# Chapter Four: Reactions in Aqueous Solution

**Learning Outcomes:**

➢Identify compounds as acids or bases, and as strong, weak, or nonelectrolytes

➢Recognize reactions by type and be able to predict the products of simple acid–base, precipitation, and redox reactions.

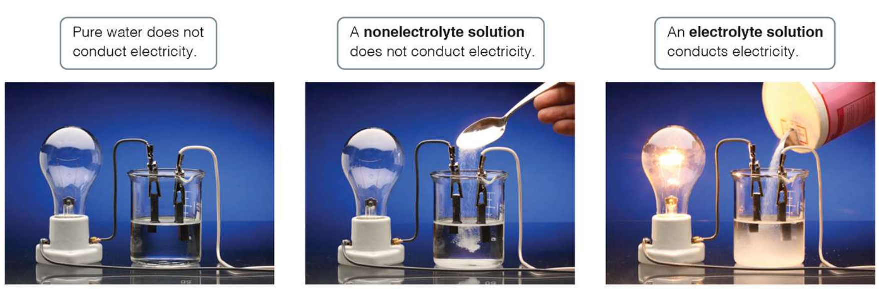
➢Calculate molarity and use it to convert between moles of a substance in solution and volume of the solution.

➢Describe how to carry out a dilution to achieve a desired solution concentration.

➢Describe how to perform and interpret the results of a titration.

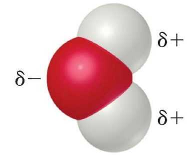
## Solutions

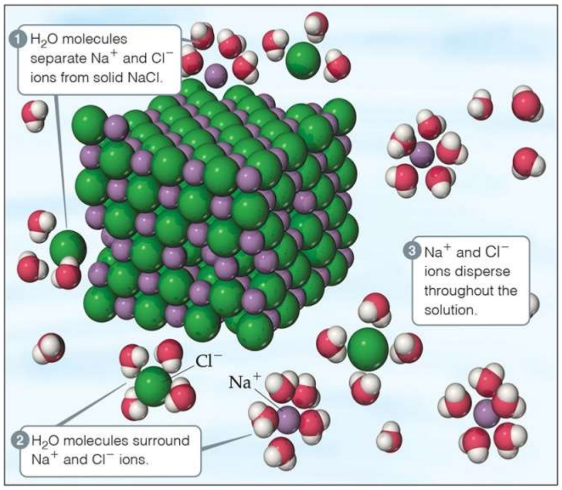
- **Solution**: A homogeneous mixture of two or more pure substances.
- **Solvent**: substance present in the greatest quantity.
- **Solute**: substance dissolved in the solvent.
- **Electrolyte**: Substance whose aqueous solutions contain ions (e.g. NaCl)
- **Nonelectrolyte**: Substance that does not form ions in solution (e.g. $C_{12}H_{22}O_{11}$)



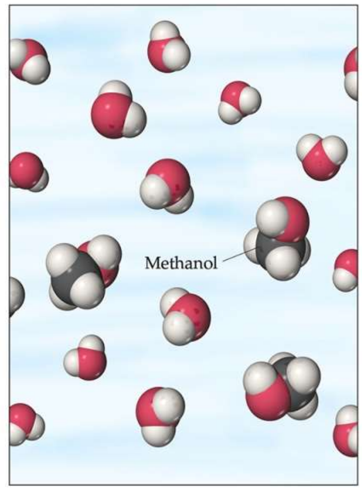

Pure water, $H_2O(l)$ | Sucrose solution, $C_{12}H_{22}O_{11}(aq)$ | Sodium chloride solution, $NaCl(aq)$

# Dissolution in water




**(a)** Ionic compounds like sodium chloride, NaCl, form ions when they dissolve.




**(b)** Molecular substances like methanol, $CH_3OH$, dissolve without forming ions.

# Electrolytes

- A strong electrolyte dissociates completely when dissolved in water.

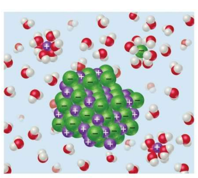
$$HCl\ (aq) \longrightarrow H^+\ (aq)\ +\ Cl^-\ (aq)$$

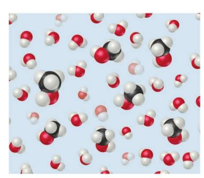
- A weak electrolyte only dissociates partially when dissolved in water.

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq)\ +\ CH_3COO^-\ (aq)$$

**TABLE 4.3 Summary of the Electrolytic Behavior of Common Soluble Ionic and Molecular Compounds**

| | Strong Electrolyte | Weak Electrolyte | Nonelectrolyte |
|---|---|---|---|
| **Ionic** | All | None | None |
| **Molecular** | Strong acids (see Table 4.2) | Weak acids, weak bases | All other compounds |





# Solubility of Ionic Compounds

- Not all ionic compounds dissolve in water.
- A list of *solubility guidelines* is used to decide what combination of ions will dissolve.

