

Chemistry 3A

Introductory General Chemistry

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- Word Equations
- Chemical Equations
- Balancing Equations
- Predicting Reactions: Single & Double Displacement Reactions
- Writing Chemical Equations for Reactions in Solution
 - Complete Chemical Equations
 - Complete Ionic Equations
 - Net Ionic Equations
- Oxidation/Reduction
 - How to understand them and to apply them

Chemical Reactions & Conservation Laws

- **Chemical reactions** are expressed in a way just as mathematics uses equations: to show something is connected at a time before with something that comes after
- A **reaction** is an expression of substances that react—the **reactants**—and the result of the reaction—the **products**

Reactants → Products

- The expression of these is about the **conservation laws** of **mass (matter)**, **energy**, and **electric charge**

Equations in Words

- Chemical reactions are expressed essentially as equations, and the expression can be in words
- Silver metal solid is reacted with sulfur with the result it forms silver sulfide
 - If you have ever seen tarnish on silver metal set, you see silver sulfur compound
 - When natural gas (methane) is burned in a Bunsen burner, the gas reacts with oxygen (O_2) in the air to produce carbon dioxide (CO_2) and water (H_2O)
- A problem with equations as words is that they can not indicate the quantitative nature of reactions

See also <https://youtu.be/vTq4sgGd2QU>



Figure 10.1.2: You can see dark spots of tarnished (silver sulfide) forming on this ring as it reacts with sulfur compounds in the air. (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

Methane + oxygen \rightarrow carbon dioxide + water



Figure 10.1.3: A Bunsen burner is commonly used to heat substances in a chemistry lab. Methane is reacted with oxygen to form carbon dioxide and water. (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

Steps in Chemistry = Recipe

Yum! Yum!

- Your book wants to point out that steps in laboratory work such as a chemical synthesis align with a metaphor of making a delicious preparation of shrimp gumbo
- Chemists are probably good in the kitchen as well because they must carefully, meticulously gather the ingredients and then “cook” them in the correct way to get an exacting result



Figure 10.2.1 (Credit: jons2 at pdphoto.org; Source: http://commons.wikimedia.org/wiki/File:Shrimp_gumbo.jpg(opens in new window); License: Public Domain)

Chemical Equations

- Chemical equations start with using chemical formula which express matter as the symbols of the elements of the **Periodic Table**
- The reactants and products as compounds are a sketch of the reaction. This is the **skeleton equation**



- The next step is to indicate the physical state of the compounds:



- (s) = solid, (l) = liquid, (g) = gas,
 (aq) = compound in aqueous phase

Symbols in Chemical Equations

It is important to understand the symbols used in chemical reaction equations

Table 10.2.1: Symbols Used in Chemical Equations

Symbols	Description
+	Used to separate multiple reactants or products.
→	Yield sign; separates reactants from products.
⇌	Replaces the yield sign for reversible reactions that reach equilibrium.
(s)	Reactant or product in the solid state.
(l)	Reactant or product in the liquid state.
(g)	Reactant or product in the gaseous state.
(aq)	Reactant or product in an aqueous solution (dissolved in water).
$\text{Pt} \rightarrow$	Formula written above the arrow is used as a catalyst in the reaction.
$\Delta \rightarrow$	Triangle indicates that the reaction is being heated.

See also <https://youtu.be/ZcF8E8aAOGs>

Balancing Equations

- With the skeleton equation up on the whiteboard, it is time to apply the laws of the conservation of mass (electric charge & energy can be examined later)
- One of the most important beginnings in chemistry is writing reactions (equations) that show the formation of compounds from their elemental forms

practice exercises calculating the enthalpy of formation is often seen with this

- The elemental form of carbon is C (s). The elemental form of hydrogen is H₂ (g)
- From these two, the formation of methane CH₄ (g) is shown



- The equation is missing mass balance however, which it must have on both sides of the reaction arrow
- There is one atom of C on both sides, so that's OK, but there are 2 atoms of H on left side, but 4 atoms on the right. The left needs 2 more atoms, which can be done by doing the following:



Details of Balancing Equations

- In the previous slide, a **2** was added to the $\text{H}_2 (g)$ reactant to achieve the balance of atoms on both sides of the reaction arrow



- This **2** and *any whole number/integer* placed in front of a **chemical compound** in a **chemical equation** is called a **coefficient**

This is also term in mathematics for a number placed in front of a variable in an algebraic expression

- Putting a coefficient in front of a compound has the effect of multiplying the number of each atom in the compound by the number of the coefficient, and if the atom is subscripted, by that subscript number too
- $2 \text{H}_2 = 2 \times 2 \text{H} = 4 \text{H atoms}$
 $2 \text{CO}_2 = 2 \times 1 \text{C} = 2 \text{C atoms}; 2 \times 2 \text{O} = 4 \text{O atoms}$
 $4 \text{H}_2\text{O} = 4 \times 2 \text{H} = 8 \text{H atoms}; 4 \times 1 \text{O} = 4 \text{O atoms}$
 $3 \text{MnO}_4 = 3 \times 1 \text{Mn} = 3 \text{Mn atoms}; 3 \times 4 \text{O} = 12 \text{O atoms}$

Steps To Balancing Equations

1. Set up the skeleton equation: write down the correct chemical formulas on each side of the reaction arrow, the reactants and products
2. Identify all atoms and count the number of atoms on the reactant and product side

If polyatomic ions are unchanged on both sides, count it as a unit

3. Begin the balancing by focusing on elements that occur in only one compound on one side

For instance, oxygen often appears in more than one compound on one side the arrow: do not start with balancing oxygen atoms

4. Balancing can ONLY be done by using coefficients: changing subscripts changes the chemical nature of a compound, and this is not permitted
5. When satisfied of completion, verify the numbers of atoms on both sides of reaction arrow
6. Make sure coefficients have lowest possible ratio, while remaining integers

Practice Balancing Equations

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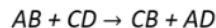
Types of Reactions

- Chemical reactions will fall under certain types/categories on one level, and then on an additional level with question “what is happening with atoms?”
- On an additional level, the question is “what process is happening?”
- You will learn to identify these types or categories of reactions

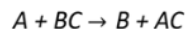
Scheme 1

What is happening with the atoms?

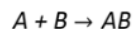
Double Displacement (“DD”)



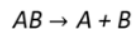
Single Displacement (“SD”)



Combination



Decomposition



Scheme 2

What overall process is taking place?

Precipitation

A “DD” reaction that forms a solid product

Acid-Base/Neutralization

A “DD” reaction between an acid and base.

Gas Evolution

A “DD” reaction that forms a gaseous product.

No Reaction

A “DD” reaction with only aqueous products.

Oxidation/Reduction (Redox)

*A reaction where electrons are transferred.
(Often “SD”, Combination, or Decomposition)*

Combustion

A Redox reaction with gaseous oxygen.

Combination Reactions



- This reaction type is about **synthesis**: two substances combine to form a single (third) compound
- Sodium metal solid reacts with chlorine gas to form the solid sodium chloride



Oxide Formation: A Combination Reaction

- Oxygen O_2 in the air reacting with numerous elements is perhaps one of the most important significant of reactions



This reaction was one of your recent lab experiments!!



Decomposition Reactions



- The **decomposition reaction** type appears to be the very opposite of the **combination reaction**
- One substance (shown as “parts” of A and B) is “decomposed” to form two or more substances/compounds
- Many of these reactions require an input of energy—an “activation energy”—for the reaction to proceed

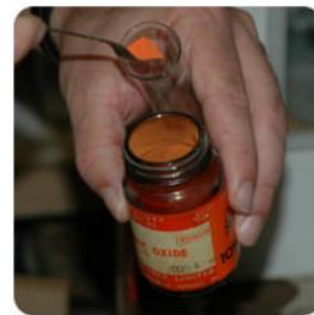


Figure 10.4.2.2: Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas. (Credit: Ben Mills (User:Benjah-bmm27/Wikimedia Commons);



A compound decomposes to elements in this reaction

Decomposition Reactions

- **Decomposition reaction** include compounds decomposing to compounds:



- Here **metal oxides** are formed from their **hydroxides**



- Acids like the unstable **carbonic acid** will decompose quickly to **nonmetal oxides** and **water**



- **Potassium chlorate** is a well-known decomposition reaction



- The **electrolysis** of **water** is a well-known decomposition



Combustion Reactions



- **Combustion reactions** always involve **gaseous oxygen** (O_2) as a reactant
- Humans learned the hard way with the Hindenberg airship disaster that hydrogen gas (H_2) also gets combusted



- Are you a gas griller? Here is the **combustion** of **propane**:



Among the many important things to learn in chemistry, one of these is just how much **oxygen** is involved in much of chemistry

