

Oxidation Reduction

Unit 9

Oxidation Reduction

often abbreviated as RedOx, a shorthand way to express that oxidation and reduction *must* occur simultaneously

Reduction:

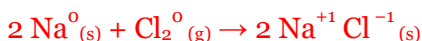
- occurs when atoms *gain* electrons (e^-)
- the oxidation state is *reduced*

Oxidation:

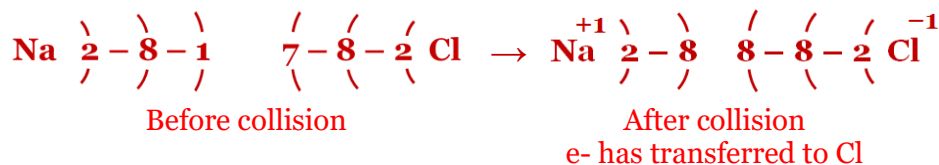
- to react with oxygen, originally
- occurs when atoms *lose* electrons (e^-), in modern usage
- the oxidation state *increases*

For redox reactions to occur, some atoms must gain e^- while other atoms must lose e^- and since charge is conserved, the number of e^- lost *must* equal the number of e^- gained. Since e^- are negative, the oxidation numbers of atoms that *gain* e^- are *reduced* while the oxidation numbers of atoms that *lose* e^- are *increased*.

Example:



From collision theory, we know that the Na and Cl atoms must collide:



Oxidizing and Reducing Agents

The species that is reduced is called the *oxidizing agent* (Cl_2 in the example above)
the oxidizing agent causes the other reactant to become oxidized

The species that is oxidized is called the *reducing agent* (Na in the example above)
the oxidizing agent causes the other reactant to become oxidized

Losing Electrons is Oxidation (LEO)

Gaining Electrons is Reduction (GER)

Mnemonic for RedOx is LEO says GER

Oxidation Number Review

1. The oxidation number of any free element is zero

- $\text{Na}_{(s)}$ 0
- O 0
- O_2 0
- O_3 0

2. The oxidation number of a monatomic ion is equal to its charge

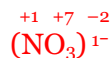
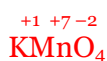
- Na^{1+} +1
- O^{2-} -2
- Al^{3+} +3
- Hg_2^{2+} +1 (Hg_2^{2+} is not monatomic)

3. Fluorine has an oxidation number of -1 in all its compounds
 - F_2 O (see rule #1)
 - MgF_2 F^{-1}
 - OF_2 F^{-1}
4. Group 1 and Group 2 metals have oxidation numbers equal to their group number in all their compounds
 - $Mg_{(s)}$ Mg^0 (see rule #1)
 - CaF_2 Ca^{+2}
 - Li_2O Li^{+1}
 - Na_2SO_4 Na^{+1}
5. Hydrogen will have an oxidation number of +1 or -1; check the electronegativity of the other element
 - H_2 H^0 (see rule #1)
 - H_2SO_4 H^{+1} (see Table E for charge on the polyatomic SO_4^{2-})
 - NaH H^{-1} (see rule #5 for Na)
 - $LiAlH_4$ H^{-1} (Al will always be +3 in compounds)
 - H_2O_2 H^{+1} (a peroxide)
6. Oxygen is the second most electronegative element and will have an oxidation number of -2 in *almost* all its compounds; exceptions are F, peroxides, and superoxides
 - $MgO_{(s)}$ O^{-2}
 - Na_2SO_4 O^{-2}
 - H_2O_2 O^{-1} (a peroxide)
 - KO_2 $O^{-1/2}$ (a superoxide)
 - OF_2 O^{+2} (F is the most electronegative element)
7. The most electronegative element in a compound will usually behave like a monatomic ion
 - H_2SO_4 O^{-2}
 - K_3SO_3 O^{-2}
 - CaC_2 C^{-1}
 - NH_3 N^{-3}
8. The algebraic sum of the oxidation numbers in molecules will equal 0 or will equal the charge of a polyatomic ion
 - H_2SO_4 $2 H^{+1} + S^{+6} + 4 O^{-2} = 0$
 - $KMnO_4$ $K^{+1} + Mn^{+7} + 4 O^{-2} = 0$
 - H_2O_2 $2 H^{+1} + 2 O^{-1} = 0$
 - Hg_2Cl_2 $2 Hg^{+1} + 2 Cl^{-1} = 0$
 - NO_3^{-1} $N^{+5} + 3 O^{-2} = -1$

Writing oxidation numbers:

- write the oxidation number for one atom of each element
- write the oxidation number as a superscript above each element

