Chapter 4: Aqueous Solutions (Chs 4 and 5 in Jespersen, Ch4 in Chang)

Solutions in which water is the dissolving medium are called aqueous solutions.

There are three major types of chemical processes occurring in aqueous solutions:

precipitation reactions (*insoluble* product)

acid-base reactions (transfer of H^+s)

redox reactions (transfer of *electrons*)

General Properties of Aqueous Solutions

solution – a *homogeneous* mixture of two or more substances.

solvent – usually the component that is present in greater quantity.

solute(s) – the other substance(s) in the solution (*ionic* or *molecular*); present in *smaller* quantities.

saturated solution – at a given temperature, the *solution* that results when the *maximum* amount of a substance has dissolved in a solvent.

Electrolytic Properties

electrolyte – a substance whose aqueous solutions contains ions and hence *conducts electricity*. E.g. NaCl.

nonelectrolyte – a substance that does **not** form ions when it dissolves in water, and so aqueous solutions of nonelectrolytes *do not conduct electricity*. E.g. Glucose, $C_6H_{12}O_6$.
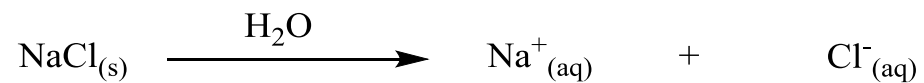

$CuSO_4$ and Water; Ions present;
electricity is conducted – bulb on.

Sugar and Water; No Ions present;
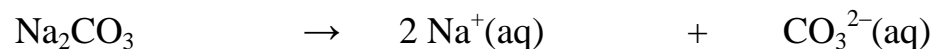electricity is **not** conducted – bulb off.

Ionic Compounds in Water

Ionic compounds *dissociate* into their component ions as they dissolve in water.

$$NaCl_{(s)} \xrightarrow{\quad H_2O \quad} Na^+_{(aq)} \quad + \quad Cl^-_{(aq)}$$

The ions become hydrated. Each ion is surrounded by water molecules, with the negative pole of the water oriented towards the cation and the positive pole oriented towards the anion.
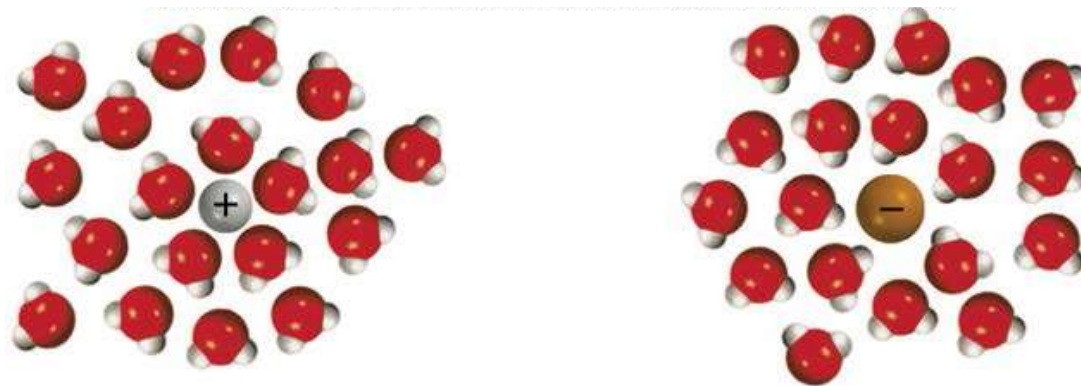
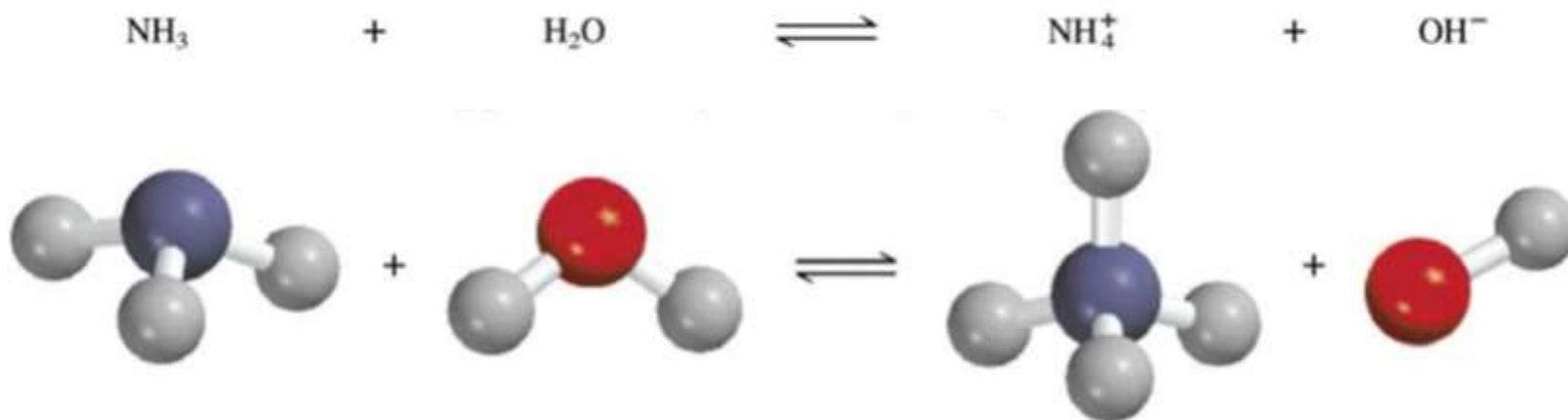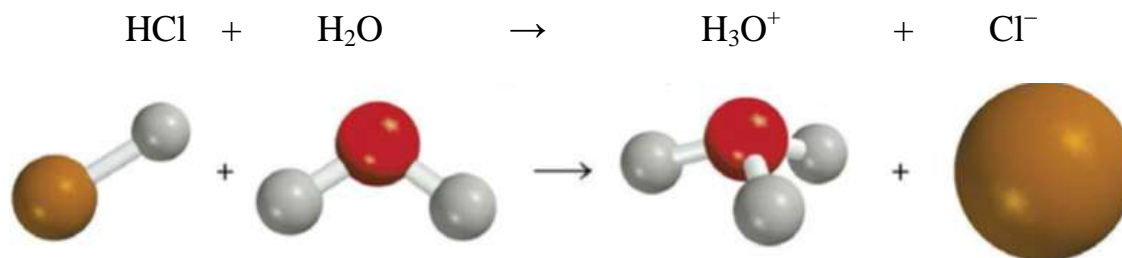Other examples of ionic compounds dissociating into their component ions:

$$Na_2CO_3 \quad \rightarrow \quad 2\ Na^+(aq) \quad + \quad CO_3^{2-}(aq)$$

$$(NH_4)_2SO_4 \quad \rightarrow \quad 2\ NH_4^+(aq) \quad + \quad SO_4^{2-}(aq)$$

Molecular Compounds in Water

Most molecular compounds do **not** form ions when they dissolve in water; they are nonelectrolytes.

Important <u>exceptions</u> are acids and compounds such as ammonia that *react* with water to form ions.

$$\text{HCl} \quad + \quad \text{H}_2\text{O} \quad \longrightarrow \quad \text{H}_3\text{O}^+ \quad + \quad \text{Cl}^-$$

$$\text{NH}_3 \quad + \quad \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{NH}_4^+ \quad + \quad \text{OH}^-$$

Strong and Weak Electrolytes

Strong electrolytes exist in solution *completely* (or nearly completely) as ions. E.g. KBr, HCl.

Weak electrolytes produce *small concentrations* of ions when they dissolve.

Do not confuse the *extent* to which an electrolyte dissolves with whether it is a strong or weak electrolyte.

(Weak electrolytes still fully dissolve).

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Chemical equilibrium - chemical equilibrium is the state in which both reactants and products are present in concentrations which have *no further tendency to change* with time.

Usually, this state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally **not** zero, but **equal**.

Thus, there are no *net* changes in the *concentrations* of the reactant(s) and product(s).