**TABLE 4.1 Solubility Guidelines for Common Ionic Compounds in Water**

| Soluble Ionic Compounds | | Important Exceptions |
|---|---|---|
| Compounds containing | $NO_3^-$ | None |
| | $CH_3COO^-$ | None |
| | $Cl^-$ | Compounds of $Ag^+$, $Hg_2^{2+}$, and $Pb^{2+}$ |
| | $Br^-$ | Compounds of $Ag^+$, $Hg_2^{2+}$, and $Pb^{2+}$ |
| | $I^-$ | Compounds of $Ag^+$, $Hg_2^{2+}$, and $Pb^{2+}$ |
| | $SO_4^{2-}$ | Compounds of $Sr^{2+}$, $Ba^{2+}$, $Hg_2^{2+}$, and $Pb^{2+}$ |
| **Insoluble Ionic Compounds** | | **Important Exceptions** |
| Compounds containing | $S^{2-}$ | Compounds of $NH_4^+$, the alkali metal cations,$Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ |
| | $CO_3^{2-}$ | Compounds of $NH_4^+$ and the alkali metal cations |
| | $PO_4^{3-}$ | Compounds of $NH_4^+$ and the alkali metal cations |
| | $OH^-$ | Compounds of $NH_4^+$, the alkali metal cations,$Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ |

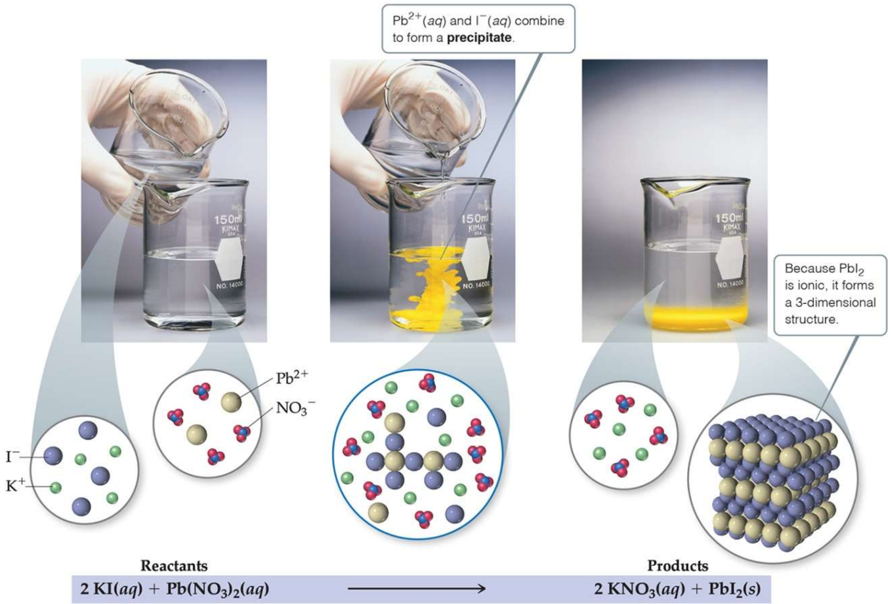
You need to know the solubility guidelines on this table.

# Precipitation Reactions

- A **precipitation reaction** involves the formation of an insoluble product or products from the reaction of soluble reactants. The solid is called a **precipitate**.
- Example: Mixing $AgNO_3$ and LiCl, both of which are soluble, produces insoluble AgCl.

$$AgNO_3(aq) + LiCl(aq) \rightarrow AgCl(s) + LiNO_3(aq)$$

## Precipitation Reaction




## Precipitation Reactions

What insoluble compound, if any, will form when solutions of $Pb(NO_3)_2$ and $Na_2SO_4$ are mixed?

1) Note the ions present in the reactants.
2) Consider the possible cation-anion combinations.
3) Use Table 4.1 to determine if any of the combinations is insoluble.
4) Write the chemical equation.

*Anions*      *Cations*

| | $Na^+$ | $Pb^{2+}$ |
|---|---|---|
| $NO_3^-$ | soluble $NaNO_3$ | soluble $Pb(NO_3)_2$ |
| $SO_4^{2-}$ | soluble $Na_2SO_4$ | insoluble $PbSO_4$ |

$Pb(NO_3)_2\,(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$

## Metathesis (Exchange) Reactions

- Metathesis comes from a Greek word that means “to transpose”. The ions in the reactant compounds exchange, or transpose, ions
- The **molecular equation** lists the reactants and products in the overall reaction and includes the states of matter.

$$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

1) Use the chemical formulas of the reactants to determine which ions are present.
2) Write formulas for the products: cation from one reactant, anion from the other. Use charges to write proper subscripts.
3) Check solubility rules. If either product is insoluble, a precipitate forms.
4) Balance the equation.