18					
Helium 2 He 4.003					
13	14	15	16	17	
Boron 5 B 10.81 2.0	Carbon 6 C 12.011 2.5	Nitrogen 7 N 14.007 3.0	Oxygen 8 O 15.999 3.5	Fluorine 9 F 18.998 4.0	Neon 10 Ne 20.180 —
13	14	15	16	17	18
Aluminum Al 26.98 1.5	Silicon Si 28.09 1.8	Phosphorus P 30.97 2.1	Sulfur S 32.06 2.5	Chlorine Cl 35.45 3.0	Argon Ar 39.95 —
31	32	33	34	35	36
Gallium Ga	Germanium Ge	Arsenic As	Selenium Se	Bromine Br	Krypton Kr



Figure 10.4.3.2: Explosion of the Hindenberg. (Credit: Courtesy of Gus Pasquerella/US Navy; Source: <https://www.flickr.com/photos/usnavy/10400000000/>)

Single Replacement Reactions

- **Silver** tarnishes. The metal reacts with **hydrogen sulfide** (H_2S) which is always present in small amounts in the air



- This is an example of a **single-replacement reaction**

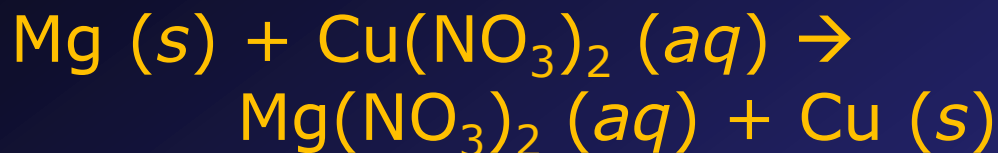


- One (usually **metal**) **element A** replaces a similar (also **metal**) **element B** in a compound
- If **A** is a **nonmetal**, it will replace the **nonmetal** that is **B** with **C**



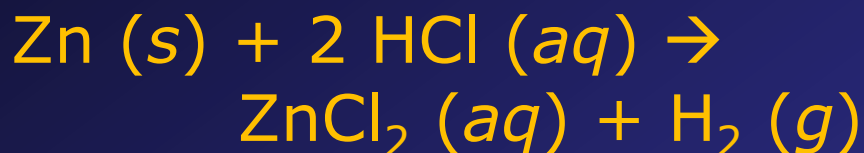
Single Replacement Reactions

- Metal Replacement



Mg more reactive than Cu and replaces it

- Hydrogen Replacement



Acidic proton is replaced by active metal

Water is not usually considered an acid, but some metals are so reactive that they replace the H in H_2O to form the metal hydroxide



Figure 10.4.4.2: Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Credit: User: Chemicalinterest/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Zn_reaction_with_HCl.JPG(opens in new window); License: Public Domain)



Figure 10.4.4.3: Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite. (Credit: User:Ajhalls/Wikimedia Commons; License: Public Domain)

Single Replacement Reactions

• Halogen Replacement

The interesting thing about this reaction is that **diatomic chlorine molecule** replaces **bromine ion** to produce **chloride ion** and **diatomic bromine molecule** (it actually takes electrons away from **Br** in an oxidation reaction)

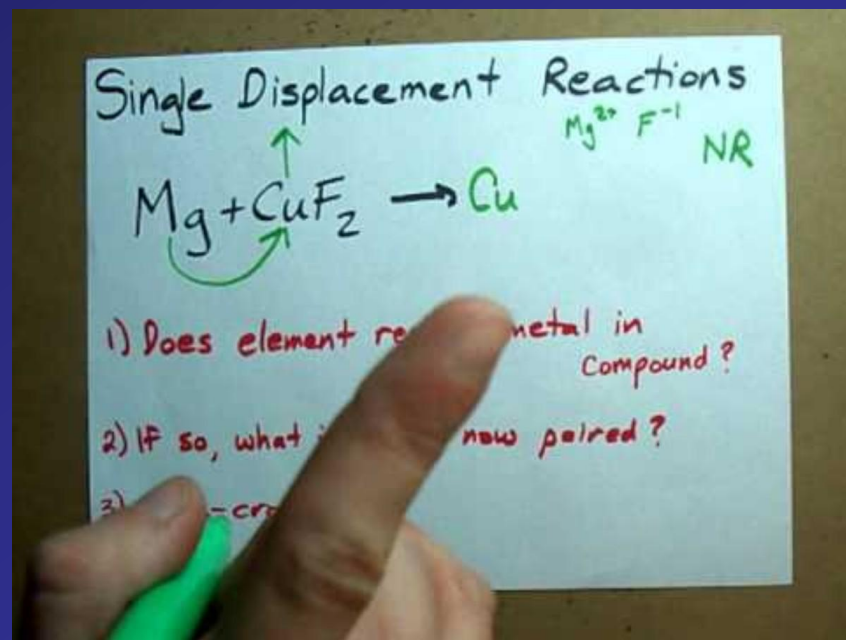


Cl_2 will do the same to **NaI**.

Fluorine (F_2) will do the same to **NaCl** or **NaBr** or **NaI**.

And **Br_2** will do the same to **NaI**.
All these elements are in same **Group** (column), and they show a reactivity based on the period (row) they are in

Reactivity decreases with increasing period



Double Replacement Reactions



- This reaction is when the **cations** and **anions** of **two ionic compounds** exchange places to form **two** different **ionic compounds**
 - **A** & **C** are the **cations**, **B** and **D** are the **anions**
 - These reactions happen when one of the **products** is a **precipitate**, **gas** or a **molecule** like **H₂O**

- **Precipitate**

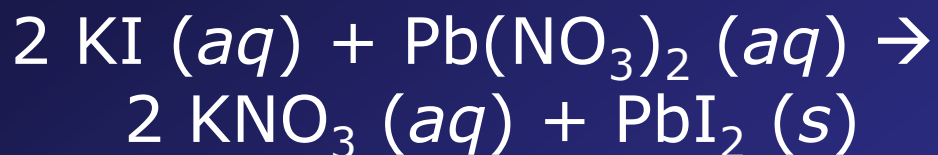


Figure 10.4.5.2: Formation of lead iodide precipitate. (Credit: Paige Powers - "Lead Iodide"; Source:

Pb²⁺ and I⁻ ions strongly bind and form a solid

Double Replacement Reactions

- Gas Formation



The H_2S gas bubbling out actually drives the action further to the right, promoting the reaction

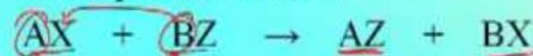
- Molecular Compound Formation



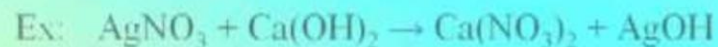
This is actually a classic reaction of a **strong acid** with a **strong base** to produce a **salt** and **water**

II. Types of Chem. Rxns

D. Double Replacement Rxns



- Positive ions from each compound switch places



Predicting Single Displacement Reactions

- The **hydrogen** and **halogen single replacement reactions** were discussed a couple of slides back
- For **ionic compounds**, elements of the same type will replace elements of that type
 - **Metal cations/elements** replace **metal cations**
 - **Nonmetal anions/elements** replace **nonmetal anions**
- $\text{FeCl}_2 + \text{Ca} \rightarrow ?$
 $\text{CaCl}_2 + \text{Fe}$
- $\text{CaBr}_2 + \text{F}_2 \rightarrow ?$
 $\text{CaF}_2 + \text{Br}_2$
- $\text{FeI}_2 + \text{Cl}_2 \rightarrow ?$
 $\text{FeCl}_2 + \text{I}_2$
- $\text{AlPO}_4 + \text{Mg} \rightarrow ?$
 $\text{Mg}_3(\text{PO}_4)_2 + \text{Al}$

Predicting Double Displacement Reactions

- There are patterns and trends that can be seen with these reactions making them predictable
1. Exchange anions and cations on reactant side to form new product compounds
 2. Since charge magnitude may differ on cations or anions (1+ and 2+, or 1- and 2-) between reactants and products, formulas may need to be corrected (remember the criss-cross method)
 3. Balance the equation
- Consider barium chloride (BaCl_2) and lithium sulfate (Li_2SO_4) next

Predicting Double Displacement Reactions

- 1. Exchange anions and cations on reactant side to form new product compounds*



- In specifying the products, it is vital to follow write the correct chemical formula for compounds and not worry about balance of atom numbers on both sides of arrow at the moment
- Polyatomic ions (like sulfate SO_4^{2-}) despite being composed of multiple elements must be maintained as the groups of elements they are which gives them their identity as polyatomic ions as they are connected by covalent and not ionic bonds, despite being ions as a group of nonmetal elements

Predicting Double Displacement Reactions

2. *Since charge magnitude may differ on cations or anions (1+ and 2+, or 1- and 2-) between reactants and products, formulas may need to be corrected (remember the criss-cross method)*



- The exchanged ions Ba²⁺ with SO₄²⁻, and of Li⁺ with Cl⁻, created no problem with matching charges of the ions: 1+ matched with 1- and 2+ matched with 2-
- Had this matching not of ions by charge state not occurred, determining correct subscripts to monatomic ions or polyatomic ions would have been necessary