Reversible Reaction - is a reaction where the reactants form products, which also react together to give the reactants back.

$$aA \quad + \quad bB \quad \rightleftharpoons \quad cC \quad + \quad dD$$
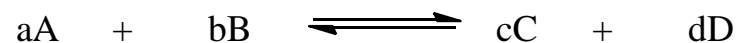
A and B can react to form C and D or/and, in the reverse reaction, C and D can react to form A and B.

Summary

- An aqueous strong electrolyte solution consists of ions that are free to move through the solvent.

- The solutes in nonelectrolyte solutions are present as molecules.

- Only a small fraction of molecules in weak electrolyte solutions are present as ions.
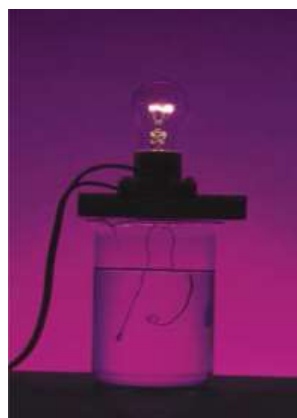
Classification of Solutes in **Aqueous** Solution

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH_3COOH	$(NH_2)_2CO$ (urea)
HNO_3	HF	CH_3OH (methanol)
$HClO_4$	HNO_2	C_2H_5OH (ethanol)
H_2SO_4*	NH_3	$C_6H_{12}O_6$ (glucose)
NaOH	$H_2O^\dagger$	$C_{12}H_{22}O_{11}$ (sucrose)
$Ba(OH)_2$		
Ionic compounds		

*H_2SO_4 has two ionizable H^+ ions, but only one is completely ionized.   †Pure water is a very weak electrolyte.

Strong electrolyte   Weak electrolyte   Nonelectrolyte
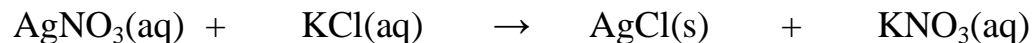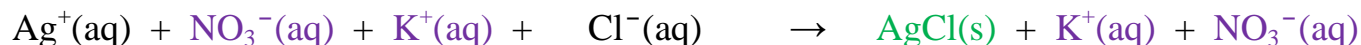
Ionic Equations

There are three types of equation that can be written for ionic reactions:

1) Molecular equation – shows complete chemical formulas of the reactants and products.

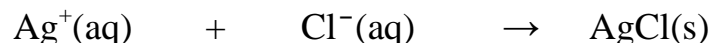$$AgNO_3(aq) \; + \qquad KCl(aq) \qquad \rightarrow \qquad AgCl(s) \qquad + \qquad KNO_3(aq)$$

2) (Complete) Ionic equation - shows *dissolved* species as free ions. (*Insoluble* solids are written together).

$$Ag^+(aq) \; + \; NO_3^-(aq) \; + \; K^+(aq) \; + \qquad Cl^-(aq) \qquad \rightarrow \qquad AgCl(s) \; + \; K^+(aq) \; + \; NO_3^-(aq)$$

This includes Spectator Ions – ions that are *present* but play *no role* in the reaction. (Here NO_3^- and K^+).

3) Net ionic equation - shows only the species that *actually take part* in the reaction.

$$Ag^+(aq) \qquad + \qquad Cl^-(aq) \qquad \rightarrow \qquad AgCl(s)$$

To arrive at the net ionic equation:

1. Write a **balanced** molecular equation for the reaction.

2. Rewrite the equation to show the ions that form in solution when each soluble strong electrolyte dissociates (*ionizes*) into its component ions. *Only dissolved strong electrolytes are written in ionic form.*
    so *NH₃(aq)* but *Na⁺(aq) + Cl⁻(aq)*

3. Identify and **cancel** the spectator ions that occur on both sides of the equation.

Precipitation Reactions

Reactions that result in the formation of an *insoluble* product are known as precipitation reactions.

A precipitate is an *insoluble solid* formed by a reaction in *solution*.

E.g. $Pb(NO_3)_2(aq)$ + $2\ KI(aq)$ $\rightarrow$ $PbI_2(s) \downarrow$ + $2\ KNO_3(aq)$

$$Pb(NO_3)_2(aq) \quad + \quad 2\ KI(aq) \quad \longrightarrow \quad PbI_2(s) \downarrow \quad + \quad 2\ KNO_3(aq)$$
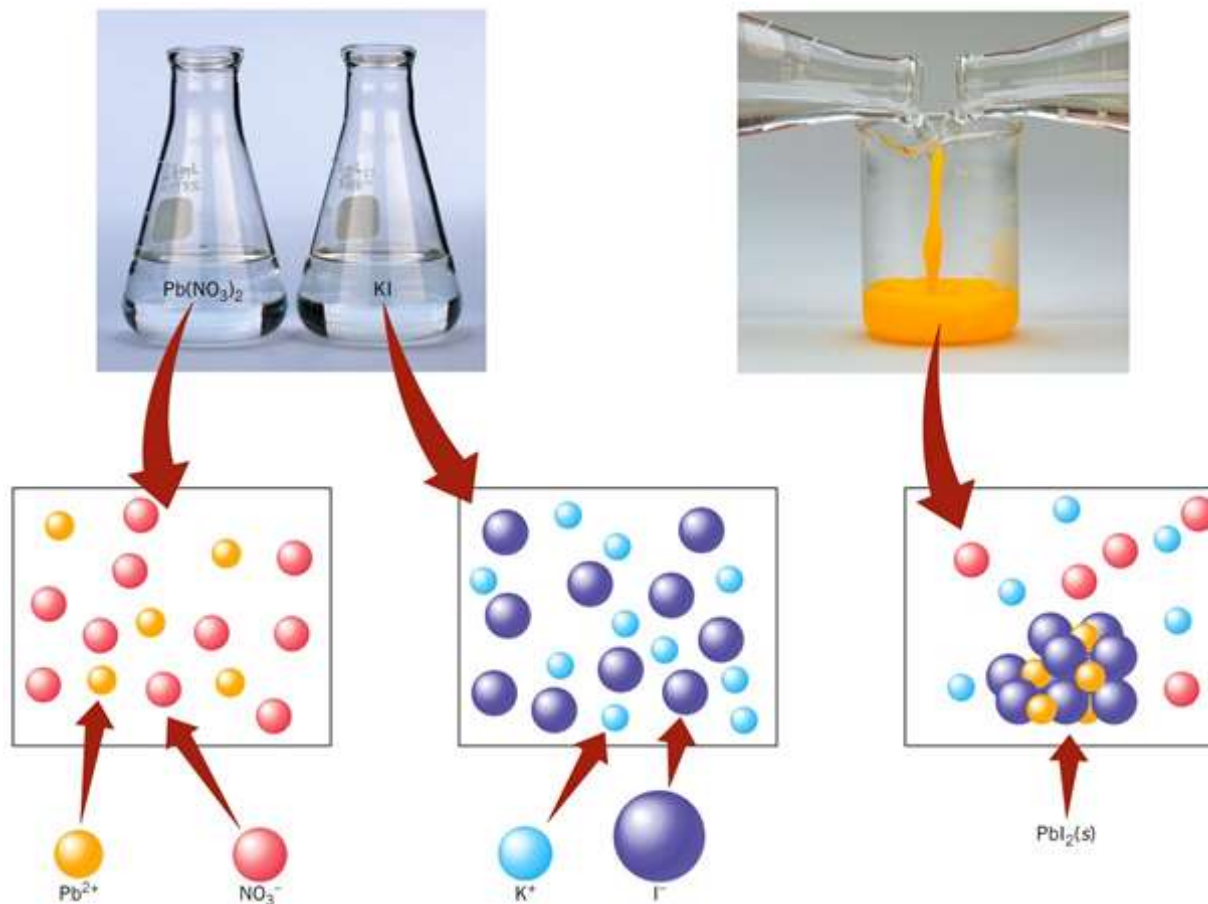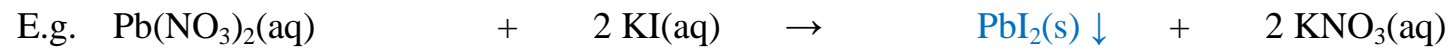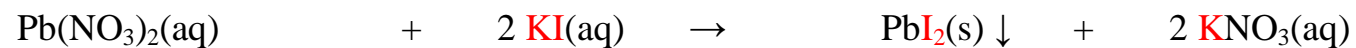
This is an example of a metathesis reaction (also called a double replacement), a reaction that involves the *exchange of parts* between the *two* compounds.

