.

Oxidation State

- Used interchangeably with oxidation number
- Indicates charge on monatomic ions
- Iron (III) means +3 oxidation state of Fe or Fe^{3+}

Using Oxidation Numbers to Recognize Redox Reactions

- Sometimes literal electron transfer:

decrease reduction

increase oxidation

$$\overset{+2}{Cu^{2+}} + \overset{0}{Zn} \longrightarrow \overset{+2}{Zn^{2+}} + \overset{0}{Cu}$$

Cu: oxidation number decreases by 2
$\Leftrightarrow$ reduction

Zn: oxidation number increases by 2
$\Leftrightarrow$ oxidation

Using Oxidation Numbers to Recognize Redox Reactions

- Sometimes electron transferred in "formal" sense.

O: decrease reduction

C: increase oxidation

$$\overset{-4}{C}\overset{+1}{H_4} + 2\overset{0}{O_2} \longrightarrow \overset{+4}{C}\overset{-2}{O_2} + 2\overset{+1}{H_2}\overset{-2}{O}$$

  - **O:** oxidation number decreases by 2 $\Leftrightarrow$ reduction
  - **C:** oxidation number increases by 8 $\Leftrightarrow$ oxidation

Acids as Oxidizing Agents

- Metals often react with acid
  - Form metal ions &
  - Molecular hydrogen gas

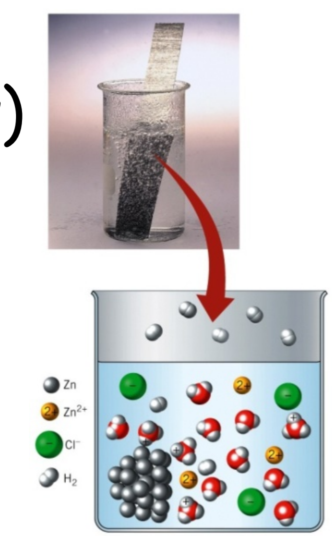
Molecular Equation

$$Zn(s) + 2HCl(aq) \rightarrow H_2(g) + ZnCl_2(aq)$$

Net Ionic Equation

$$Zn(s) + 2H^{+}(aq) \rightarrow H_2(g) + Zn^{2+}(aq)$$

- M ⇔ oxidized
- H^+ ⇔ reduced
- H^+ ⇔ oxidizing reagent
- Zn ⇔ reducing reagent



Anion Determines Oxidizing Power

- Acids are divided into 2 classes:

1. **Nonoxidizing Acids**
   - Anion is weaker oxidizing agent than H_3O^+
   - Only redox reaction is
     - $2H^+ + 2e^- \longrightarrow H_2$ or
     - $2H_3O^+ + 2e^- \longrightarrow H_2 + 2H_2O$
   - $HCl(aq)$, $HBr(aq)$, $HI(aq)$
   - $H_3PO_4(aq)$
   - Cold, dilute $H_2SO_4(aq)$
   - Most organic acids (e.g., $HC_2H_3O_2$)

Oxidizing Acids

- Anion is stronger oxidizing agent than H_3O^+
  - Used to react metals that are less active than H_2
  - No H_2 gas formed
  - $HNO_3(aq)$
    - Concentrated
    - Dilute
    - Very dilute, with strong reducing agent
  - $H_2SO_4(aq)$
    - Hot, conc'd, with strong reducing agent
    - Hot, concentrated

Redox Reactions of Metals

- Acids reacting with metal
  - Special case of more general phenomena

Single Replacement Reaction

- Reaction where one element replaces another
- **A + BC → AC + B**

1. Metal *A* can replace metal B
   - If *A* is **more active** metal, *or*
2. Nonmetal *A* can replace nonmetal *C*
   - If *A* is **more active** than *C*

Oxidation of Metals by Acids

- **Ease** of oxidation process depends on **metal**
  - Metals that react with HCl or H_2SO_4
    - Easily oxidized by H^+
    - **More active** than hydrogen (H_2)

  Ex. Mg, Zn, alkali metals

$$Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$$

$$2Na(s) + 2H^+(aq) \longrightarrow 2Na^+(aq) + H_2(g)$$

  - Metals that don't react with HCl or H_2SO_4
    - Not oxidized by H^+
    - **Less** active than H_2

  Ex. Cu, Pt

Activity Series of Metals

- Cu less active, can't replace Zn^{2+}
  - Can't reduce Zn^{2+}
  - $Cu(s) + Zn^{2+}(aq) \longrightarrow$ No reaction
- General phenomenon
  - Element that is more easily oxidized will displace one that is less easily oxidized from its compounds

Activity Series

- Metals at bottom more easily oxidized (more active) than those at top
- This means that given element will be displaced from its compounds by any metal **below** it in table

Activity Series of Some Metals

Table 6.3 Activity Series for Some Metals (and Hydrogen)