Examples:

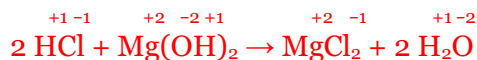


RedOx Reactions

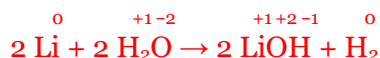
Identifying oxidation and reduction:

1. Start with a balanced equation
2. Write oxidation states for all the elements
3. Use the change in oxidation states to identify oxidation and reduction

Examples:



No oxidation states change, so this is not a redox equation



Li⁰ oxidation state increases from 0 → +1 oxidation (Li⁰ is the reducing agent)

H⁺¹ oxidation state decreases from +1 → 0 reduction (H⁺¹ is the oxidizing agent)

Reducing agent: a substance that reduces another substance

reducing agents get oxidized

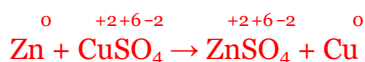
Oxidizing agent: a substance that oxidizes another substance

oxidizing agents get reduced

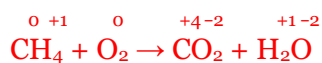
Use reaction types to help identify redox reactions

Single replacement and combustion reactions are *always* redox reactions

Examples:



Single replacement

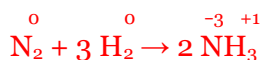


Combustion

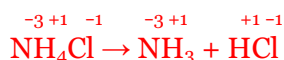
Note that both reactions have elemental reactants that form compounds

Synthesis and decomposition reactions are *may* be redox reactions

Examples:



Is redox

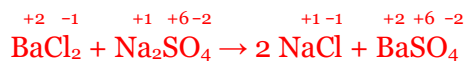


Is not redox

Reactions that start with elements and end with compounds (or vice versa) are redox

Double replacement reactions are *never* redox reactions

Example:



Is not redox

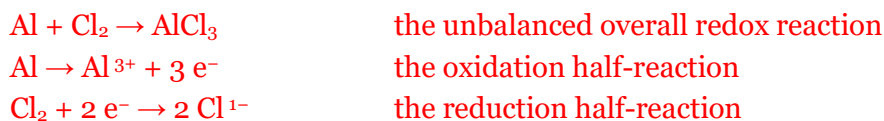
Half-Reactions

Redox has both oxidation and reduction, and so is often written as two half-reactions

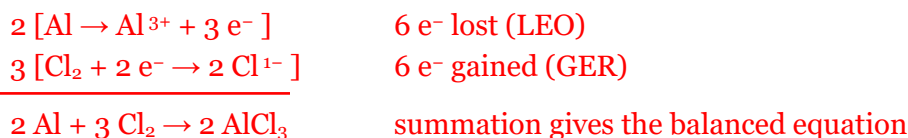
- one half-reaction shows oxidation (loss of e⁻)
- the other half-reaction shows reduction (gaining e⁻)
- half-reactions leave out *spectator ions*

Spectator ion: an ion that remains unchanged on both the reactant and product sides of an equation

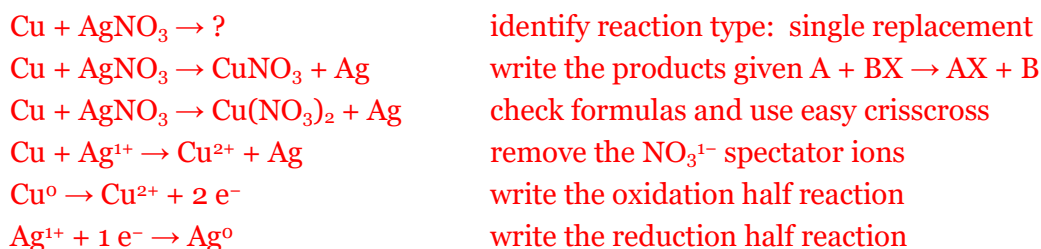
Example 1: write the oxidation and reduction half-reactions



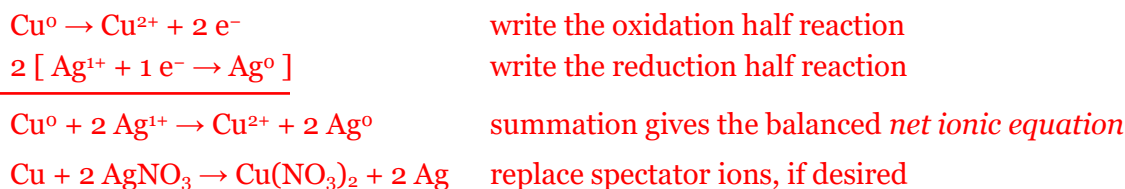
Conservation of charge *must* be observed