The cations have exchanged anions.

Solubility Guidelines for Ionic Compounds

The solubility of a substance is the *amount* of that *substance* that can be *dissolved* in a given quantity of *solvent*.

Any substance with a solubility of less than 0.001 mol/L will be referred to as insoluble (**in water**).

Solubility Guidelines

A compound is <u>probably</u> soluble (in water) if it contains one of the following cations:

- Group 1A cation: Li^+, Na^+, K^+, Rb^+, Cs^+

- Ammonium ion: NH_4^+

A compound is <u>probably</u> soluble if it contains one of the following anions:

- Nitrate (NO_3^-), perchlorate (ClO_4^-), chlorate (ClO_3^-), acetate ($CH_3CO_2^-$) anions.

- Halides: Cl^-, Br^-, I^- *Except Ag^+, Hg_2^{2+} and Pb^{2+} compounds*

- Sulfate (SO_4^{2}-)   *Except Ba^{2+}, Hg_2^{2+}, Ca^{2+}, Sr^{2+} and Pb^{2+} sulfates.*

A compound is <u>probably</u> insoluble in water if it contains one of the following anions:

- Carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), chromate (CrO_4^{2-}), sulfide (S^{2-})

   Except compounds containing alkali metal (Group 1A) ions, and the ammonium ion.

- Ionic metal hydroxides (OH^-) and ionic metal oxides (O^{2-})

   Except compounds containing alkali metal (Group 1A) ions and Ca^{2+}, Sr^{2+} and Ba^{2+} ions.

Solubility Rules (in table form) for Common Ionic Compounds (in Water at 25°C)

Soluble Compounds	Insoluble Exceptions
Compounds containing alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) and the ammonium ion (NH_4^+)	
Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-)	
Halides (Cl^-, Br^-, I^-)	Halides of Ag^+, Hg_2^{2+}, and Pb^{2+}
Sulfates (SO_4^{2-})	Sulfates of Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}

Insoluble Compounds	Soluble Exceptions
Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), sulfides (S^{2-})	Compounds containing alkali metal ions and the ammonium ion
Hydroxides (OH^-)	Compounds containing alkali metal ions and the Ba^{2+} ion

Acid-Base Reactions

One of the oldest chemical distinctions is the difference between *acids* and *bases*.

Acids

- Have a sour taste

- Cause litmus to change from blue to red

- React with certain metals to produce hydrogen gas

- React with carbonates and bicarbonates to produce carbon dioxide.

Bases

- Have a bitter taste

- Feel slippery. E.g. soap

- Cause litmus to change from red to blue

Acids

Acids are substances that are able to ionize in *aqueous* solutions to form a hydrogen ion (H^+) and thereby *increase the concentration of* $H^+(aq)$ *ions* (Arrhenius definition).

The Bronsted definition is that an acid is a proton donor.

(Note: proton = H^+ = Hydrogen ion = Hydrogen cation)

When an acid is in *aqueous* solution, the H^+ becomes the *hydronium ion* H_3O^+.

$$HCl(g) \quad + \quad H_2O(l) \quad \rightarrow \quad H_3O^+(aq) \quad + \quad Cl^-(aq).$$
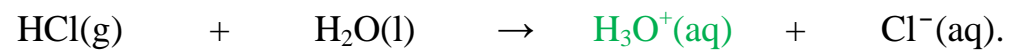
Protic acids are species that generate H^+ or H_3O^+ ions.

Different acids can generate *different* amounts of these species…

Monoprotic acid - each unit of acid yields one hydrogen ion.

$$HCl(aq) \quad\longrightarrow\quad H^+(aq) \quad+\quad Cl^-(aq)$$

Diprotic acid - each unit of acid gives up two H^+ ions, in two *separate* steps.

$$H_2SO_4(aq) \quad\longrightarrow\quad H^+(aq) \quad+\quad HSO_4^-(aq)$$

$$HSO_4^-(aq) \quad\longrightarrow\quad H^+(aq) \quad+\quad SO_4^{2-}(aq)$$
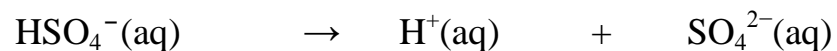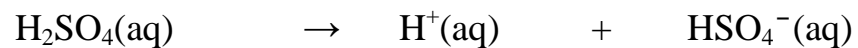
Triprotic acids - yield three H^+ ions.

$$H_3PO_4(aq) \quad\longrightarrow\quad H^+(aq\ ) \quad+\quad H_2PO_4^-(aq)$$

$$H_2PO_4^-(aq\ ) \quad\longrightarrow\quad H^+(aq) \quad+\quad HPO_4^{2-}(aq)$$

$$HPO_4^{2-}(aq) \quad\longrightarrow\quad H^+(aq) \quad+\quad PO_4^{3-}(aq)$$
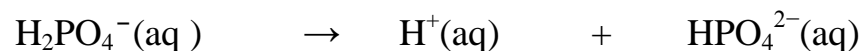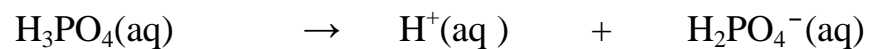
Bases increase the concentration of OH¯(aq) ions in water. (Arrhenius definition of a base)

Bases are substances that accept (*react with*) H$^+$ ions. (Bronsted definition)

$$NH_3(aq) \quad + \quad H_2O(l) \quad \rightarrow \quad NH_4^+(aq) \quad + \quad OH^-(aq)$$

$$H^+(aq) \quad + \quad OH^-(aq) \quad \rightarrow \quad H_2O(l)$$
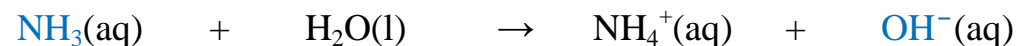
Strong and Weak Acids and Bases

Acids (and bases) that are **strong** electrolytes are called **strong** acids (and **strong** bases).

Those that are **weak** electrolytes are called **weak** acids and **weak** bases.

Weak acids are NOT *completely* deprotonated (ionized) in solution.

E.g. HF (hydrofluoric acid), HNO_2 (nitrous acid), H_3PO_4 (Phosphoric acid), CH_3COOH (enthanoic/acetic acid).

Common **strong** acids

Molecular Formula	Acid Name	Anion	Name of Anion
HCl	Hydrochloric acid	Cl^-	Chloride
HBr	Hydrobromic acid	Br^-	Bromide
HI	Hydroiodic acid	I^-	Iodide
HNO_3	Nitric acid	NO_3^-	Nitrate
$HClO_4$	Perchloric acid	ClO_4^-	Perchlorate
$HClO_3$	Chloric acid	ClO_3^-	Chlorate
H_2SO_4	Sulfuric acid	SO_4^{2-}	Sulfate

Notice the difference between *hydrochloric acid* and *chloric acid*.

Notice the difference between HCl(g) (hydrogen chloride) and HCl(aq) (hydrochloric acid).

Nonmetal Oxides are **acidic** since they react with water to produce acidic molecules (which act as acids).

E.g. SO_3(g)   + H_2O(l)   → H_2SO_4(aq)   sulfuric acid

N_2O_5(g)   + H_2O(l)   →   2 HNO_3(aq)   nitric acid

CO_2(g)   + H_2O(l)   → H_2CO_3(aq)   carbonic acid
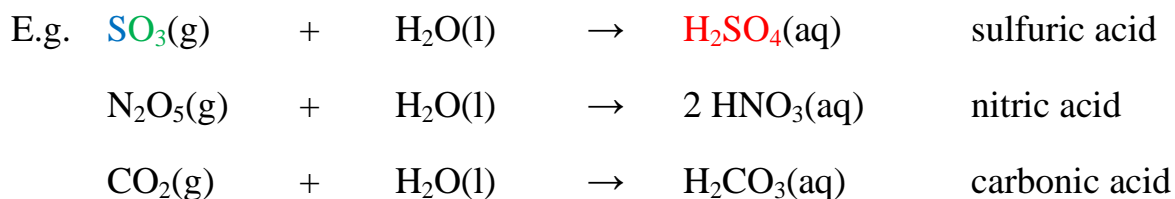
Bases

Strong bases: - all of the Group 1A hydroxides, (LiOH, NaOH, KOH, RbOH, CsOH).