## Complete Ionic Equation

- In the complete ionic equation all strong electrolytes (strong acids, strong bases, and soluble ionic salts) are dissociated into their ions.
- This more accurately reflects the species that are found in the reaction mixture.

$$Ag^+ (aq) + NO_3^- (aq) + K^+ (aq) + Cl^- (aq) \longrightarrow AgCl\,(s) + K^+ (aq) + NO_3^- (aq)$$

## Net Ionic Equation

- To form the net ionic equation, cross out anything that does not change from the left side of the equation to the right.

$$Ag^{+}(aq) + \cancel{NO_3^{-}}(aq) + \cancel{K^{+}}(aq) + Cl^{-}(aq) \longrightarrow$$
$$AgCl\,(s) + \cancel{K^{+}}(aq) + \cancel{NO_3^{-}}(aq)$$

- The only things left in the equation are those things that change (i.e., react) during the course of the reaction.

$$Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl\,(s)$$

- Those things that didn't change (and were deleted from the net ionic equation) are called spectator ions.

## Writing Net Ionic Equations

1. Write a balanced molecular equation.
2. Dissociate all strong electrolytes.
3. Cross out anything that remains unchanged from the left side to the right side of the equation (spectator ions).
4. Write the net ionic equation with the species that remain.

## *Example*

Overall equation:

$Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow$
$PbSO_4(s) + 2NaNO_3(aq)$

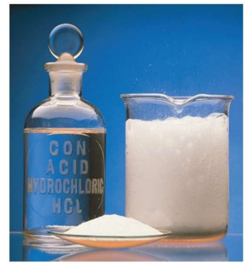
Write the net ionic equation.

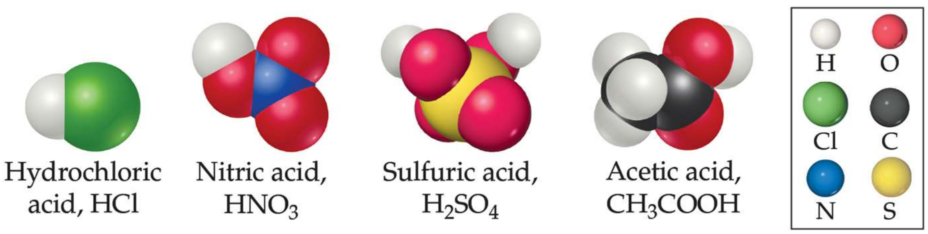
## *Example*

Write the net ionic equation for the reaction of HCl(aq) and KOH(aq).

# Acids

- Substances that ionize in aqueous solution and increase the concentration of $H^+$ when dissolved in water (Arrhenius).
- Proton donors (Brønsted–Lowry).



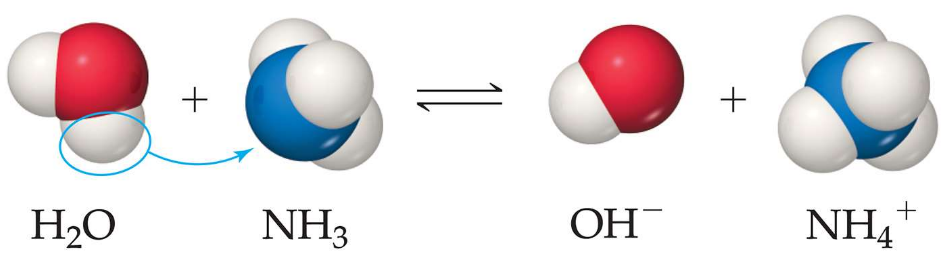

monoprotic acid

diprotic acid

# Bases

- Substances that increase the concentration of $OH^-$ when dissolved in water (Arrhenius).
- Proton acceptors, react with $H^+$ (Brønsted–Lowry).


Substances do not have to contain $OH^-$ to be a base.



## Classification: Strong and Weak

- Strong acids completely dissociate in water, whereas weak acids partially dissociate.
- Strong bases dissociate to metal cations and hydroxide anions in water; weak bases only partially react to produce hydroxide anions

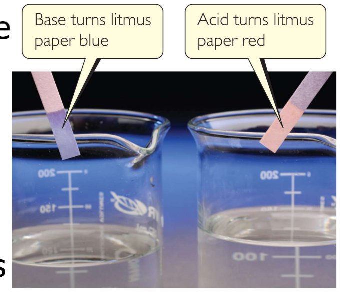



**TABLE 4.2 Common Strong Acids and Bases**

| Strong Acids | Strong Bases |
|---|---|
| Hydrochloric acid, $HCl$ | Group 1A metal hydroxides [$LiOH$, $NaOH$, $KOH$, $RbOH$, $CsOH$] |
| Hydrobromic acid, $HBr$ | Heavy group 2A metal hydroxides [$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$] |
| Hydroiodic acid, $HI$ | |
| Chloric acid, $HClO_3$ | |
| Perchloric acid, $HClO_4$ | |
| Nitric acid, $HNO_3$ | |
| Sulfuric acid (first proton), $H_2SO_4$ | |