Predicting Double Displacement Reactions

3. *Balance the equation*



- At this point, the compounds are determined. Subscripts to monatomic or polyatomic ions will not be changed
- To achieve balance, coefficients will be determined (added) to the compounds to obtain the necessary result
- In the current reaction, it was only necessary to balance with two of the LiCl ionic compound

Practice: Predicting Double Replacement

Predict mixing of: $\text{RbOH (aq)} + \text{CoCl}_2 \text{ (aq)}$

1. *Exchange cations/anions*



Note that hydroxide is parenthesized to show as a polyatomic ion it should not have its elements separated

2. *Adjust formulas (subscripts) of products to correct for ion charge states*



RbCl needed no correction, but cobalt is a 2+ ion and hydroxide (OH) is a 1- ion, so two OH groups were needed

3. *Balance equation and add phase indicators*



No coefficients were found to be needed since there was a balance of atoms/elements on both sides. The only thing added was the phase indicators, in particular to show that a precipitate in cobalt(II) hydroxide was formed

Practice: Predicting Double Replacement

Predict mixing of: $\text{SrBr}_2 (aq) + \text{Al}(\text{NO}_3)_3 (aq)$

1. *Exchange cations/anions*



Note there is NO subscripts on the product side: only one of each of the cations and anions, keeping in mind nitrate is polyatomic ion so parentheses are put around it to note that, keep track of it

2. *Adjust formulas (subscripts) of products to correct for ion charge states*



The compounds have now been "criss-crossed" to reflect correct subscripts of monatomic/polyatomic numbers

3. *Balance equation*



The balance of this equation was selected to be the most difficult of reactions. Usually balancing is not difficult but this was a big test. There was one of each of Sr and Al on both sides, so balancing does not start there. With $(\text{NO}_3)_3$ reactant and $(\text{NO}_3)_2$ product, do a criss-cross of coefficients $[2 (\text{NO}_3)_3]$ and $[3 (\text{NO}_3)_2]$. And reactant Br_2 and product Br_3 , do same: $[3 \text{Br}_2]$ and $[2 \text{Br}_3]$ and it all works!

Precipitation Reactions

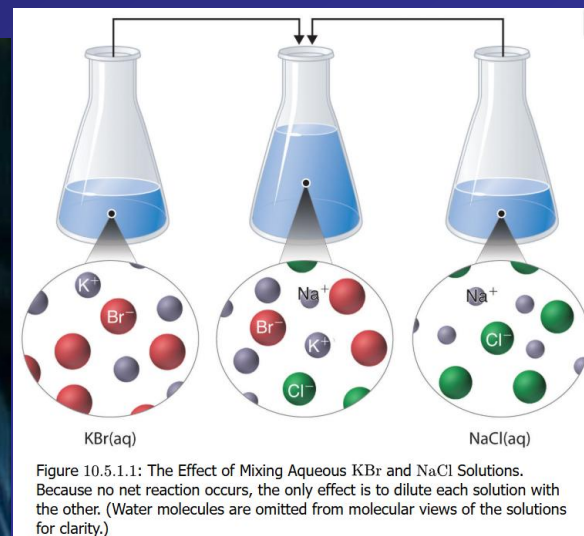


- Precipitations are double displacement reactions with one of products being insoluble



This is an unbalanced equation (can you balance it?)

- Not all mixing of compounds in solutions results in precipitations
- Mixing KBr and NaCl solutions results in no reaction except K^+ , Na^+ , Br^- , and Cl^- ions in solution, all at half original concentrations



Practice: Precipitation Reactions

The 3 steps of the double displacement add a 4th step (actually at the 3rd step) to determine if a product is a precipitate according to solubility rules on your Green Sheet

- $\text{Sr}(\text{OH})_2 (aq)$ is added to $\text{FeCl}_2 (aq)$

1. *Exchange ions*



2. *Check exchanged ion charges, fix subscripts*



Both metals are 2+ ions, both anions 1-

3. *Check solubility (precipitate) and note the phases*



Metal hydroxides like Fe are insoluble

4. *Balance by finding coefficients*



Balancing not needed

Practice: Precipitation Reactions

- K_3PO_4 solid added to mercury(II) perchlorate, $\text{Hg}(\text{ClO}_4)_2 (aq)$

1. *Exchange ions*



2. *Check exchanged ion charges, fix subscripts*



K^+ matches ClO_4^- , 3 Hg^{2+} needed for 2 PO_4^{3-}

3. *Check solubility (precipitate) and note the phases*



Chlorates are soluble, phosphates of mercury are not

4. *Balance by finding coefficients*



Start with add 3 K to product side, then 3 Hg to reactant side; then see that $3 \times 2 = 6$ perchlorates are on reactant side, so put 6 in front of KClO_4 ; also need 2 PO_4 groups, so put 2 in front of K_3PO_4 , verify that there are now $2 \times 3 = 6$ K on reactants and you see $6 \times 1 = 6$ K on products. DONE!

Practice: Precipitation Reactions

- Solid sodium fluoride added to aqueous solution of ammonium formate

1. *Exchange ions*



2. *Check exchanged ion charges, fix subscripts*



All ions found to be 1+ or 1-

3. *Check solubility (precipitate) and note the phases*



Everything soluble, no precipitate

4. *Balance by finding coefficients*



No balancing was required in this step either

Practice: Precipitation Reactions

- Mix aqueous solutions of calcium bromide and cesium carbonate

1. *Exchange ions*



2. *Check exchanged ion charges, fix subscripts*



The exchange actually matched +2 with -2, and +1 with -1

3. *Check solubility (precipitate) and note the phases*



Carbonates are insoluble for Ca^{2+} , bromides are soluble for Cs^+

4. *Balance by finding coefficients*



Inspection shows Ca and CO_3 are balanced; add 2 to CsBr to balance Cs atom. The addition caused a balance of Br to the left; DONE

Acid-Base Neutralization

- **Acids** react with **bases** to **neutralize** each other with the products being a **salt** and **water**



Neutralize nitric acid with calcium hydroxide

1. *Exchange ions*



2. *Check exchanged ion charges for product, fix subscripts*



3. *Balance by finding coefficients*



Ca has one on both sides; next check H atom: 2 on right, $2 \times 1 + 1 = 3$ on left, so try putting 2 for HNO_3 making it 4 H atoms on left, so put 2 in front of H_2O on right; check N atoms: 2 on left and 2 on right (good); check O atoms: $2 \times 1 + 3 \times 2 = 8$ on left, same check is good on right, DONE!

Practice: Acid-Base Neutralization

- Placeholder here

Gas-Evolving Reactions

- Reactions of acids with carbonate salts usually produce a gas like carbon dioxide



In the figure on the right, CO_2 created or released by the addition of the carbonate salt (Na_2CO_3) to dilute acid (HCl) in the tube on the stand (left) leaves the tube through the stopper into tubing that connects to a stoppered tube on the right which contains calcium hydroxide [$\text{Ca}(\text{OH})_2$] on the right. Because CaCO_3 is insoluble, a precipitate forms making the solution milky

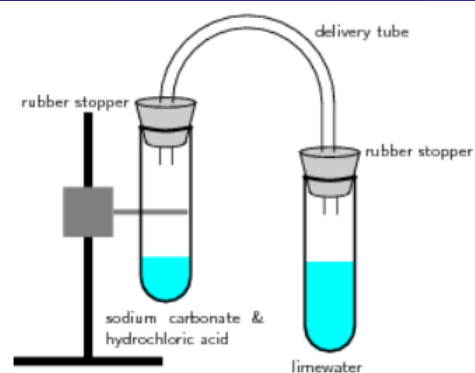


Figure 10.5.2.1: Reaction of acids with carbonates. In this reaction setup, lime water (water + calcium hydroxide) is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

Gas-Evolving Reactions

Reactant Type	Intermediate Product	Evolved Gas	Example
sulfide	none	H ₂ S	$2 \text{HCl (aq)} + \text{K}_2\text{S} \rightarrow \text{H}_2\text{S (g)} + 2 \text{KCl (aq)}$
carbonates, bicarbonates	H ₂ CO ₃	CO ₂	$2 \text{HCl (aq)} + \text{K}_2\text{CO}_3 \rightarrow \text{H}_2\text{O (l)} + \text{CO}_2 \text{ (g)} + 2 \text{KCl (aq)}$
sulfites, bisulfites	H ₂ SO ₃	SO ₂	$2 \text{HCl (aq)} + \text{K}_2\text{SO}_4 \rightarrow \text{H}_2\text{O (l)} + \text{SO}_2 \text{ (g)} + 2 \text{KCl (aq)}$
ammonia	NH ₄ OH	NH ₃	$\text{NH}_4\text{Cl (aq)} + \text{KOH} \rightarrow \text{H}_2\text{O (l)} + \text{NH}_3 \text{ (g)} + 2 \text{KCl (aq)}$

