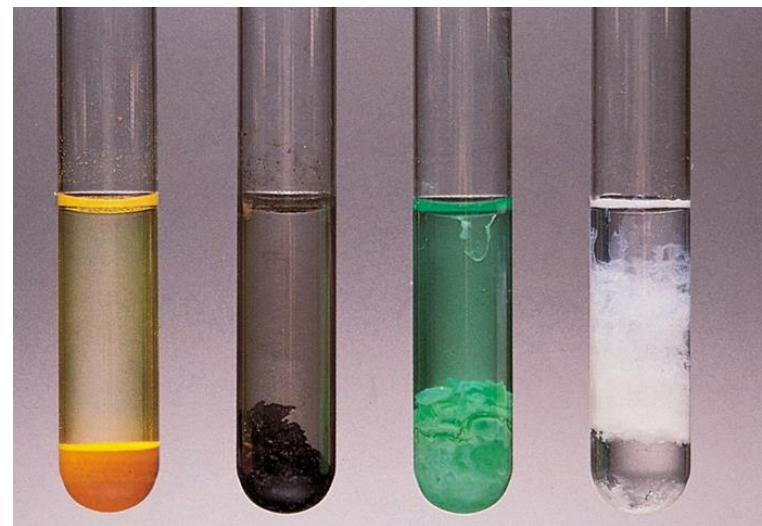




Reactions in Aqueous Solution

Chapter 4



- Many chemical reactions and virtually all biological processes take place in **water** – the so called **universal solvent**.
- **Three** categories of reactions occur in aqueous solutions:
 - **precipitations reactions**
 - **acid-base reactions**
 - **redox reactions**
- We begin with ***general properties of aqueous solutions***.

Solution, Solute & Solvent

A **solution** is a homogenous mixture of 2 or more substances.

The **solute** is the substance present in the **smaller** amount.

The **solvent** is the substance present in the **larger** amount.

<u>Solution</u>	<u>Solvent</u>	<u>Solute</u>
Air (g)	N_2	O_2 , Ar, CH_4
Soft drink (l)	H_2O	Sugar, CO_2
Soft Solder (s)	Pb	Sn



aqueous solutions
of $KMnO_4$

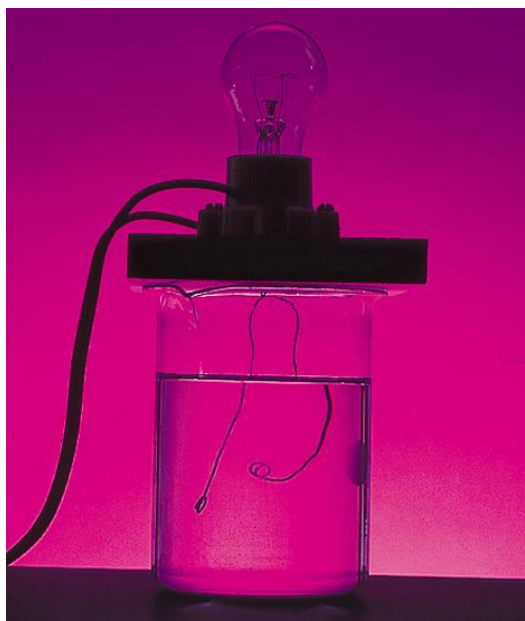
Solution, Solute & Solvent

- So, a solution may be:
 - **gaseous** (such as air)
 - **liquid** (such as seawater)
 - **solid** (such as an alloy)
- Here we will discuss only **aqueous solution**
 - in which *the **solute** is a **solid** or **liquid**, and the **solvent** is **water***
- All solute that dissolve in water fit into **two** types:
 - **Electrolyte** and **Nonelectrolyte**
- Electrolytes are of **two** categories:
 - **Strong electrolyte** and **Weak electrolyte**

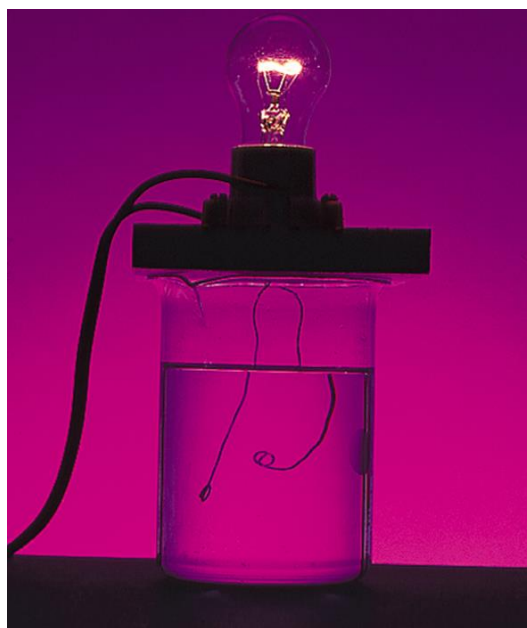
Electrolyte & Nonelectrolyte

An **electrolyte** is a substance that, when dissolved in water, results in a solution that can conduct electricity.