## Strong and Weak Electrolyte

**TABLE 4.3 Summary of the Electrolytic Behavior of Common Soluble Ionic and Molecular Compounds**

| | Strong Electrolyte | Weak Electrolyte | Nonelectrolyte |
|---|---|---|---|
| **Ionic** | All | None | None |
| **Molecular** | Strong acids (see Table 4.2) | Weak acids, weak bases | All other compounds |

# Neutralization Reactions

Generally, when solutions of an acid and a base are combined, the products are a salt and water.

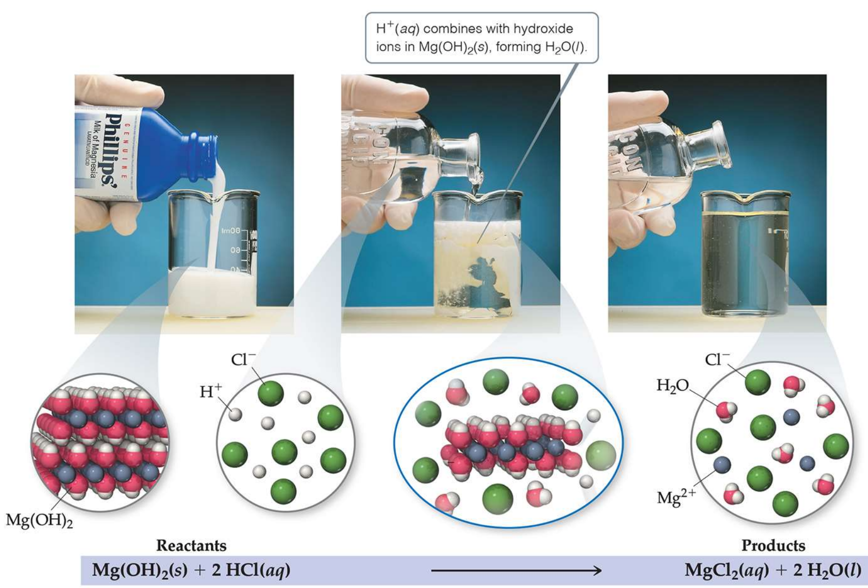
- Can be written as molecular, complete ionic, or net ionic equations.

$$\underset{\text{(acid)}}{HCl(aq)} + \underset{\text{(base)}}{NaOH(aq)} \longrightarrow \underset{\text{(water)}}{H_2O(l)} + \underset{\text{(salt)}}{NaCl(aq)}$$

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + Na^+(aq) + Cl^-(aq)$$

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

# Neutralization Reactions



# Gas-Forming Reactions

- These reactions do not give the product expected for a metathesis reaction.
- The expected product decomposes to give a gaseous product (e.g. $CO_2$, $SO_2$, or $H_2S$).

$$CaCO_3\,(s) + 2HCl\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

$$NaHCO_3\,(aq) + HBr\,(aq) \longrightarrow NaBr\,(aq) + CO_2\,(g) + H_2O\,(l)$$

$$SrSO_3\,(s) + 2\,HI\,(aq) \longrightarrow SrI_2\,(aq) + SO_2\,(g) + H_2O\,(l)$$

$$Na_2S\,(aq) + H_2SO_4\,(aq) \rightarrow Na_2SO_4\,(aq) + H_2S\,(g)$$

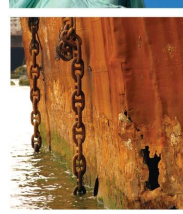
# Redox Reactions

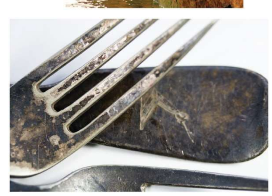
**Manufacturing metals**

**Batteries**

**Fuels**

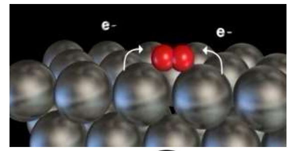
**Corrosion**

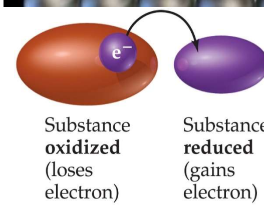


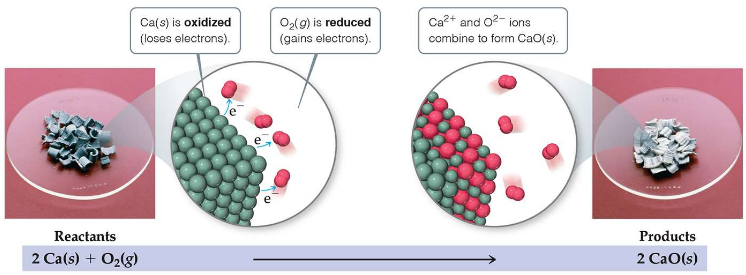


# Oxidation-Reduction Reactions

- An oxidation occurs when an atom or ion *loses* electrons.
- A reduction occurs when an atom or ion *gains* electrons.
- One cannot occur without the other.