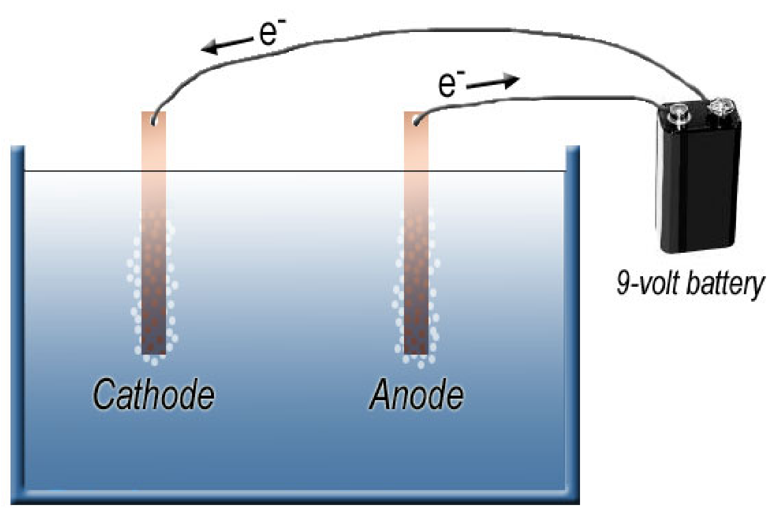
Activity	Element	Oxidation Product
Least Active; Do not react with nonoxidizing acids	Gold	Au^{3+}
	Mercury	Hg^{2+}
	Silver	Ag^{+}
	Copper	Cu^{2+}
	HYDROGEN	H^{+}
	Lead	Pb^{2+}
	Tin	Sn^{2+}
	Cobalt	Co^{2+}
	Cadmium	Cd^{2+}
	Iron	Fe^{2+}
React with nonoxidizing acids	Chromium	Cr^{3+}
	Zinc	Zn^{2+}
	Manganese	Mn^{2+}
	Aluminum	Al^{3+}
	Magnesium	Mg^{2+}
	Sodium	Na^{+}
	Calcium	Ca^{2+}
React with water to produce hydrogen	Strontium	Sr^{2+}
	Barium	Ba^{2+}
	Cesium	Cs^{+}
	Potassium	K^{+}
Most Active	Rubidium	Rb^{+}

Increasing ease of oxidation of the metal

Increasing ease of reduction of the ion

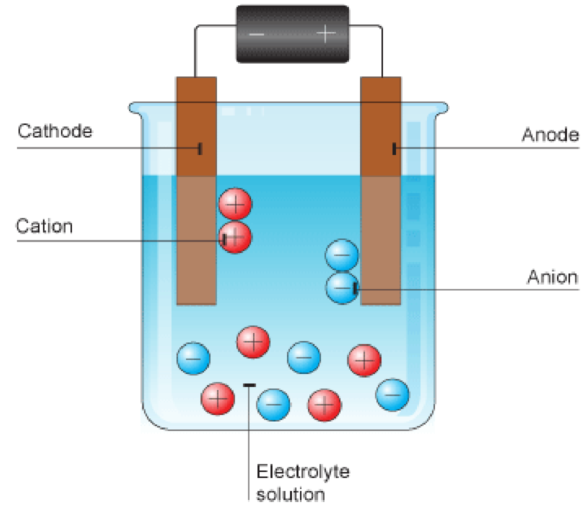
Electrolysis

- Oxidation-reduction process by which an electric current is passed through a substance to cause a chemical change.
- The chemical change is one in which the substance loses or gains an electron.

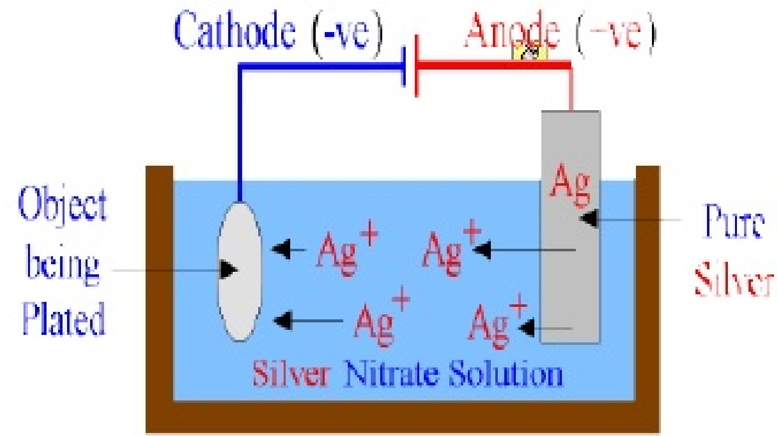


Set-up for electrolysis experiment

Electrolysis



- The process uses an apparatus consisting of positive and negative electrodes which are separated from each other in a solution.
- Electric current enters through the negatively charged electrode (**cathode**).
- Positively charged parts of the solution travel to the cathode, combine with the electrons, and are transformed into neutral molecules.
- The negatively charged parts of the solution travel to the positive electrode (**anode**), give up electrons, and are transformed into neutral molecules.



- Silver atom the anode releases electrons to form silver ions ,Ag^+ and moves into the silver nitrate solution: $Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-$
  The anode becomes thinner/ smaller

- Silver ion, Ag^+ move to the cathode receives electron to form silver atom :
  $$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$$
  Silver is deposited onto the surface of the object as the object becomes silver plated.

- The rate at which the silver atoms become silver ions at the anode is the same as the rate at which the silver ions become silver atoms at the cathode

- The concentration of the silver nitrate solution therefore remains unchanged.