- for Group 2A: only Ba(OH)$_2$ is soluble.

Be(OH)$_2$ and Mg(OH)$_2$ are *insoluble*

Ca(OH)$_2$ and Sr(OH)$_2$ are *slightly soluble*.

Weak bases: The most common weak base is Ammonia (NH$_3$).

Many other weak bases are *derivatives* of ammonia called amines. E.g. (CH$_3$)$_3$N, C$_5$H$_5$N, C$_6$H$_5$NH$_2$.

$$NH_3(aq) \quad + \quad H_2O(l) \quad \rightarrow \quad NH_4{}^+(aq) \quad + \quad OH^-(aq)$$
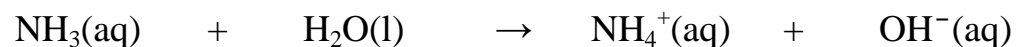
(*Soluble*) Metal Oxides are **basic**, since they produce metal hydroxides (which act as bases).

E.g.   CaO(s)   +   H$_2$O(l)   →   Ca(OH)$_2$(aq)
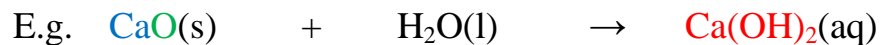
Neutralization Reactions and Salts

A neutralization reaction occurs when a solution of an acid and a base are mixed to produce a salt (*and water if the base is strong*).

Strong base and **strong acid**

$$HCl(aq) \quad + \quad NaOH(aq) \quad \rightarrow \quad H_2O(l) \quad + \quad NaCl(aq)$$

(acid)   (base)   (water)   (salt)

net ionic eqn: $\quad \mathbf{H^+(aq)} \quad + \quad \mathbf{OH^-(aq)} \quad \rightarrow \quad \mathbf{H_2O(l)}$
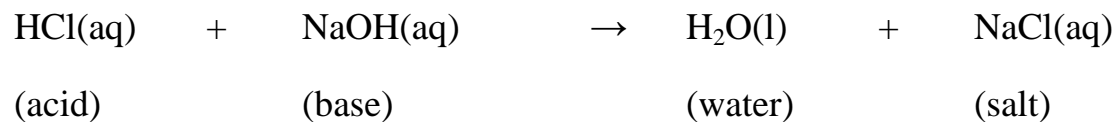
It is important to pay attention to stoichiometry (number of *acidic* or *basic* components per unit):

$$HCl(aq) \quad + \quad NaOH(aq) \quad \rightarrow \quad H_2O(l) \quad + \quad NaCl(aq)$$

$$\mathbf{2}\,HCl(aq) \quad + \quad Ba(OH)_2(aq) \quad \rightarrow \quad \mathbf{2}\,H_2O(l) \quad + \quad BaCl_2(aq)$$

$$H_2SO_4(aq) \quad + \quad \mathbf{2}\,NaOH(aq) \quad \rightarrow \quad \mathbf{2}\,H_2O(l) \quad + \quad Na_2SO_4(aq)$$
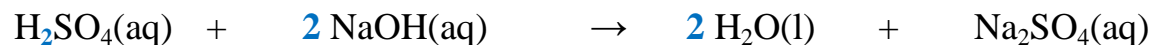
Weak acid and **strong base** (*weak* acids are **not** *completely* ionized in aqueous solution)

molec. eq   HCN(aq)   +   NaOH(aq) $\rightarrow$ $H_2O(l)$ +   NaCN(aq)

ionic eq   HCN(aq)   + $Na^+(aq)$ $+ OH^-(aq)$ $\rightarrow$ $H_2O(l)$ + $Na^+(aq)$ + $CN^-(aq)$

net ionic eq   **HCN(aq)   + $OH^-(aq)$ $\rightarrow$ $H_2O(l)$ + $CN^-(aq)$**
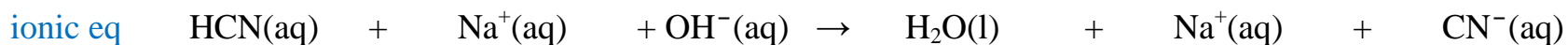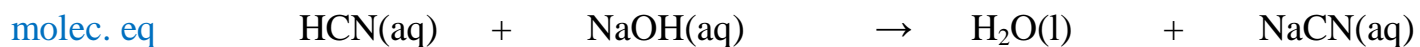
Strong acid and weak base

$HNO_3(aq)$ + $NH_3(aq)$ $\rightarrow$ $NH_4NO_3(aq)$
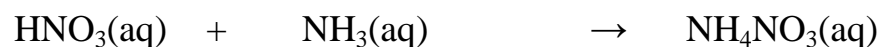
In aqueous solution, NH_3 reacts with water to produce NH_4^+ and OH^-, so really the above is:

$HNO_3(aq)$ + $NH_4^+(aq)$ + $OH^-(aq)$ $\rightarrow$ $H_2O(l)$ + $NH_4NO_3(aq)$
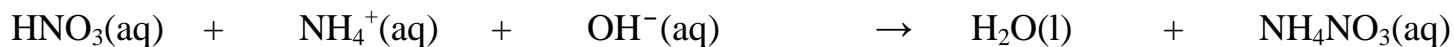
Acid-Base Reactions with Gas Formation

Some salts with *carbonate*, *bicarbonate*, *sulfite* or *sulfide* anions will react with acids to form gases.

Sulfides

$$2\ HCl(aq) \quad + \quad Na_2S(aq) \quad\quad \rightarrow \quad H_2S(g) \uparrow \quad + \quad 2\ NaCl(aq)$$

$$2\ H^+(aq) \quad + \quad S^{2-}(aq) \quad\quad \rightarrow \quad H_2S(g) \uparrow$$
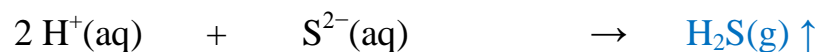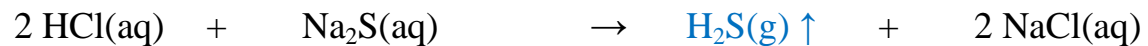
Carbonates and Bicarbonates

Na_2CO_3 – washing soda; $NaHCO_3$ – bicarbonate of soda or sodium bicarbonate

$$HCl(aq) \quad + \quad NaHCO_3(aq) \quad \rightarrow \quad H_2CO_3(aq) \quad + \quad NaCl(aq)$$

$$H_2CO_3(aq) \quad\quad \rightarrow \quad H_2O(l) \quad + \quad CO_2(g) \uparrow$$

Sulfites

$$2\ HCl(aq) \quad + \quad Na_2SO_3(aq) \quad \rightarrow \quad SO_2(g) \uparrow \quad + \quad 2\ NaCl(aq) \quad + \quad H_2O(l)$$
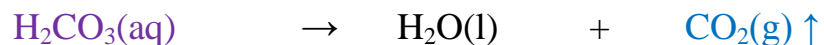
Oxidation–Reduction (REDOX) Reactions

Acid/Base reactions are characterized by proton transfer.

Redox reactions are characterized by electron transfer.

The *loss* of electrons by a substance is called oxidation.

The *gain* of electrons by a substance is reduction.

Oxidation of one substance is **always** accompanied by the reduction of another as electrons are transferred between them.

LEO-GER   **L**oss of **E**lectrons **O**xidation - **G**ain of **E**lectrons **R**eduction

OIL RIG   **O**xidation **I**s **L**oss of electrons; **R**eduction **I**s **G**ain of electrons

Substances that are *oxidized* are called reducing agents.

Substances that are *reduced* are called oxidizing agents.

Oxidation Numbers

To keep track of the electrons in redox reactions, we assign oxidation numbers (or *oxidation states*):

The oxidation number of an atom in a substance is the actual charge of the atom **if** it were a monatomic ion.