# Oxidation Numbers

To determine if an oxidation-reduction reaction has occurred, we assign an **oxidation number** to each element in a neutral compound or charged entity.

- The **oxidation number** may be a positive or negative number.
- The sum of the oxidation numbers in a neutral compound is 0.
- The sum of the oxidation numbers in a polyatomic ion is the **charge** on the ion.
- An **oxidation-reduction reaction** is one in which some of the elements **change** oxidation number during the course of the reaction.
- In a balanced equation the sum of the changes in oxidation numbers is zero.

$$\text{Oxidation number}\quad \underset{0}{\mathrm{Mg}}(s) + 2\,\underset{+1}{\mathrm{H}}\underset{-1}{\mathrm{Cl}}(aq) \longrightarrow \underset{+2}{\mathrm{Mg}}\underset{-1}{\mathrm{Cl_2}}(aq) + \underset{0}{\mathrm{H_2}}(g)$$

## Oxidation Numbers

Rules to assign oxidation numbers (ox. #).

1. Each atom in free element has ox. # = 0.

   Zn    $O_2$    $O_3$    $I_2$    $S_8$    $P_4$

2. In simple ions, ox. # = charge on ion.

   -1 for $Cl^-$    +2 for $Mg^{2+}$

3a. The ox. # of O is normally -2, except in peroxides.

   O is -2 in NO    O is -1 in $Na_2O_2$

## Oxidation Numbers

3b. The ox. # of H is +1 when bonded to nonmetals and -1 when bonded to metals.

   H is +1 in $CH_4$    H is -1 in $CaH_2$

3c. The ox. # of F is ALWAYS -1 with all other elements.

   $FeF_3$    $PF_5$    $SF_6$    $OF_2$

The ox. # of Cl, Br and I are always -1, except when combined with O or F, then are positive.