Example 2: write the oxidation and reduction half-reactions leaving out spectator ions



Conservation of charge *must* be observed



Electrochemical Cells

There are two types of electrochemical cells:

- voltaic cells, sometimes called galvanic cells, spontaneously convert chemical energy into electrical energy
- electrolytic cells are nonspontaneous and require energy to operate

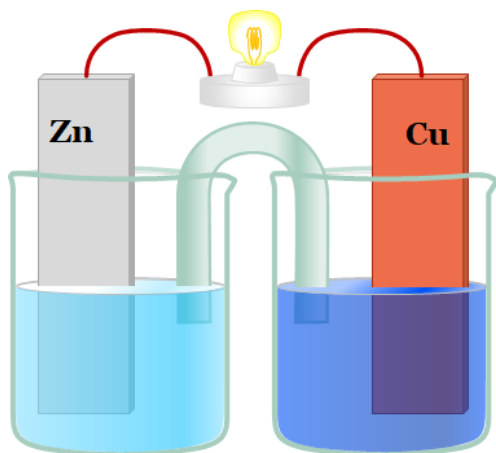
In both types of electrochemical cells:

- anode – the site where oxidation occurs “Annie the ox”
- cathode – the site where reduction occurs “Red cat”
- there must be a complete circuit

Voltaic cells: a redox reaction *produces* electricity

- requires *two* half-cells with (usually) metallic electrodes
 - anode – oxidation occurs at the metal that occurs higher on Table J
 - cathode – reduction occurs at the metal that is lower on Table J
- a functioning cell *must* form a complete circuit
 - electrons will flow from the anode through a connecting wire to the cathode
 - from the oxidation site to the reduction site (LEO to GER)
 - from LEO to GER
 - from the anode to the cathode
 - ions will complete the circuit by moving through a salt bridge
- check for spontaneous reaction by using Table J
 - the metal higher up on Table J *must* be oxidized (will be the anode)

Example voltaic cell: the Daniell cell



Description of the operation of a Daniell cell:

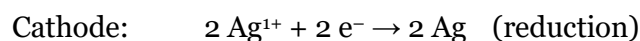
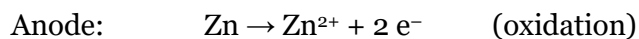
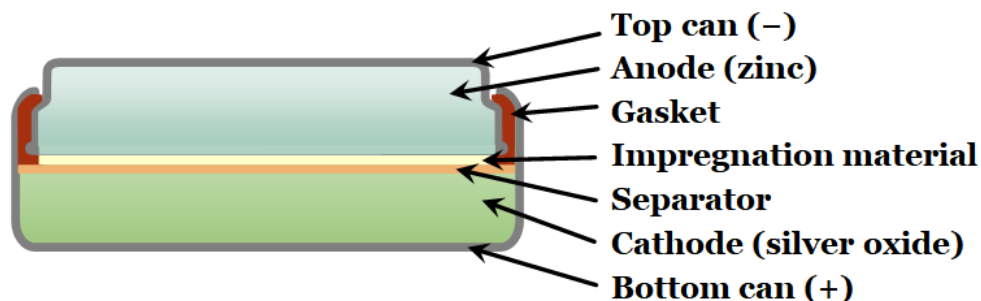
1. Zn oxidizes: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
Zn metal becomes $\text{Zn}^{2+}_{(\text{aq})}$
Zn electrode loses mass
2. e^- flow through wire to Cu electrode
3. $\text{Cu}^{2+}_{(\text{aq})}$ reduces: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 $\text{Cu}^{2+}_{(\text{aq})}$ becomes Cu metal
Cu electrode gains mass
4. Ions flow between the half-cells
through the salt bridge in both
directions (- to left, + to right)

Operating a Daniell cell causes the Zn anode loses mass and the Cu cathode gains mass

Zinc atoms in the metal strip lose electrons (become oxidized) and become Zn^{2+} ions which dissolve away to form a water solution

Copper ions in solution touch the copper metal and gain electrons becoming metal atoms which become part of the copper strip

Example voltaic cell: the silver oxide button battery



Comparing electrochemical cells:

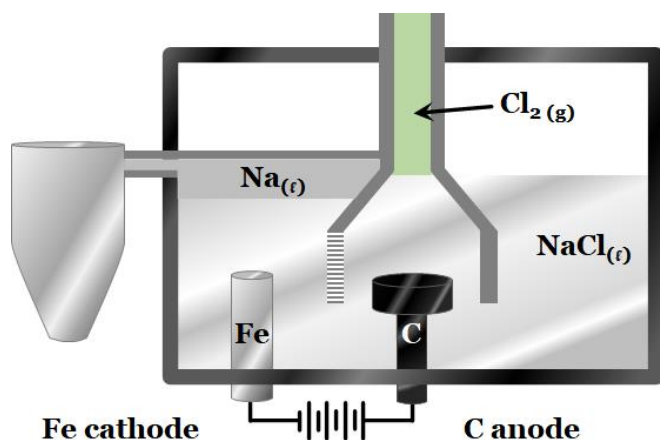
Voltaic cells: *designed* to be spontaneous

- metals are selected so the cell *will* run (see Table J)
- produces electricity (exothermic)
- the cathode will be positive (+) and the anode will be negative (-)

Electrolytic cells: are a *forced* reaction

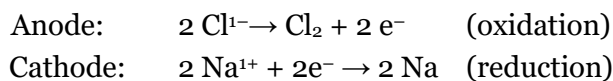
- will require an *energy* source
- uses electricity (endothermic)
- “Annie the ox” and “red cat” will still be true, *but*
- the charges are reversed, the cathode will be negative (-) and the anode will be positive (+)
- uses: recharging batteries, produce gases (H_2 , O_2 , Cl_2), refine metals, and electroplating

Example electrolytic cell: the Downs cell (which produces sodium metal and chlorine gas)



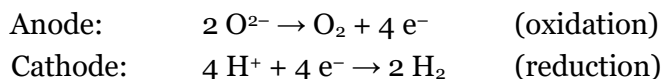
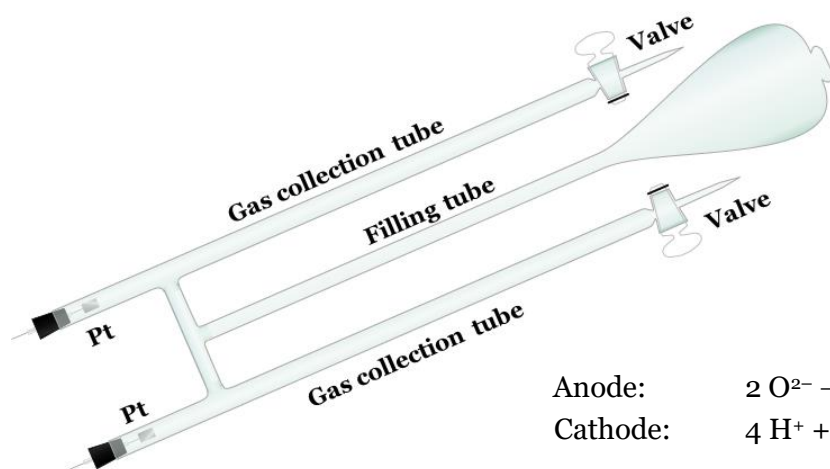
Description of the operation of a Downs cell:

1. Cl^- oxidizes: $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
Positive C anode takes e^- from Cl^-
 $\text{Cl}_2(\text{g})$ exits up chimney
2. e^- from source enter Fe cathode
3. Na^+ reduces: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Negative cathode gives $\text{Na}^+ \text{e}^-$
 $\text{Na}^+ \rightarrow \text{Na}(\text{l})$ metal spills into tank
4. liquid ions flow to oppositely charged electrodes

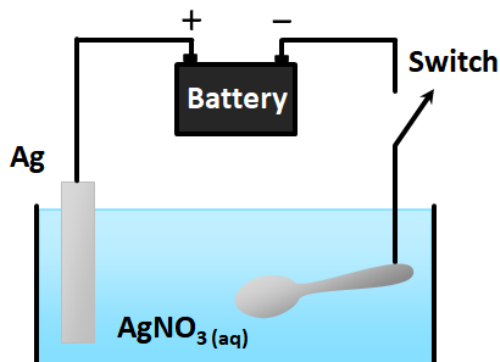


Electrolysis: separating elements from natural sources (such as ores) using an electrolytic cell

Example electrolytic cell: the Hoffman tube (which produces $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ from water)



Example electrolytic cell: electroplating a spoon with silver



Description of electroplating:

1. Make the metal object to be plated the cathode (-)
2. Negative cathode attracts Ag^+ ions
3. Reduction: $\text{Ag}^+ + 1\text{e}^- \rightarrow \text{Ag}$