*(The oxidation number of an atom is the charge that the atom would have **if** the compound was composed of ions).*

8 Rules for *Assigning* Oxidation Numbers (In this **hierarchy** *upper* rules supersede *lower* rules).

    1) Oxidation numbers must *add up* to the *charge* on the molecule/formula unit/ion.

    2) All the atoms of the free element have oxidation states of zero.

    3) Metals in groups **1A** have oxidation states of **+1**, **2A** are **+2**, and **Al** is **+3**.

    4) In compounds, **H** has oxidation state of **+1**, **F** has **–1**.

    5) Oxygen has **–2** oxidation number.

    6) Group **7A** elements have **–1** oxidation numbers.

    7) Group **6A** elements have **–2** oxidation numbers.

    8) Group **5A** elements have **–3** oxidation numbers.

E.g. NO_3^- Oxidation number of **N** is **+5**   since $-1 = X + 3(-2)$, so $X = $ **+5**.

       NH_3 Oxidation number of **N** is **–3**   since $0 = X + 3(+1)$, so $X = -3$.

       $Cr_2O_7^{2-}$ Oxidation number of **Cr** is **+6**   since $-2 = 2X + 7(-2)$, so $2X = +12$, so $X = +6$.
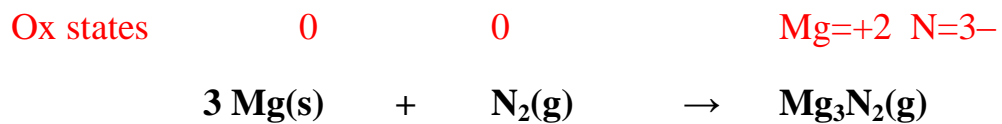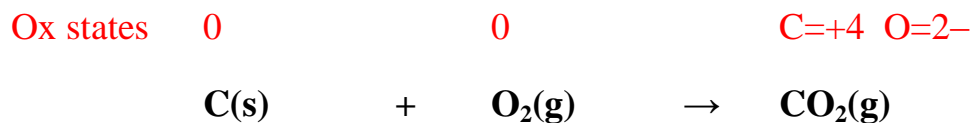
For Redox reactions:

- Oxidation states become *changed*.

- Oxidation *and* reduction always occur simultaneously.

- **Total** number of electrons *lost* by one substance equals **total** number of electrons *gained* by second substance.

- For a redox reaction to occur, something must *accept* electrons that are *lost* by the other substance.

Types of Redox Reactions

There are five common types of redox reaction (*combination, decomposition, combustion, disproportionation* and *displacement*.

1) Combination reactions (a reaction in which *two reactants combine to form one product*).

Ox states   0   0   C=+4 O=2–

               C(s)   **+**   **O_2(g)**   **→**   **CO_2(g)**

Ox states   0   0   Mg=+2 N=3–

            3 Mg(s)   **+**   **N_2(g)**   **→**   **Mg_3N_2(g)**

2) Decomposition reactions (a reaction in which a *single compound breaks down into two or more elements or new compounds*).

Ox states   Cl=+5 O=2–   Cl=1–   O = 0 K^+=+1

                     2 $KClO_3$(s)   **→**   **2 KCl(s)**   **+**   **3 O_2(g)**
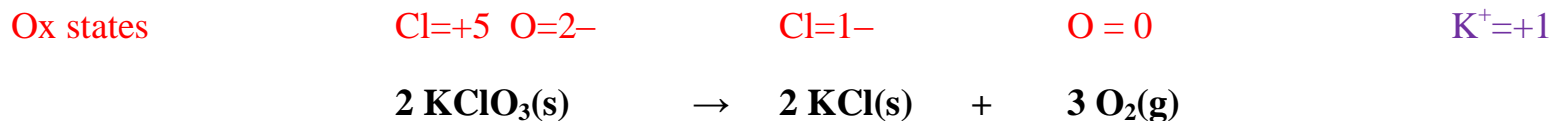
3) Combustion reactions are where a substance reacts with *oxygen*, usually with the *release of heat and light* to produce a *flame*.

E.g. Burning of propane for heating and cooking:

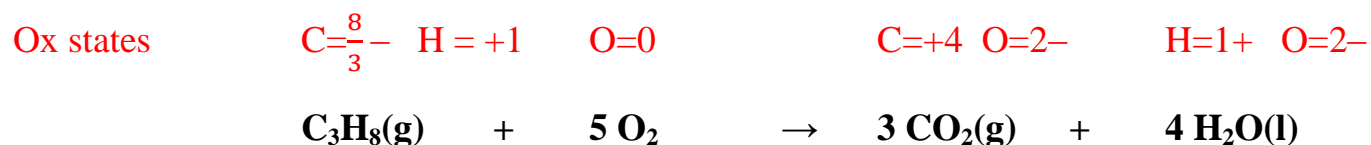Ox states $C=\frac{8}{3}-$ $H=+1$ $O=0$ $C=+4$ $O=2-$ $H=1+$ $O=2-$

        $C_3H_8(g)$ + $5\,O_2$ → $3\,CO_2(g)$ + $4\,H_2O(l)$

(C 8– ⇒ 12+, loss of 20e⁻ ; O 0 ⇒ 12– and 8– which = 20–, gain of 20e⁻)

4) Disproportionation reactions (a reaction where one substance is *oxidized* **and** *reduced* in the *same* reaction).

            Cl_2 + H_2O →   HCl   +   HOCl

Ox.Nu. Cl   0   →   –1   +1

            $Hg_2S(s)$ →   Hg(l)   +   HgS(s)

Ox.Nu. Hg   +1   →   0   +2
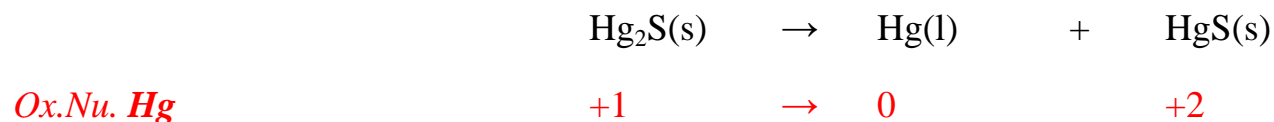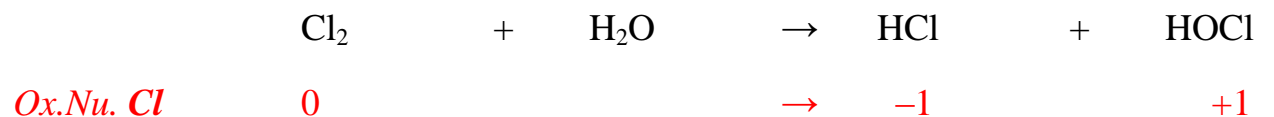
5) Displacement reactions (a reaction where an *ion* in solution is *displaced* (or replaced) through *oxidation* of an *element*).

Common types are metal, hydrogen and halogen *displacements*.

5a) Metal displacement - *Oxidation* of metals (metal → metal *cation*) by acids and salts:

$$M \quad + \quad BX \quad \rightarrow \quad MX \quad + \quad B$$

$$Zn(s) \quad + \quad 2\ HBr(aq) \quad \rightarrow \quad ZnBr_2(aq) \quad + \quad H_2(g)$$

$$Mn(s) \quad + \quad Pb(NO_3)_2(aq) \quad \rightarrow \quad Mn(NO_3)_2(aq) \quad + \quad Pb(s)$$
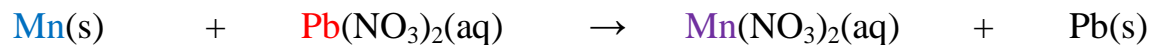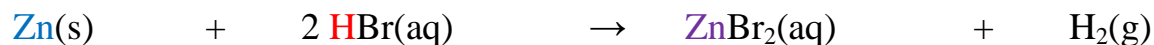
Remember that whenever one substance is *oxidized*, some other substance must be *reduced*.

Above, Zn is *oxidized* (oxidation number $0 \rightarrow +2$); H is *reduced* ($+1 \rightarrow 0$).