4. Algebraic sum of oxidation numbers

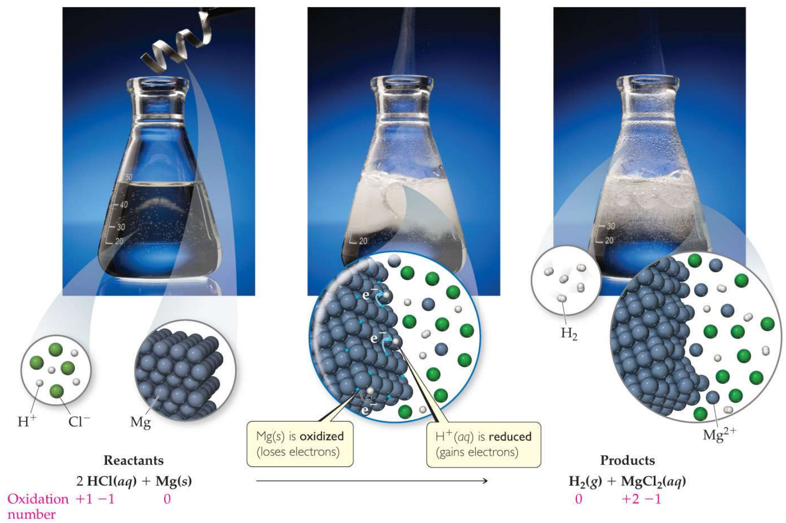
   = 0 for a neutral compound

   = overall charge for an ion

# Displacement Reactions

$$Mg(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

Oxidation number 0 +1 −1 +2 −1 0




# Activity Series

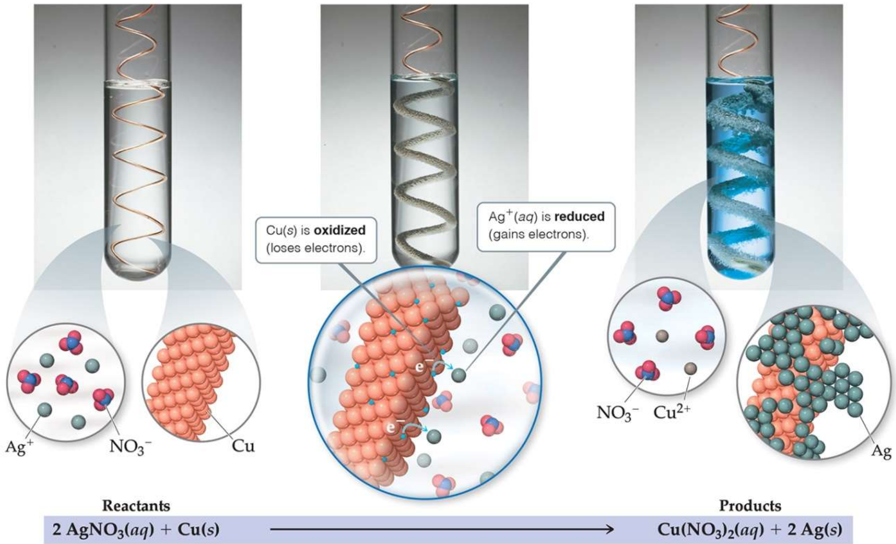
**TABLE 4.5 Activity Series of Metals in Aqueous Solution**

| Metal | Oxidation Reaction |
|---|---|
| Lithium | $Li(s) \longrightarrow Li^+(aq) + e^-$ |
| Potassium | $K(s) \longrightarrow K^+(aq) + e^-$ |
| Barium | $Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^-$ |
| Calcium | $Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$ |
| Sodium | $Na(s) \longrightarrow Na^+(aq) + e^-$ |
| Magnesium | $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$ |
| Aluminum | $Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$ |
| Manganese | $Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^-$ |
| Zinc | $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ |
| Chromium | $Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$ |
| Iron | $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ |
| Cobalt | $Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$ |
| Nickel | $Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$ |
| Tin | $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$ |
| Lead | $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$ |
| Hydrogen | $H_2(g) \longrightarrow 2\,H^+(aq) + 2e^-$ |
| Copper | $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$ |
| Silver | $Ag(s) \longrightarrow Ag^+(aq) + e^-$ |
| Mercury | $Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^-$ |
| Platinum | $Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^-$ |
| Gold | $Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$ |

Ease of oxidation increases

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

# Displacement Reactions




Elements higher on the activity series are more reactive. They will exist as ions. The element below will exist as the element.

# Molarity

- Two solutions can contain the same compounds but be quite different because the proportions of those compounds are different.
- Molarity is one way to measure the amount dissolved, or the concentration of a solution.

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{volume of solution in liters}}$$

**Molarity** (*M*) is often expressed as the number of moles of solute in one liter of *solution*.

## *Example: Molarity of a Solution*

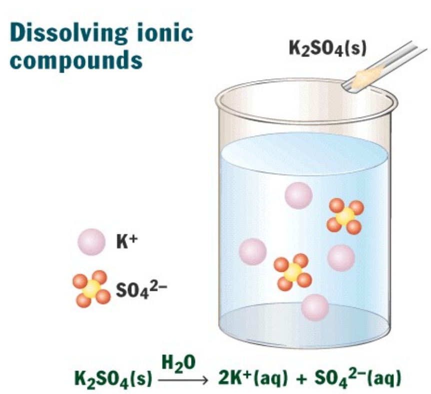
What is the molar concentration of NaF in a solution prepared by dissolving 2.51 g of NaF in enough water to form 200. mL of solution?

Mass of NaF $\xrightarrow[\text{of NaF}]{\text{Molar mass}}$ Moles of NaF $\xrightarrow[\text{of solution}]{\text{Volume (L)}}$ Molarity of NaF solution

## Molarity of Ions

One mole of $K_2SO_4$ dissolves in water to form two moles of $K^+$ ions and one mole of $SO_4^{2-}$ ions.

$$K_2SO_4(s) \xrightarrow{H_2O} 2K^+(aq) + SO_4^{2-}(aq)$$



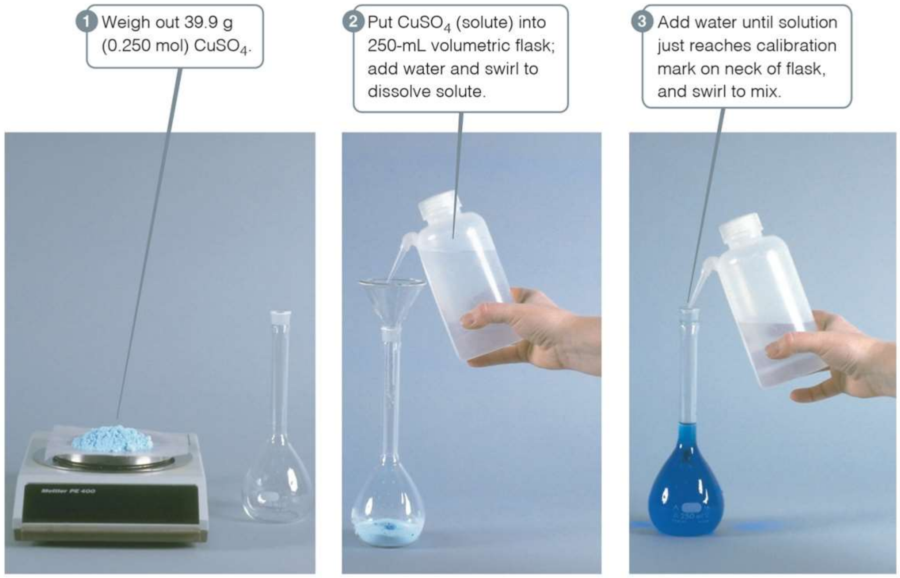
## *Example: Molarity of Ions in a Solution*