A **nonelectrolyte** is a substance that, when dissolved, results in a solution that does not conduct electricity.



nonelectrolyte



weak electrolyte



strong electrolyte

Electrolyte & Nonelectrolyte

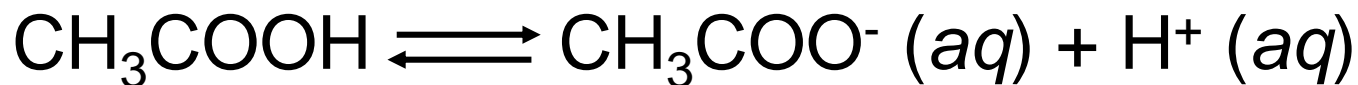
Conduct electricity in solution?

Cations (+) and **Anions (-)**

Strong Electrolyte – 100% dissociation

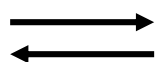
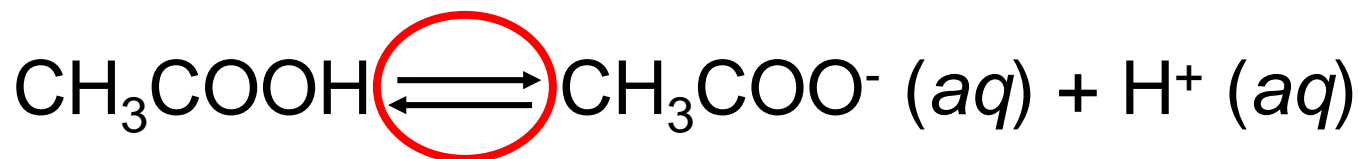


Weak Electrolyte – not completely dissociated



Electrolyte & Nonelectrolyte

Ionization of acetic acid



A ***reversible*** reaction. The reaction can occur in both directions.

Reaches an ***equilibrium***.

Acetic acid is a ***weak electrolyte*** because its ionization in water is incomplete.

Electrolyte & Nonelectrolyte

Nonelectrolyte does not conduct electricity?

No **cations (+)** and **anions (-)** in solution

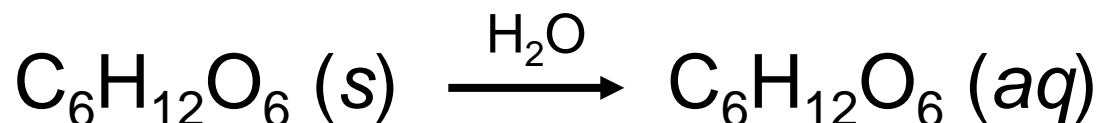


TABLE 4.1 Classification of Solutes in Aqueous Solution

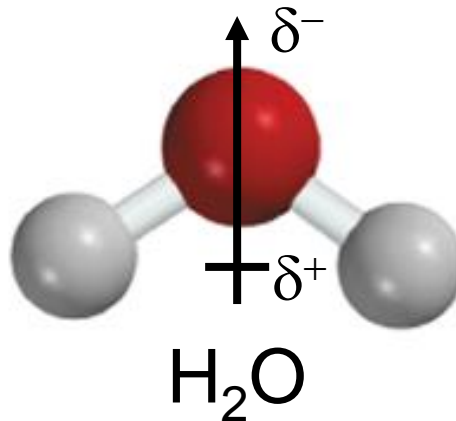
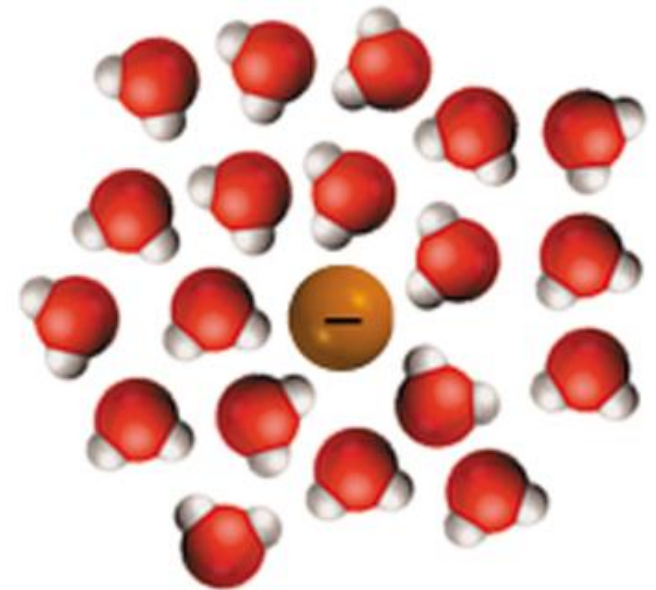
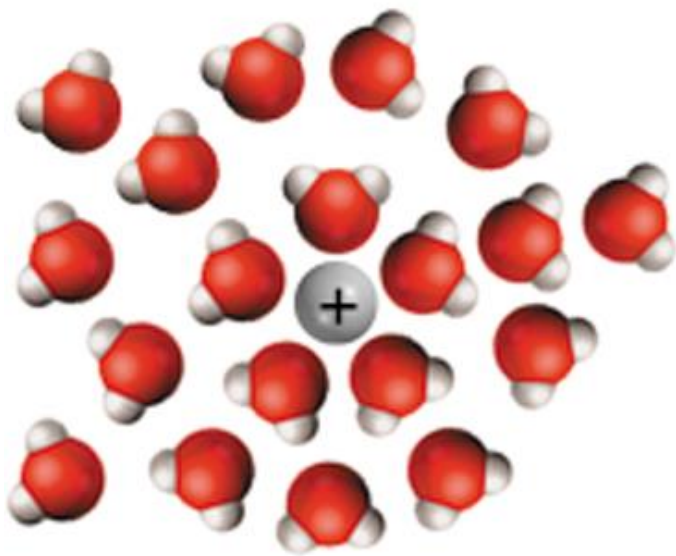
Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH ₃ COOH	(NH ₂) ₂ CO (urea)
HNO ₃	HF	CH ₃ OH (methanol)
HClO ₄	HNO ₂	C ₂ H ₅ OH (ethanol)
H ₂ SO ₄ [*]	NH ₃	C ₆ H ₁₂ O ₆ (glucose)
NaOH	H ₂ O [†]	C ₁₂ H ₂₂ O ₁₁ (sucrose)
Ba(OH) ₂		
Ionic compounds		