Mn is *oxidized* (oxidation number $0 \rightarrow +2$); Pb is *reduced* ($+2 \rightarrow 0$).

How do I know "what can oxidize what" ?

There is the activity series…

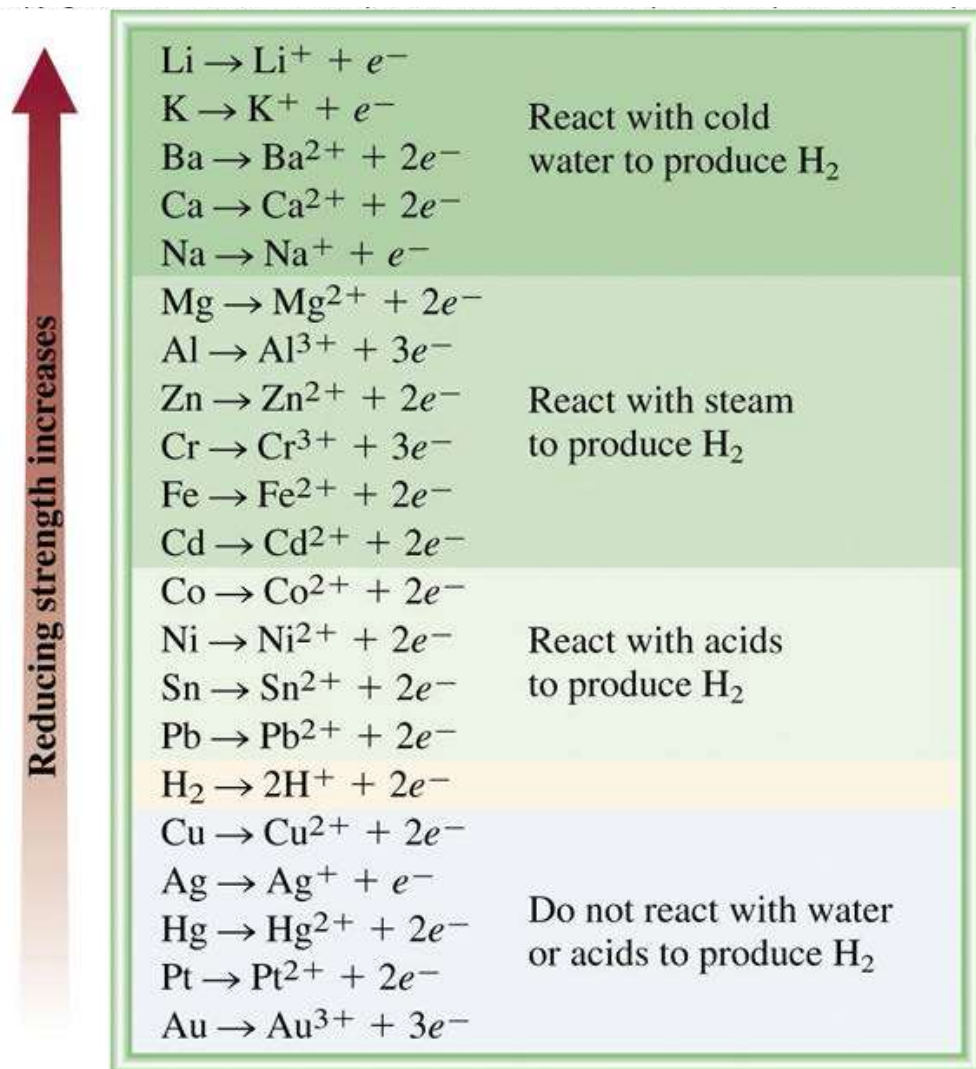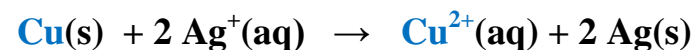**The Activity Series (The *electrochemical* series)**

Any metal on the list can be oxidized by the ions of elements *below* it.

Reducing strength increases ↑		
$Li \rightarrow Li^+ + e^-$		
$K \rightarrow K^+ + e^-$	React with cold	
$Ba \rightarrow Ba^{2+} + 2e^-$	water to produce H_2	
$Ca \rightarrow Ca^{2+} + 2e^-$		
$Na \rightarrow Na^+ + e^-$		
$Mg \rightarrow Mg^{2+} + 2e^-$		
$Al \rightarrow Al^{3+} + 3e^-$		
$Zn \rightarrow Zn^{2+} + 2e^-$	React with steam	
$Cr \rightarrow Cr^{3+} + 3e^-$	to produce H_2	
$Fe \rightarrow Fe^{2+} + 2e^-$		
$Cd \rightarrow Cd^{2+} + 2e^-$		
$Co \rightarrow Co^{2+} + 2e^-$		
$Ni \rightarrow Ni^{2+} + 2e^-$	React with acids	
$Sn \rightarrow Sn^{2+} + 2e^-$	to produce H_2	
$Pb \rightarrow Pb^{2+} + 2e^-$		
$H_2 \rightarrow 2H^+ + 2e^-$		
$Cu \rightarrow Cu^{2+} + 2e^-$		
$Ag \rightarrow Ag^+ + e^-$		
$Hg \rightarrow Hg^{2+} + 2e^-$	Do not react with water	
$Pt \rightarrow Pt^{2+} + 2e^-$	or acids to produce H_2	
$Au \rightarrow Au^{3+} + 3e^-$		

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

(Cu is *higher* on activity series than Ag).

But

$$Cu(s) + Zn^{2+}(aq) \rightarrow \text{No Reaction}$$

(Zn is higher on activity series than Cu).

From these reactions the following activity series can be constructed: Zn > Cu > Ag

Notice the *element* that ends up as the cation is the one *higher* up in the activity series.

$$2 \ Na(s) \quad + \quad Sn^{2+}(aq) \qquad \rightarrow \qquad 2 \ Na^{+}(aq) \quad + \quad Sn(s)$$

5b) Hydrogen Displacement

• *Alkali metals* and some *alkaline earth metals* (Ca, Sr, and Ba) react with *water* to produce **hydrogen gas**.

Ox states   Na=0   H=+1   Na=+1   H=0

$$2 \ Na(s) \quad + \quad 2 \ H_2O(l) \quad \rightarrow \quad 2 \ NaOH(aq) \quad + \quad \textbf{H}_2\textbf{(g)}$$
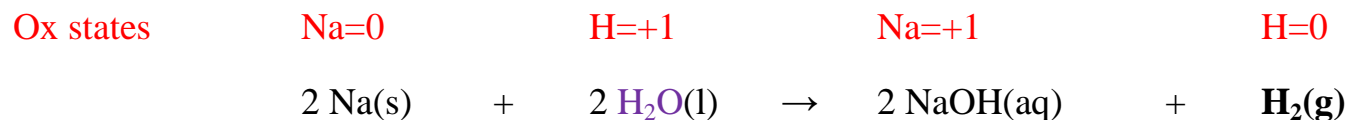
• Some metals that *don't* react with *water* (e.g. Fe, Zn, Mg) will react with *acids* to produce **hydrogen gas**.

Ox states   Zn=0   H=+1   Zn=+2   H=0

$$Zn(s) \quad + \quad 2 \ HCl(aq) \quad \rightarrow \quad ZnCl_2(aq) \quad + \quad \textbf{H}_2\textbf{(g)}$$
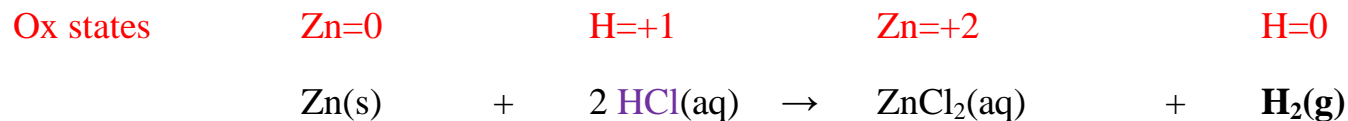
5c) Halogen Displacement – Uses another activity series:

Oxidizing strengths: $F_2 > Cl_2 > Br_2 > I_2$

(Chlorine can oxidize Bromide to Bromine).