In the following pair of solutions, indicate which has a higher concentration of $K^+$ ions. A 0.100 M $K_2SO_4$ solution or a 0.150 M KCl solution.

## *Example: Molarity of Ions in Mixed Solutions*

Indicate the concentration of each ion present in the solution formed by mixing 34.6 mL of 0.100 M $K_2SO_4$ and 18.3 mL of 0.150 M KCl.

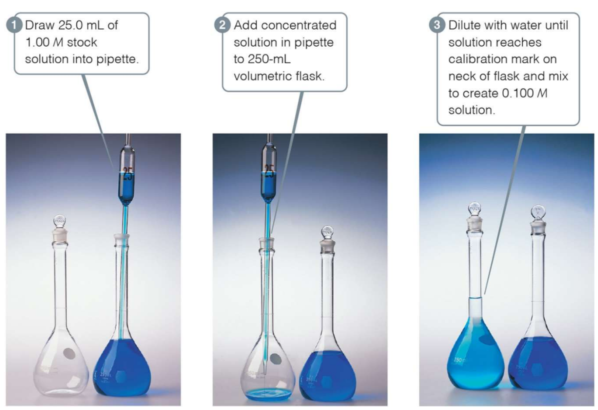
# Preparing a Solution




# Dilution

Solutions of lower concentration can be prepared by dilution of more concentrated solutions of known molarity

**Volume (L) of dilute solution** $\xrightarrow[\text{of dilute}]{\text{Molarity}}$ **Moles of solute** $\xrightarrow[\text{of concentrated}]{\text{Molarity}}$ **Volume (L) concentrated solution**



# Dilution

In a dilution problem: moles of solute in dilute solution = moles of solute in the concentrated solution

$$M_{conc} \times V_{conc} = M_{dil} \times V_{dil}$$

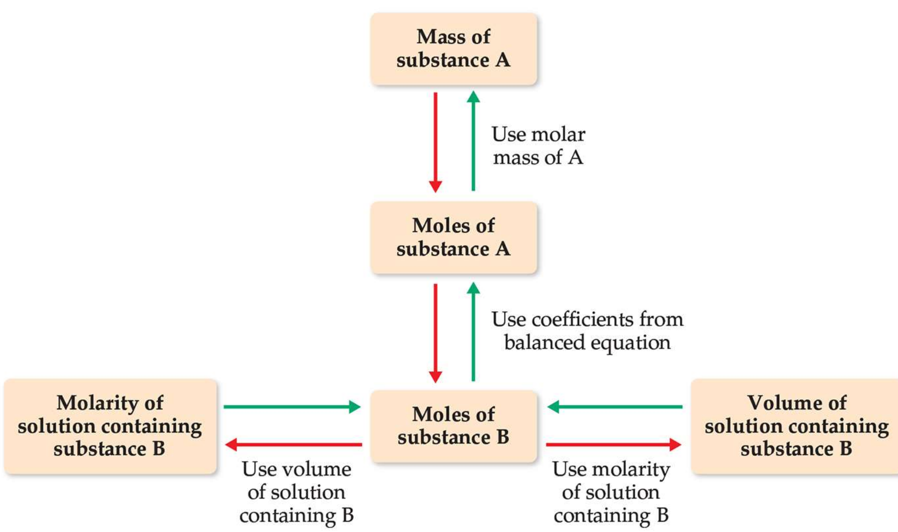
Use this formula only for dilution problems, <u>not</u> for problems involving reaction equations.

## *Examples*

1) Describe how you would prepare a 50.0 mL solution of 4.00 M $K_2SO_4$. Calculate the volume of 4.00 M $K_2SO_4$ that is needed to prepare 600. mL of a 0.0200 M solution of $K_2SO_4$. Calculate the molar concentration of $K^+$ ions in the 0.0200 M solution.

2) A 35.0 mL sample of 1.00 M KBr and a 60.0 mL sample of 0.600 M KBr are mixed. The solution is then heated to evaporate water until the total volume is 50.0 mL. What is the molarity of the KBr in the final solution?