Gas-Evolving **REDOX** Reactions

- Reactions of acids with metals also generate a gas:



This reaction is really a case of **oxidation** of the **metal**, and the **reduction** of **protons** to form **hydrogen gas**

Oxidation is when electrons are *taken from* an element/atom in a reaction (the **redox reaction**)

Reduction is when electrons are *gained by* an element/atom in a reaction (the **redox reaction**)

The two **half-reactions**



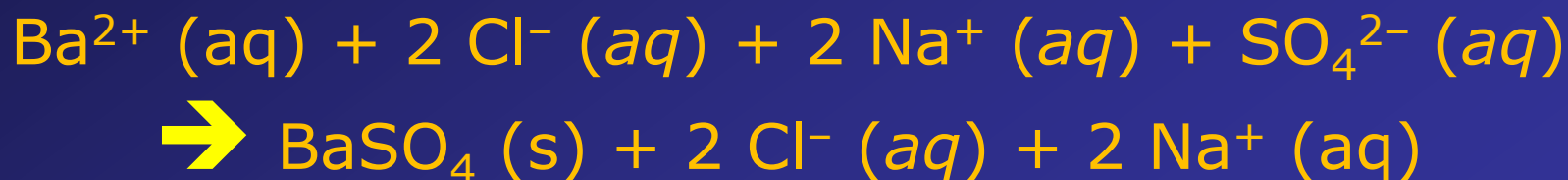
Writing Equations for Reactions

- For the precipitation reaction of barium chloride mixed with sodium sulfate, it is written to illustrate the essence of the reaction. Call this the **complete chemical equation**

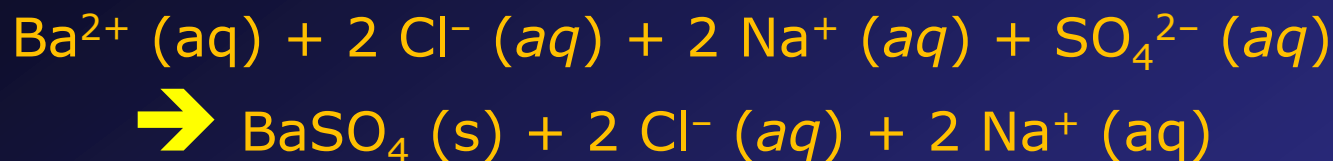


- But what really happens when compound is dissolved in an aqueous solution is that compounds do not exist in this way but are dissolved ions in solution.

Call this the **complete ionic equation**



Writing Equations for Reactions



1. On the reactant and product sides, ions (Ba^{2+} , Cl^{-} , Na^{+} , SO_4^{2-}) are present in dissolved form which you have determined to be the true form
2. Stoichiometry is preserved: BaCl_2 was solid, and it yielded Ba^{2+} and 2Cl^{-} . The same for Na_2SO_4 : SO_4^{2-} and 2Na^{+}
3. Ba^{2+} and SO_4^{2-} are not shown on the product side as ions because they form a solid (precipitate) which is BaSO_4
4. Na^{+} and Cl^{-} do not participate in the reaction and in effect cancel each other on both sides of the chemical equation or reaction arrow: these are **spectator ions**
5. The reaction can instead be written as a **net ionic equation** as follows, removing the spectator ions:



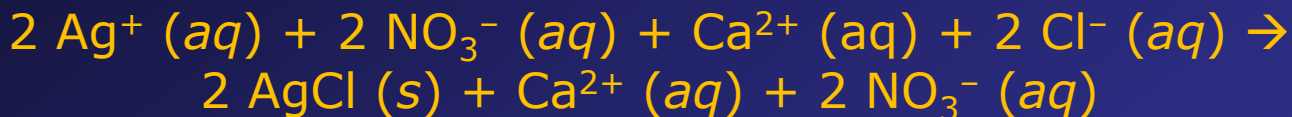
Practice Writing Equations

For the precipitation reaction with AgNO_3 and CaCl_2 , write the three equations: complete chemical equation, complete ionic equation, and net ionic equation

complete chemical equation



complete ionic equation



net ionic equation

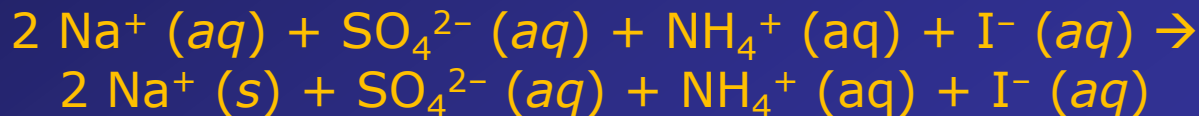


Write the three equations (if needed) for Na_2SO_4 and NH_4I

complete chemical equation



complete ionic equation



net ionic equation

none: everything soluble, all spectator ions

Writing Equations for Reactions

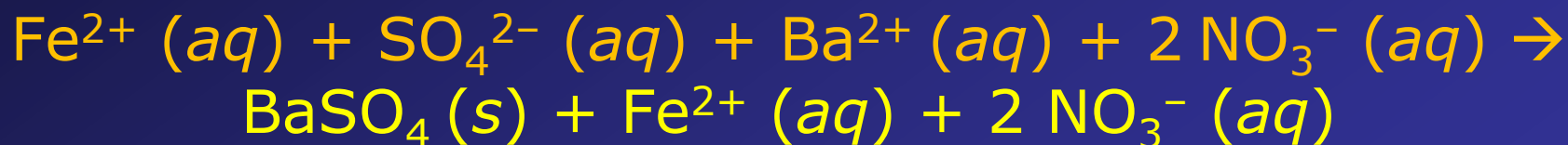
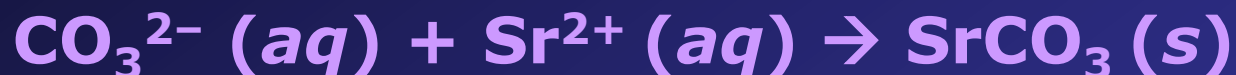
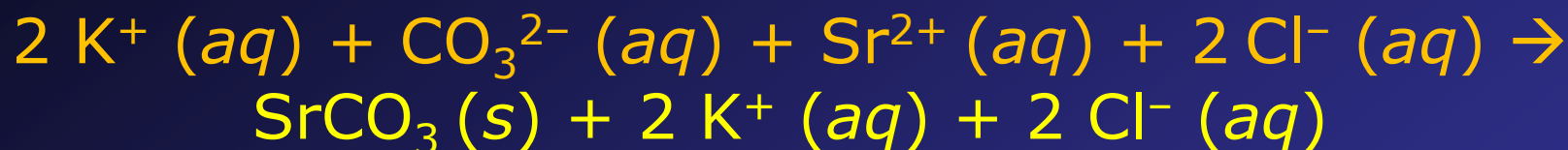
- Precipitation reactions are often used to test the presence of ions in solution
- Adding BaCl_2 to a solution and the formation of a precipitate could indicate sulfate (SO_4^{2-}) ion presence
- Since Ba^{2+} can precipitate with other counter anions, how do we know it is BaSO_4 ? It is when the unknown solution is first acidified: all precipitates of barium dissolves in dilute acid but not the sulfate
- Halides of silver can be distinguished by the color of their precipitates when AgNO_3 added to an acidified unknown halide (image right)



Figure 10.6.1: The three common silver halide precipitates: AgI , AgBr and AgCl (left to right). The silver halides precipitate out of solution, but often form suspensions before settling. (CC BY-SA 3.0; [Cychr](#)).

Practice: Net Ionic Equations

- Show the balanced net ionic equations



Oxidation-Reduction

- Oxidation is a process that is attributed to observations of corrosion (“rusting”) and combustion
- Reduction was a term applied to converting metal ores (salts of metals) to the pure metal, which involved a reduction in the mass of the ore
- A copper wire in a silver nitrate solution will take on fuzzy or furry appearance and the solution colored blue

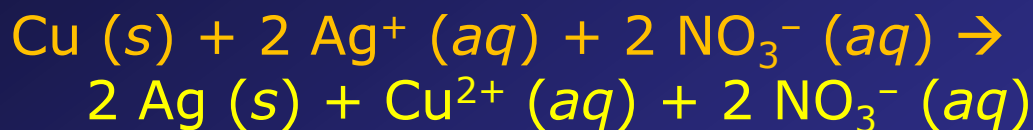


Figure 10.7.1: *Reaction of copper wire in a silver nitrate solution.*



LEO / GER

Need a way to remember that elements **losing electrons** is **oxidation** and elements (usually **OXYGEN**) **gaining the electrons** is **reduction**?