Ox states	Cl=0		Br=1−		Cl=1−		Br=0
	$Cl_2(g)$	+	$2 \, KBr(aq)$	$\rightarrow$	$2 \, KCl(aq)$	+	$Br_2(l)$

But $Cl_2(g)$ + $2 \, KF(aq)$ $\rightarrow$ no reaction
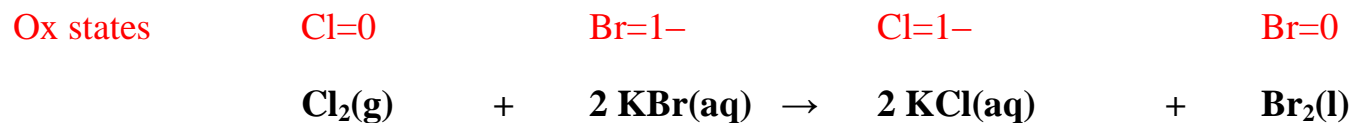
Concentrations of Reactants in Solution

Molarity is the most common way of describing "*concentrations*".

The concentration of a solution is defined as the *amount of solute* present in a *given amount of solvent* (or solution).

$$\textbf{Molarity} \quad = \quad \frac{\textbf{moles of solute}}{\textbf{volume of solution in L}}$$

Molarity (M), also known as *molar concentration* is the *number of moles of solute per liter of solution*, with units therefore of moles per liter.

$\Rightarrow$ 2.0 M means two molar, which means two moles per liter.

Expressing the Concentration of an electrolyte

The concentration of an electrolyte in solution can be specified either in terms of the *compound used* to make the solution or in terms of the *ions* that the solution contains.

E.g. $1.0 \text{ M } Na_2SO_4$ or $2.0 \text{ M } Na^+$ or $1.0 \text{ M } SO_4^{2-}$

Often *square brackets* are used to indicate *concentration* in *moles per liter*.

So for above, $[Na_2SO_4] = 1.0 \text{ M}$

In practice, solutions of defined concentration are prepared using standard volumetric flasks.
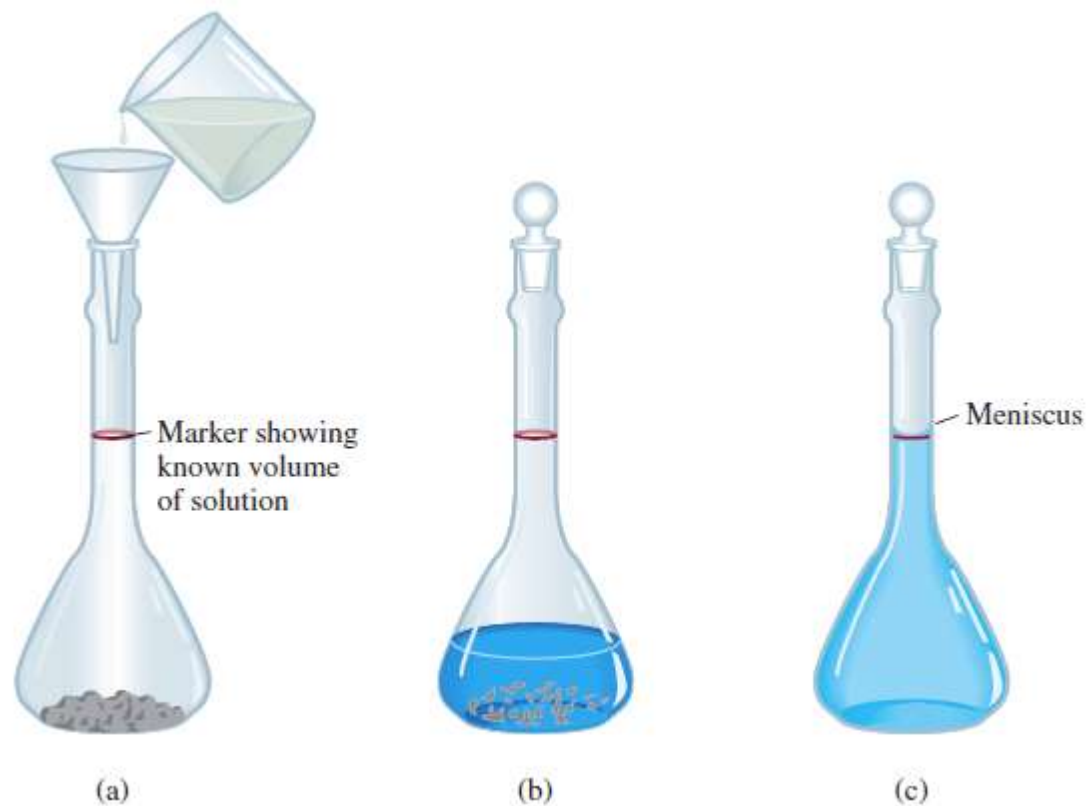
Typically you will:

(a) add your known amount of solute to the flask;

(b) add water slowly, with swirling to encourage dissolving;

(c) once all the solid is completely dissolved, then add sufficient water to fill up to the mark.

Interconverting Molarity, Moles, and Volume

Molarity provides the conversion factor between number of moles, and volume (in **L**).
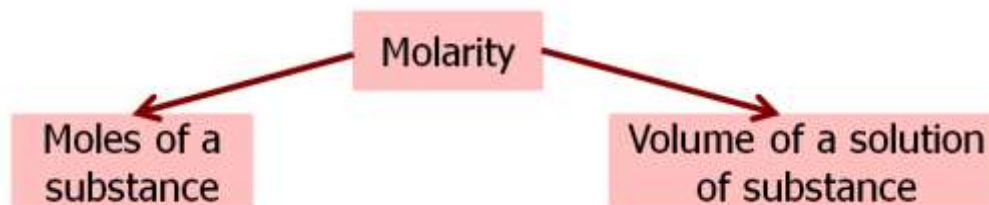
Using dimensional analysis:

$$\textbf{moles} = \textbf{liters} \times \textbf{molarity} \qquad \text{and} \qquad moles = liters \times \frac{moles}{liter}$$

Problem: How many moles of solute are present in a 35.00 mL of 1.200 M HNO_3 solution?

$$35.00 \text{ mL} \quad \times \quad \frac{1 \text{ L}}{1000 \text{ mL}} \quad \times \quad \frac{1.200 \text{ mol } HNO_3}{L} \qquad = 4.200 \times 10^{-2} \text{ mol}$$

Convert to L

$$= 0.04200 \text{ mol } HNO_3$$

Diluting Concentrated Solutions

Solutions of *lower concentration* can be obtained by adding water to *more concentrated* solutions, a process called dilution.

The number of moles of solute *does not change*, they just become contained in a *larger* volume of solvent.

Moles of solute **before** dilution =   moles of solute **after** dilution.

Moles   =   molarity × volume

$$M_i \times V_i = M_f \times V_f \qquad\qquad V_i = \frac{M_f \times V_f}{M_i}$$

Where i = initial, and f = final

Problem: A bottle of 12.0 M hydrochloric acid has only 35.7 mL left in it. What will the new HCl concentration be if the solution is diluted to 250.0 mL?

$$M_f = \frac{M_i \times V_i}{V_f} = \frac{(12.0 \text{ M HCl}) (35.7 \text{ mL})}{250.0 \text{ mL}} = 1.71 \text{ M HCl}$$

Problem: What is the volume of solution that would result by diluting 70.00 mL of 0.0913 M NaOH to a concentration of 0.0150 M?

$$V_f = \frac{M_i \times V_i}{M_f} = \frac{(0.0913 \text{ M NaOH}) (70.00 \text{ mL})}{0.0150 \text{ M}} = 426. \text{ mL}$$

Now that we are expert in moles, concentration and volumes, we can apply these quantitative aspects to something that is **useful**.

The following are two techniques (*gravimetric analysis* and *titrations*) that provide for Quantitative Analysis, which is the *determination* of the *amount* (or concentration) of a particular substance in a sample.

Gravimetric Analysis - an analytical technique based on the *measurement* of *mass*.