# Molarities in Stoichiometric Calculations



## Stoichiometry Calculations for Reactions in Solution

- Molarity is a conversion between volume (L) of solution and moles of solute. For a 2.00 molar solution of KCl:

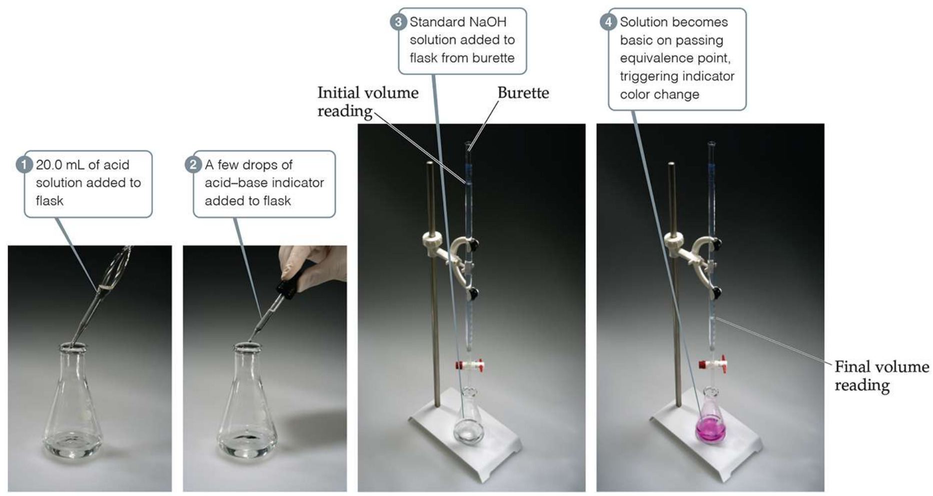
  2.00 mol KCl = 1 L KCl
- In stoichiometric calculations with equations molarity is used to calculate moles of solute from volume of solution analogous to using molar mass to calculate moles from mass of a solid.

## *Example:*

Calculate the mass of lead(II) sulfate formed in the reaction of 145 mL of 0.123 M lead(II) nitrate and excess sodium sulfate.

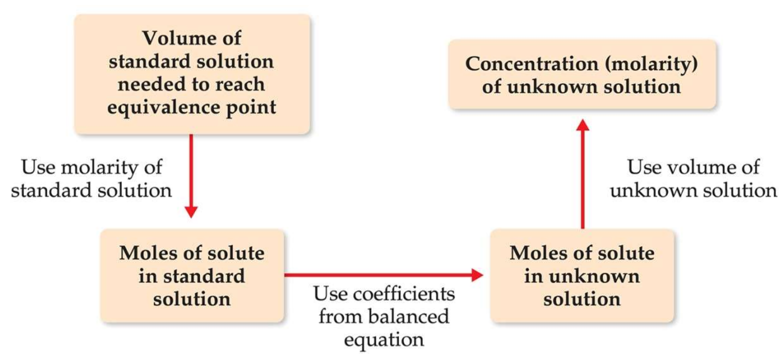
# Titration

The analytical technique in which one can calculate the concentration of a solute in a solution.




# Titrations

- In a **titration**, the concentration and volume of a *known* solution is used to determine the *unknown* concentration of a second solution.
- **Equivalence point**: the point in a titration where stoichiometrically *equivalent* amounts of the two reactants have been added.



## Titration Using Phenolphthalein Indicator

- Left: acidic solution with indicator added
- Center: end point - very slight pink color
- Right: pink color after excess base added

## Example

Calculate the molarity of an HCl solution if 26.4 mL of the solution neutralizes 30.0 mL of a 0.120 molar solution of $Ba(OH)_2$.

## Example

A 16.0 mL aliquot of a 0.220 M solution of $H_2SO_4$ is titrated with a 0.211 M NaOH solution. What volume (mL) of base will it take to reach the equivalence point?

## Example

What mass of lead(II) chloride forms in the reaction of 24.3 mL of 1.34 *M* lead(II) nitrate and 38.1 mL of 1.22 *M* sodium chloride?

## Example

Consider 6.82 g $Sr(NO_3)_2$ is dissolved in enough water to form 0.500 L solution. A 0.100 L sample is withdrawn and titrated with a 0.0335 M solution of $Na_2CrO_4$. What volume of $Na_2CrO_4$ solution is needed to precipitate all the $Sr^{2+}(aq)$ as $SrCrO_4$?

## Example

A 1.248 g limestone rock, which contains $CaCO_3$ and other compounds, is pulverized and treated with 30.00 mL of 1.035 M HCl solution. The excess acid requires 11.56 mL of 1.010 M NaOH for neutralization. Calculate the percent by mass of calcium carbonate in the rock, assuming it is the only substance reacting with the HCl solution.