"LEO goes GER"

Loss of **E**lectrons is **O**xidation

Gain of **E**lectrons is **R**eduction

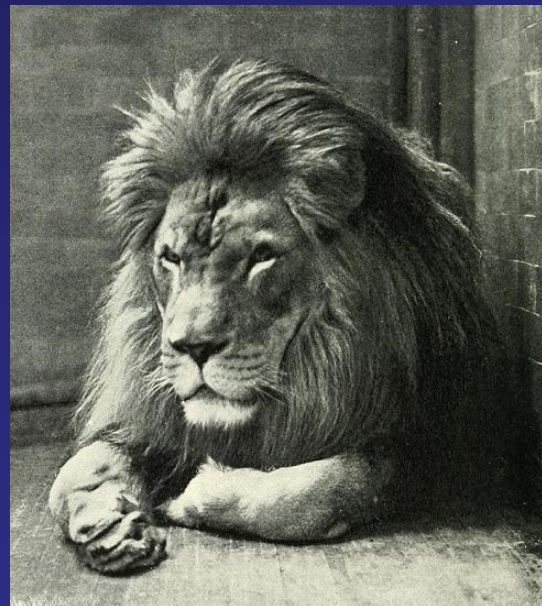
"OIL RIG"

Oxidation **I**s **L**oss, **R**eduction **I**s **G**ain



Zinc gets **oxidized** and iron(II) gets **reduced** in the reaction.

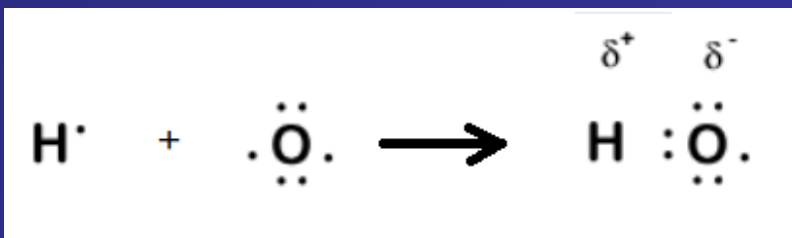
Zinc is a **reducing agent** and iron(II) is an **oxidizing agent**



Electronegativity & Oxidation

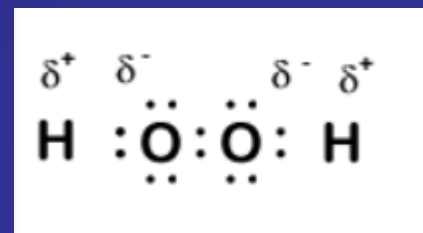
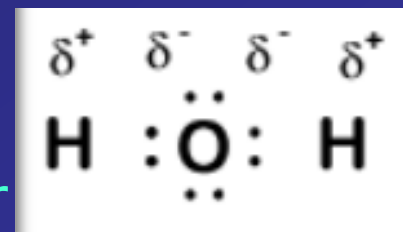
- **Electronegativity** is both a **qualitative** and **quantitative** indicator of how two elements with a covalent (shared electrons) bond will have one element pulling to itself more strongly those bonding electrons compared to the other element
- While fluorine (F) is the most electronegative of all elements, oxygen (O) is 2nd and its chemistry is vital for life
- Oxygen's ability to pull electrons to itself from other elements like hydrogen (H) gives it a special place in chemistry to refer to its properties as oxidation

Element	Electronegativity
Fluorine (F)	3.98
Oxygen (O)	3.44
Chlorine (Cl)	3.16
Nitrogen (N)	3.04
Bromine (Br)	2.96
Hydrogen (H)	2.20



Oxidation Number

- Ionic compounds are truly formed by ions in which one, typically metal element loses one or more electrons to become positively ionized (a cation) while another, typically nonmetal element gains one or more electrons to become negatively ionized (an anion)
- The transfer of electrons forms the ionic compounds which differs from two nonmetal elements that form covalent bonds that range from have no bond dipole (no polarity) to having a significant bond dipole (noticeable polarity)
- In water molecule, the hydrogen (H) atom "loses" its one electron and oxygen (O) atom "gains" that electron: H is oxidized to a **+1 oxidation number**. O has an oxidation number of **-2**: this is because it takes one electron each from the two H atoms it bonds to
- In hydrogen peroxide (H_2O_2 , $\text{H}-\text{O}-\text{O}-\text{H}$), both O atoms have oxidation number of **-1** because they can take an electron from one H atom each



Oxidation Number Rules

- There are a set of rules in determining oxidation numbers for elements in compounds

- The **oxidation number** of a **pure element**, whether monatomic, diatomic or polyatomic, is **0** (zero)
- Oxidation number of a monatomic ion is equal to the charge of the ion.
 Na^+ is **+1**, Cl^- is **-1**,
 Mg^{2+} is **+2**, O^{2-} is **-2**

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

Ionic Compound	Ions	Charge	Oxidation Number
NaCl	Na^+	+1	+1
	Cl^-	-1	-1
Mg_3N_2	Mg^{+2}	+2	+2
	N^{-3}	-3	-3

Oxidation Number Rules

3. The oxidation number of hydrogen (H) is almost always **+1** when it is a compound with a nonmetal element. It is **-1** when a compound of a metal cation as a metal hydride.
4. Oxidation number of oxygen (O) is usually **-2** with metals and most nonmetals. Exceptions are in peroxide ($-O-O-$) compounds: **-1**, and if bonded to fluorine in very highly reactive oxygen difluoride (OF_2): **+2**

Compound	Element	Oxidation Number
HCl	H	+1
	Cl	-1
H ₂ S	H	+1
	S	-2

Compound	Element	Oxidation Number
MgO magnesium oxide	Mg	+2
	O	-2
Na ₂ O sodium oxide	Na	+1
	O	-2
Na ₂ O ₂ sodium peroxide	Na	+1
	O	-1

Oxidation Number Rules

5. Sum of all oxidation numbers in any compounds is zero

This rule and prior rules allows determination of oxidation number of other elements

Mn_2O_7 is the example:

From the $\text{O} = -2$ rule, with 7 O atoms for -14 total electrons, and with

2 Mn atoms, the Mn oxidation number = $+14/2 = +7$

Compound	Element	Oxidation Number	Number of Atoms	Total
Mg_3N_2	Mg	+2	3	+6
	N	-3	2	-6
	SUM			0
Mn_2O_7	Mn	+7	2	+14
	O	-2	7	-14
	SUM			0
Cl_2O_3	Cl	+3	2	+6
	O	-2	3	-6
	SUM			0

Oxidation Number Rules

6. Sum of all oxidation numbers in a polyatomic ion is equal to charge of the ion

$$\sum \text{element oxidation number} \times \text{number of element atoms} = \text{charge on compound}$$

Cr₂O₇²⁻ is the example:

$$\begin{aligned} &\text{Cr ON} \times \text{Cr atoms} + \\ &\text{O ON} \times \text{O atoms} = \mathbf{-2} \end{aligned}$$

Apply the **O = -2** rule, and substitute the # of Cr and O atoms:

$$\text{Cr ON} \times 2 + -2 \times 7 = \mathbf{-2}$$

Now get the Cr ON with algebra:

$$\text{Cr ON} = \mathbf{+6} \text{ and O ON} = \mathbf{-2}$$

Compound	Element	Oxidation Number	Number of Atoms	Total
NO ₃ ⁻	N	+5	1	+5
	O	-2	3	-6
		SUM		-1
Cr ₂ O ₇ ²⁻	Cr	+6	2	+12
	O	-2	7	-14
		SUM		-2
SO ₄ ²⁻	S	+6	1	+6
	O	-2	4	-8
		SUM		-2

The Copper Wire Sulfur Powder Experiment

- Remember Lab Expt 4a “Law of Constant Composition”
- Copper wire reacting with sulfur was a redox reaction
- Copper atoms lose one electron each (oxidation)
- Sulfur atoms gain two electron each (reduction)

Half-reactions



Practice: Oxidation Numbers

Assign oxidation numbers (ON) to EACH ATOM according to rules

a. Cl_2

- i. Pure elements cannot take electrons from each other:



b. GeO_2

- i. When oxygen is a/the anion in the compound especially against a metal or metalloid, it is almost always **-2**



- ii. Now apply

$\sum \text{element oxidation number} \times \text{number of element atoms} = \text{charge on compound}$

$\text{Ge ON} \times \text{Ge atoms} + \text{O ON} \times \text{O atoms} = \text{charge}$

substitute:

$$\text{Ge ON} \times 1 + -2 \times 2 = 0$$



Practice: Oxidation Numbers

Assign oxidation numbers (ON) to EACH ATOM according to rules

a. $\text{Ca}(\text{NO}_3)_2$

- The ON of a metal ion particularly in Group 1 and 2 elements is the charge of its ion. $\text{Ca}^{2+} \rightarrow \text{Ca ON} = +2$
- NO_3 is a polyatomic ion with total -1 charge (thus NO_3^- is how it is represented), so the sum of the oxidation numbers on three O atoms and one N atom must be -1 .
- Oxygen has an $\text{ON} = -2$ according to rules, and there are three of them (O $\text{ON} = -2$). This totals a -6 charge.
- To determine the nitrogen ON, it must be part of the polyatomic ion NO_3^- , so $\text{N ON} + (-6) = -1$, or $\text{N ON} = +5$