Typically an ion is deliberately caused to precipitate, and then that precipitate is filtered and weighed.
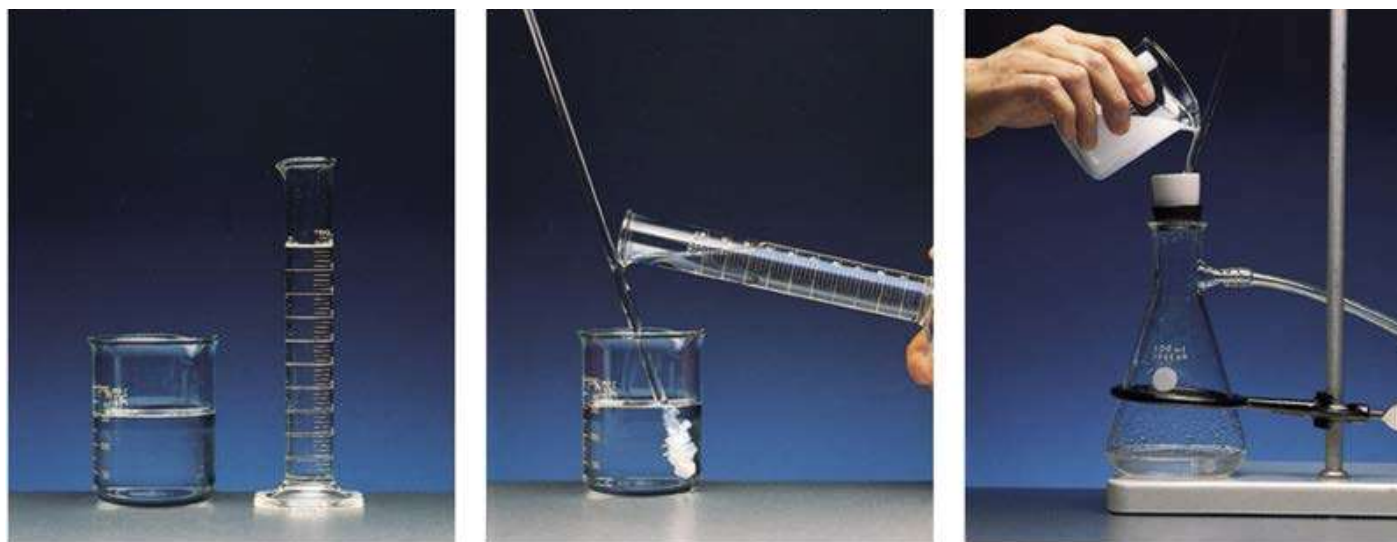
Knowing the mass and formula of the precipitate allows us to determine how many moles of the precipitate there is, which in turn allows us to determine the number of moles of the relevant cation (or anion) that we caused to precipitate.

Problem: Calculate the concentration of an aqueous KCl solution if 25.00 mL of the solution gives 0.430 g of AgCl when treated with excess $AgNO_3$.

The balanced equation is:

$$KCl(aq) \quad + \quad AgNO_3(aq) \quad \rightarrow \quad AgCl(s) \downarrow \quad + \quad KNO_3(aq)$$

Moles of KCl

$$0.430 \text{ g AgCl} \quad x \quad \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \quad x \quad \frac{1 \text{ mol KCl}}{1 \text{ mol AgCl}} \quad = \quad 3.00 \text{ x } 10^{-3} \text{ mol KCl}$$

Moles of AgCl

Molar mass of AgCl = 107.87 + 35.45
= 143.32 g/mol

$$\text{Molarity} \quad = \quad \frac{\text{moles}}{\text{volume}} \quad = \quad \frac{3.00 \text{ x } 10^{-3} \text{ mol KCl}}{25.00 \text{ mL}} \quad x \quad \frac{1000 \text{ mL}}{1 \text{ L}} \quad \begin{array}{l} = \quad 1.20 \text{ x } 10^{-1} \text{ mol/L} \\ = \quad 0.120 \text{ M} \end{array}$$

Titrations

A titration is a process where a solution of *accurately known concentration* (a standard solution), is added gradually to another solution of **unknown concentration**, until the chemical reaction between the two is *complete*.

By knowing the volume and concentration of the standard solution, and the *volume* of *unknown solution* (along with the equation of their chemical reaction), we can therefore determine the **concentration** of the **unknown** solution.

To know that the reaction is *complete* requires some type of *indication* or *sign*.

Sometimes a color change from the reactants or products can be used; other times an *indicator* is added to provide that color change.

An indicator is a species that has *distinctly different colors* in *different* media (e.g. one color in acid and a different color in base; Phenolphthalein is colorless in acidic and neutral media, but reddish pink in basic solution).

There are two common types of titration: 1) Acid-Base

                                              2) Redox Titrations.

1) Acid-Base Titrations (Where an *acid* and a *base* react to *neutralize* each other).

Problem: 34.62 mL of 0.1510 M NaOH was needed to neutralize 50.0 mL of an H_2SO_4 solution. What is the concentration of the original sulfuric acid solution?

First we need the *balanced* chemical equation…

$$2 \text{ NaOH} \quad + \quad H_2SO_4 \quad \rightarrow \quad 2 \text{ H}_2O \quad + \quad Na_2SO_4$$
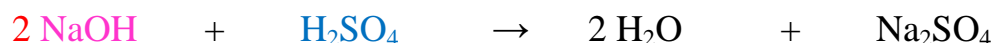
…which tells us that we need twice as many moles of NaOH compared to moles of H_2SO_4.

Moles of H_2SO_4

$$34.62 \text{ mL NaOH} \quad \text{x} \quad \frac{1 \text{ L}}{1000 \text{ mL}} \quad \text{x} \quad \frac{0.1510 \text{ mol NaOH}}{1 \text{ L}} \quad \text{x} \quad \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol NaOH}} = 2.614 \text{ x } 10^{-3} \text{ mol } H_2SO_4$$

Moles of NaOH

$$\text{Molarity} = \frac{\text{moles}}{\text{volume}} = \frac{2.614 \text{ x } 10^{-3} \text{ mol } H_2SO_4}{50.0 \text{ mL}} \text{ x } \frac{1000 \text{ mL}}{1 \text{ L}} = 5.23 \text{ x } 10^{-2} \text{ M } H_2SO_4$$

2) Redox Titrations (where a *reducing agent* and an *oxidizing reagent* react together).

The concentration of oxalate ion ($C_2O_4^{2-}$) in a sample can be determined by titration with a solution of permanganate ion (MnO_4^-) of known concentration. The *balanced* net ionic equation for this reaction is:

2 x 5e- reduction

$$2\ MnO_4^- \ +\ 5\ C_2O_4^{2-} \ +16\ H^+ \longrightarrow 2\ Mn^{2+} \ +8\ H_2O \ +\ 10\ CO_2$$

+3 (above $C_2O_4^{2-}$), +7 (below MnO_4^-), +4 (above CO_2), +2 (below Mn^{2+})

10 x 1e- oxidation

Problem: A 30.00 mL sample of an oxalate solution is found to react completely with 21.93 mL of a 0.1725 M solution of MnO_4^-. What is the oxalate ion concentration in the sample?

Moles of oxalate

$$21.93\ \text{mL MnO}_4^- \quad \times \quad \frac{1\ L}{1000\ mL} \quad \times \quad \frac{0.1725\ \text{mol MnO}_4^-}{1\ L} \times \ \frac{5\ \text{mol C}_2O_4^{2-}}{2\ \text{mol MnO}_4^-} = 9.457\ \text{x } 10^{-3}\ \text{mol C}_2O_4^{2-}$$

Moles of MnO_4^-

$$\text{Molarity} \ = \ \frac{\text{moles}}{\text{volume}} \ = \ \frac{9.457\ \text{x } 10^{-3}\ \text{mol C}_2O_4^{2-}}{30.00\ mL} \times \frac{1000\ mL}{1L} \ \begin{array}{l} = 3.152\ \text{x } 10^{-1}\ \text{M C}_2O_4^{2-} \\ = 0.3152\ \text{M C}_2O_4^{2-} \end{array}$$

Stoichiometric Calculation Summary