Solving for **N ON** another way—the better way:

$$\text{Ca ON} \times \text{Ca atoms} + \text{N ON} \times \text{N atoms} + \text{O ON} \times \text{O atoms} = \text{compound charge}$$

$$1 \times (+2) + \text{N ON} \times 2 + (-2) \times 6 = 0$$

$$\text{N ON} = -[1 \times (+2) + (-2) \times 6] / 2 = -[2 + (-12)] / 2 = +5$$

More Practice: Oxidation Numbers

Assign oxidation numbers (ON) to EACH ATOM according to rules

d. H_3PO_4

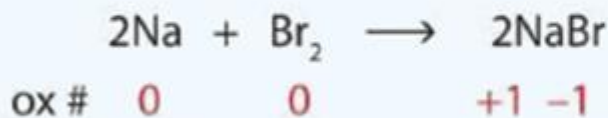
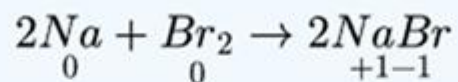
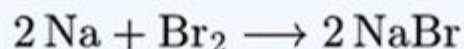
- i. ON of hydrogen in a compound with nonmetal monatomic or polyatomic group is +1 . $\text{H ON} = +1$
- ii. Oxygen has an $\text{ON} = -2$ according to rules: $\text{O ON} = -2$
- iii. Now solve for the P ON
$$\text{H ON} \times \text{H atoms} + \text{P ON} \times \text{P atoms} + \text{O ON} \times \text{O atoms} = \text{compound charge}$$
$$(+1) \times 3 + \text{P ON} \times 1 + (-2) \times 4 = 0$$
$$\text{P ON} = -[(+1) \times 3 + (-2) \times 4] = -[3 + -8] = +5$$

e. MgO

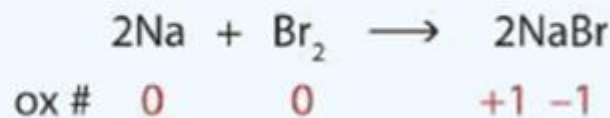
- i. One rule states that metal cations of Groups 1 and 2 have ON which is the charge of the ion. $\text{Mg}^{2+} \rightarrow \text{Mg ON} = +2$
- ii. Oxygen has an $\text{ON} = -2$ according to rules: $\text{O ON} = -2$

If There Is Oxidation, There is Reduction

- Just as there is conservation of mass/matter and of energy, there is a conservation of electric charge
- Electric charge and oxidation numbers/states must balance on both sides of the chemical reaction equation
- Where there is an oxidation, there is a reduction
- Where there is element/atom oxidized, another element/atom is reduced

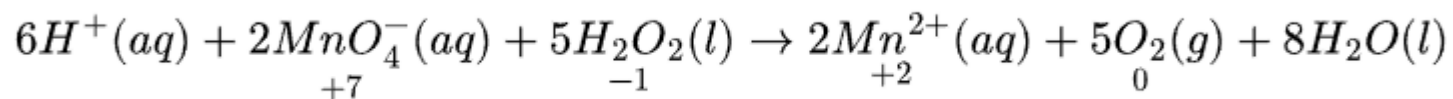
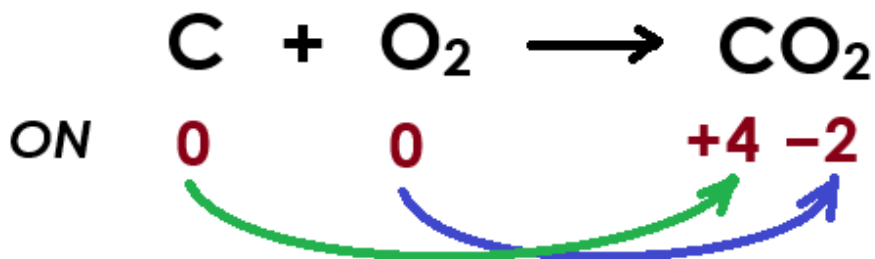


Oxidation



Reduction

What's Being Oxidized? What's Reduced?



Combustion Reactions

Make it balanced

Strategy

1. If combustion, then CO_2 (if carbon present) and H_2O are products!
2. Balance the oxidized main atom (C, H, etc) on products' side
3. Balance additional non-O atom (like H) on products' side
4. Count O atoms on products' side
 - a. If is an ODD number of O atoms, multiply everything by 2
 - b. If EVEN number (before or after doing [a]), put coefficient in front of O_2 on reactants



Redox Reactions as Two Half-Reactions

With **oxidation-reduction (redox) reactions**, they are special in the way that they are expressed as **two half-reactions**

- Because there is not only mass but charge (shown as “e⁻” or electrons), both mass (atom kind & number) and charge must balance (be conserved) on both sides of the arrow
- You normally write the oxidation (loss of electrons, the electron-producing) half-reaction first
- Follow with the reduction (gain of electrons, electron-consuming) half-reaction after
- $\text{Mg (s)} + \text{Cl}_2 \text{ (g)} \rightarrow \text{MgCl}_2 \text{ (s)}$
 - Write oxidation reaction: $\text{Mg} \rightarrow \text{Mg}^{2+}$
 - Balance it with charge (electrons): $\text{Mg} \rightarrow \text{Mg}^{2+} + 2 \text{ e}^-$
 - Write reduction reaction: $\text{Cl}_2 \rightarrow 2 \text{ Cl}^-$
 - Balance it with charge (electrons): $\text{Cl}_2 + 2 \text{ e}^- \rightarrow 2 \text{ Cl}^-$
 - Check if the electrons cancel in the half-reactions: yes
 - Write the full reaction: $\text{Mg} + \text{Cl}_2 \rightarrow \text{Mg}^{2+} + 2 \text{ Cl}^-$
 - Associate with original reaction: $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$

More Examples of Two Half-Reactions

- $\text{Cu (s)} + \text{AgNO}_3 \text{ (aq)} \rightarrow \text{Cu(NO}_3)_2 \text{ (aq)} + \text{Ag (s)}$
 - Write oxidation reaction: $\text{Cu} \rightarrow \text{Cu}^{2+}$
 - Balance it with charge (electrons): $\text{Cu} \rightarrow \text{Cu}^{2+} + 2 \text{ e}^-$
 - Write reduction reaction: $\text{Ag}^+ \rightarrow \text{Ag}$
 - Balance it with charge (electrons): $\text{Ag}^+ + 1 \text{ e}^- \rightarrow \text{Ag}$
 - Check if the electrons cancel in the half-reactions: no, need to multiply silver reduction by 2: $2 \text{ Ag}^+ + 2 \text{ e}^- \rightarrow 2 \text{ Ag}$
 - Write the full reaction: $\text{Cu} + 2 \text{ Ag}^+ \rightarrow \text{Cu}^{2+} + 2 \text{ Ag}$
 - Associate with original reaction: $\text{Cu} + 2 \text{ AgNO}_3 \rightarrow \text{Cu(NO}_3)_2 + 2 \text{ Ag}$

More Examples of Two Half-Reactions

- This redox is more complex, and it will explain why it requires an acid solution to make it happen
- $\text{MnO}_4^- (\text{aq}) + \text{Fe}^{2+} (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{Mn}^{2+} (\text{aq}) + \text{Fe}^{3+} (\text{aq}) + \text{H}_2\text{O} (\text{l})$
 - Write oxidation reaction: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$
 - Balance it with charge (electrons): $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 1 \text{e}^-$

Reduction is different: Mn ON goes from +7 to +2

- Write reduction reaction: $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$

Why don't we write it as $\text{Mn}^{7+} \rightarrow \text{Mn}^{2+}$?

- Balance ON with charge (electrons): $\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$

Have to write H^+ and H_2O in reaction. O atoms required because of MnO_4^-

- Check if the electrons cancel in the half-reactions: no, need to multiply Fe oxidation by 5: $5 \text{Fe}^{2+} \rightarrow 5 \text{Fe}^{3+} + 5 \text{e}^-$
- Write the full reaction: $5 \text{Fe}^{2+} + \text{MnO}_4^- + 8 \text{H}^+ \rightarrow 5 \text{Fe}^{3+} + \text{Mn}^{2+} + 4 \text{H}_2\text{O}$

More Examples of Two Half-Reactions

- This redox also happens in acid solution necessarily
- $\text{HNO}_3 (aq) + \text{Cu} (s) + \text{H}^+ (aq) \rightarrow \text{NO}_2 (g) + \text{Cu}^{2+} (aq) + \text{H}_2\text{O} (l)$
 - Write oxidation reaction: $\text{Cu} \rightarrow \text{Cu}^{2+}$
 - Balance it with charge (electrons): $\text{Cu} \rightarrow \text{Cu}^{2+} + 2 \text{e}^-$

Reduction is different: N ON goes from +5 to +4

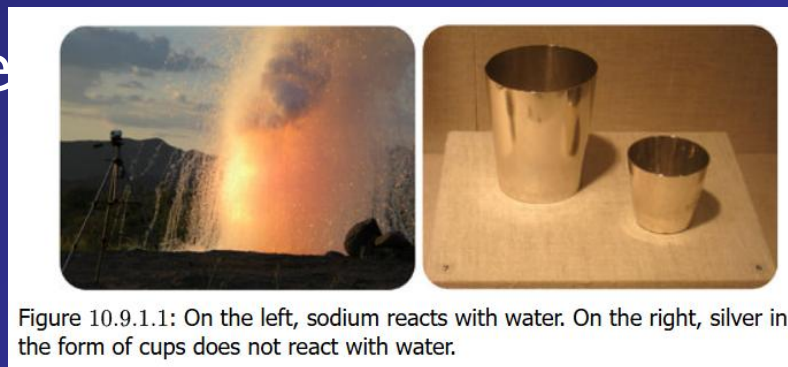
- Write reduction reaction: $\text{HNO}_3 \rightarrow \text{NO}_2$
- Balance ON with charge (electrons): $\text{HNO}_3 + \text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$

Have to write H^+ and H_2O in reaction. O atoms required because of HNO_3

- Check if the electrons cancel in the half-reactions: no, have to multiply the reduction half-reaction by two: $2 \text{HNO}_3 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{NO}_2 + 2 \text{H}_2\text{O}$
- Write the full reaction: $\text{Cu} (s) + 2 \text{HNO}_3 + 2 \text{H}^+ \rightarrow \text{Cu}^{2+} + 2 \text{NO}_2 + 2 \text{H}_2\text{O}$

Activity Series

- Both silver (Ag) and sodium (Na) can be oxidized ($\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$, $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$)
- But Na metal will react with cold water and Ag metal is completely unreactive
- The activity series for elements that show this redox reactivity has been drawn to the Periodic Table on the next slide.
- There are explanations/reasons for the patterns of the reactivity but they are beyond scope of this course



1

- Reacts with cold H_2O , replacing hydrogen
- Reacts with steam (not cold H_2O), replacing hydrogen
- Does not react with H_2O , but with acid (H^+)
- Unreactive with water or all but strongest acids (H^+)
- Reactive nonmetals: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Within colored blocks, numbers 1, 2, 3, ... indicate order of reactivity from most to least

within colored blocks, numbers 1, 2, 3, ... indicate order of reactivity from most to least

Cerium 58 Ce 140.12 1.1	Praseodymium 59 Pr 140.91 1.1	Neodymium 60 Nd 144.24 1.1	Promethium 61 Pm (145) 1.1	Samarium 62 Sm 150.36 1.2	Europium 63 Eu 151.97 1.1	Gadolinium 64 Gd 157.25 1.2	Terbium 65 Tb 158.93 1.1	Dysprosium 66 Dy 162.50 1.2	Holmium 67 Ho 164.93 1.2	Erbium 68 Er 167.26 1.2	Thulium 69 Tm 168.93 1.3	Ytterbium 70 Yb 173.04 1.1	Lutetium 71 Lu 174.97 1.1
Thorium 90 Th 232.04 1.3	Protactinium 91 Pa 231.04 1.5	Uranium 92 U 238.03 1.4	Neptunium 93 Np (237) 1.4	Plutonium 94 Pu (244) 1.3	Americium 95 Am (243) 1.3	Curium 96 Cm (247) 1.3	Berkelium 97 Bk (247) 1.3	Californium 98 Cf (251) 1.3	Einsteinium 99 Es (252) 1.3	Fermium 100 Fm (257) 1.3	Mendelevium 101 Md (259) 1.3	Nobelium 102 No (258) 1.3	Lawrencium 103 Lr (262)

***actinide

Practice: Activity Series

- Use the information from the Activity series shown in the drawn Periodic Table to make predictions about reaction



Yes: $2 \text{ Al (s)} + 3 \text{ Zn(NO}_3)_2 \text{ (aq)} \rightarrow 2 \text{ Al(NO}_3)_3 + 3 \text{ Zn (s)}$



No: Ag will not react with dilute acid



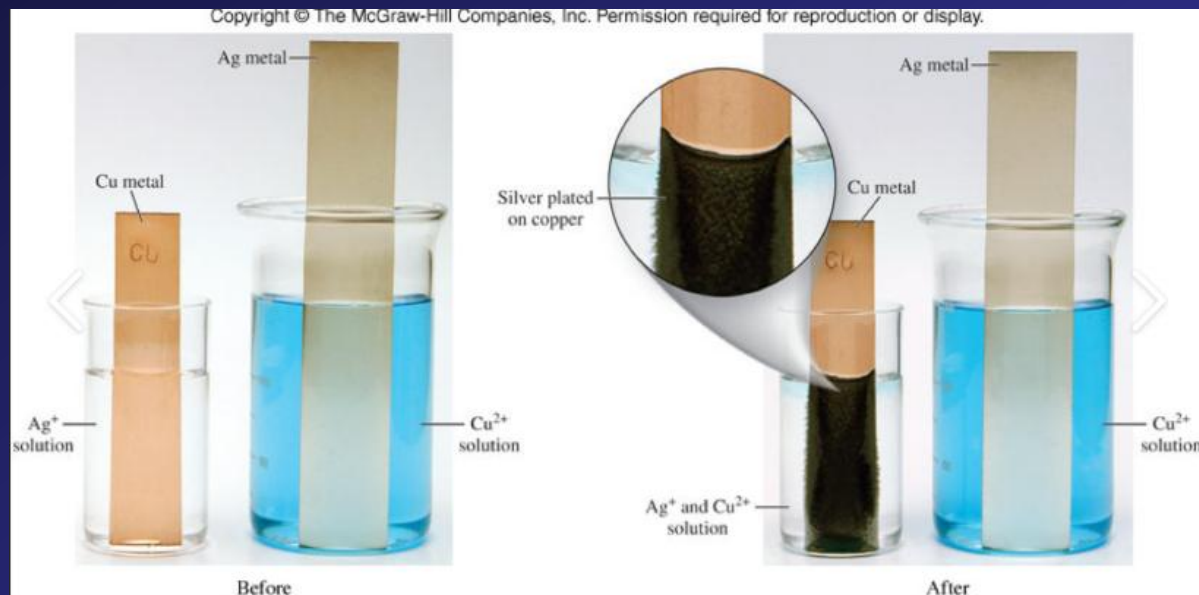
Yes: Zn is more reactive than Fe and can be oxidized



- No: gold unreactive with even acids of moderate strength

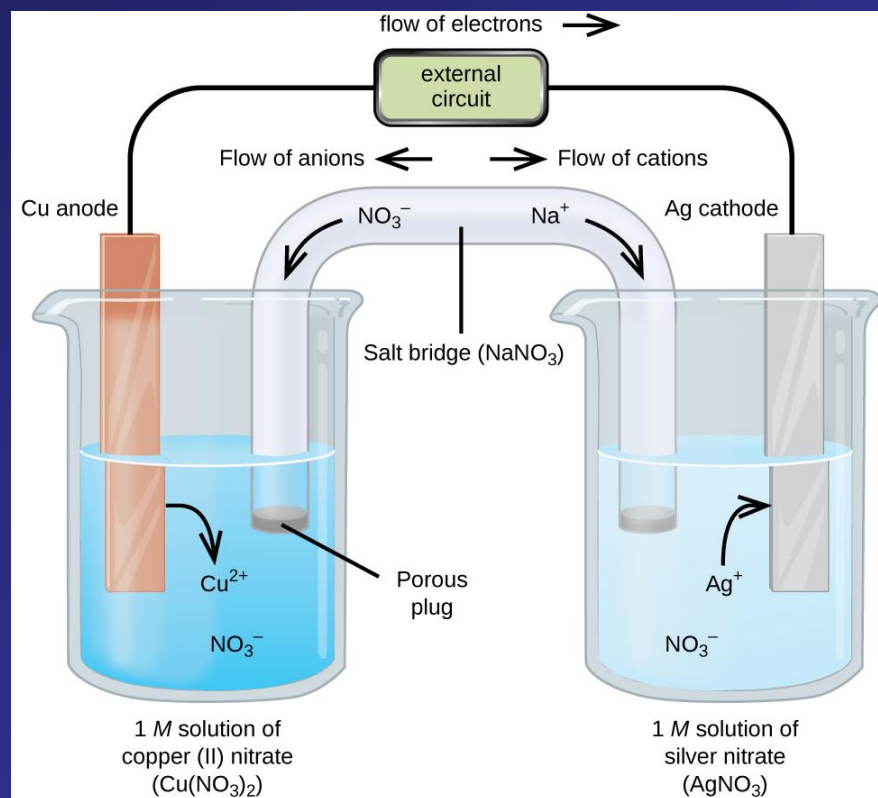
Chemistry Related to Batteries

- Batteries used in electronic devices are basically containers of chemicals that react to produce electrons that enable electric current. These reactions are redox reactions
- Reactions like the oxidation of copper in a silver solution are the basis for the chemistry:



Silver-Copper Galvanic Cell

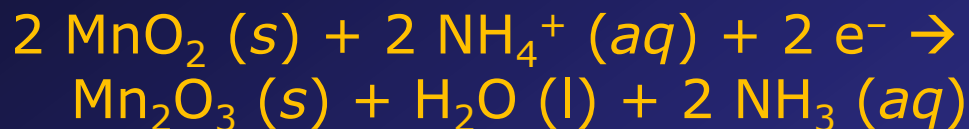
- Instead of wasting the electron flow from copper metal to silver solution, set up a compartmentalized solid copper/copper solution and solid silver/silver solution and connect these as a circuit with a wire to a device to be powered, and “salt bridge” of sodium nitrate
- The electrode where **reduction** occurs is the **cathode** (electrons gained)
- The electrode where **oxidation** occurs is the **anode** (electrons lost)



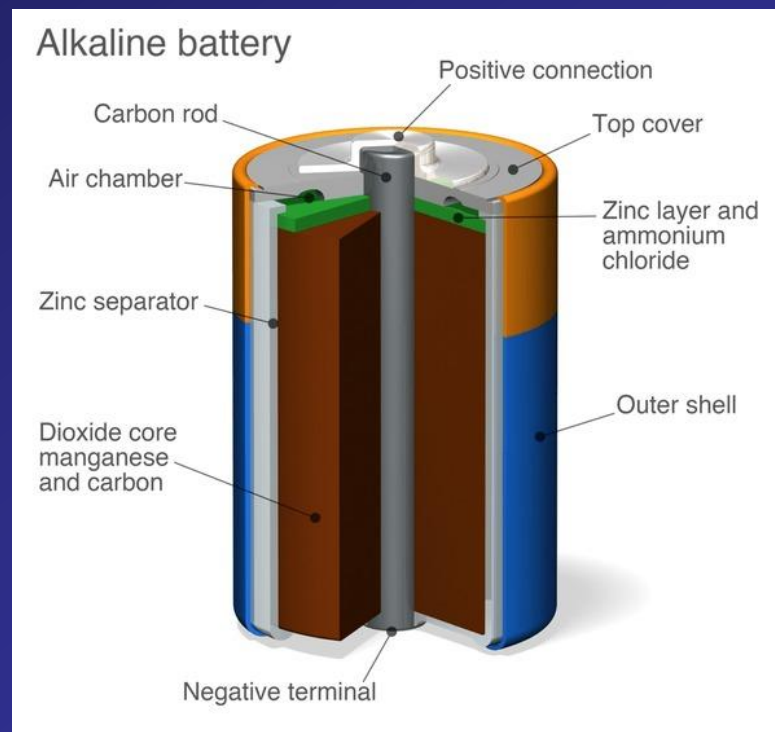
Dry Cell Battery

- Your nonrechargeable A, AA, AAA batteries are dry cell type
- Zn case is anode (neg pole), graphite rod is cathode (pos pole)
- A paste of either MnO_2 , NH_4Cl , ZnCl_2 or KOH electrolyte (alkaline type)

- Cathode:



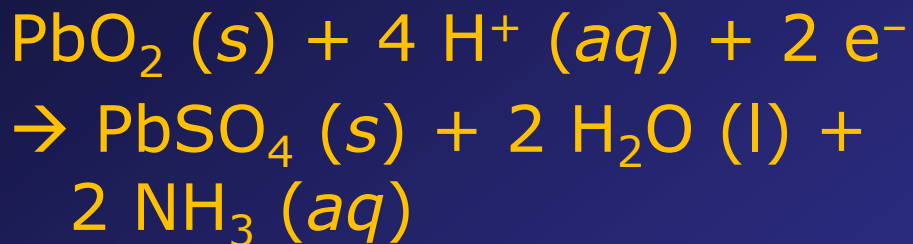
- Anode:



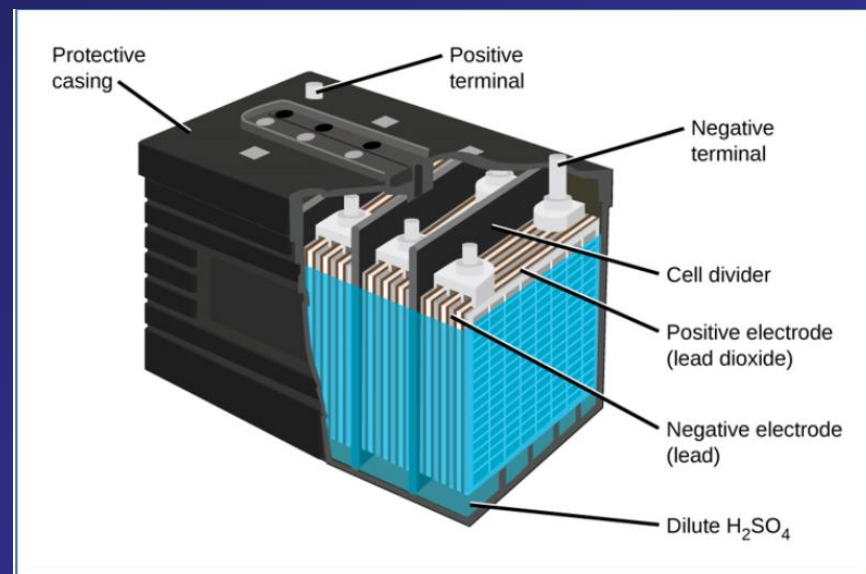
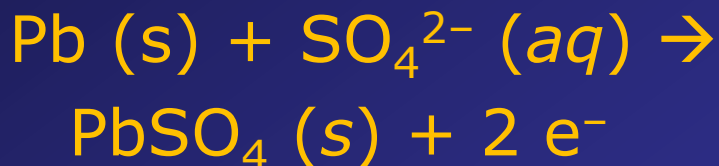
Storage Batteries

- The classic type is the rechargeable lead-acid automobile battery. Anode is grid of Pb-Sb or Pb-Ca alloy packed with spongy lead; cathode in lead(IV) oxide, in sulfuric acid electrolyte

- Cathode:



- Anode:



Fuel Cells

Works by continuously streaming H_2 and O_2 gas in the presence of a catalyst in a KOH electrolyte

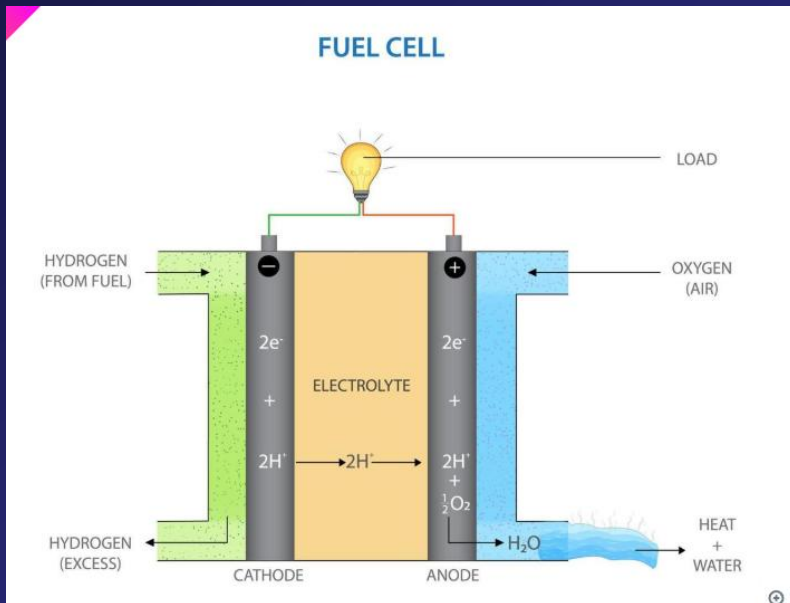
- Cathode:



- Anode:



- Net: $2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (l)$



Corrosion

- Falls in category of “undesirable” redox reactions
- The rusting of iron (Fe) is one such reaction



- Further oxidation to Fe^{3+} occurs, and this reacts with OH^{-} ions to form iron(III) oxide $[\text{Fe}_2\text{O}_3]$ and also iron(III) hydroxide $[\text{Fe}(\text{OH})_3]$

Prevention?

- Put paint, grease, plastic to cover the metal and prevent O_2 from getting access
- Put Zn or Mg on iron surface: they are more readily oxidized and Fe keeps its integrity.

Sacrificial anodes in water heaters work this way