^{*}H₂SO₄ has two ionizable H⁺ ions.

[†]Pure water is an extremely weak electrolyte.

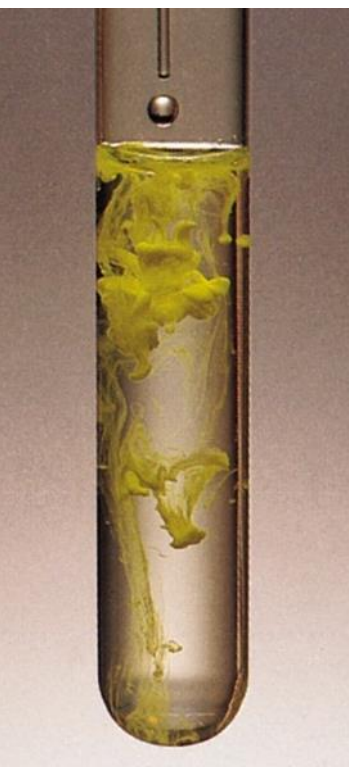
Solution Process

Hydration is the process in which an ion is surrounded by **water** molecules arranged in a specific manner.

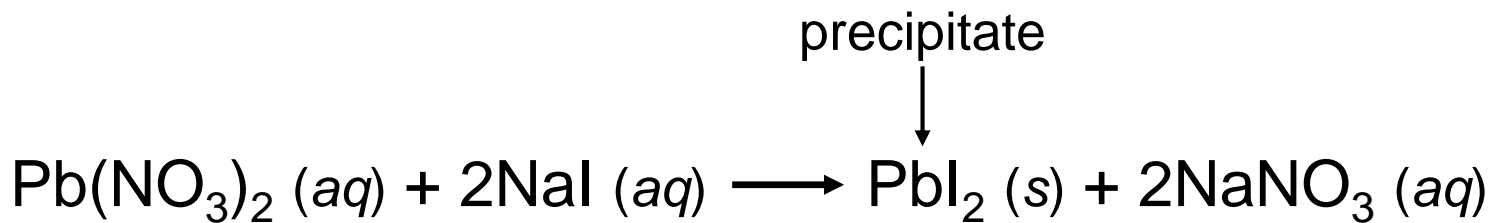


Precipitation Reactions

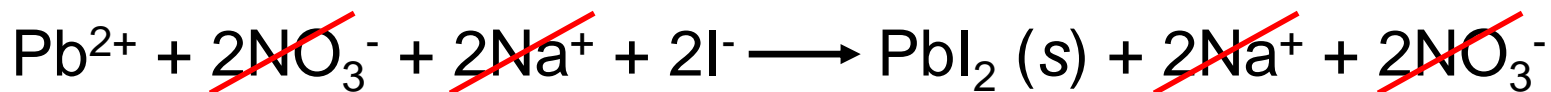
Precipitate – insoluble solid that separates from solution



PbI₂



molecular equation



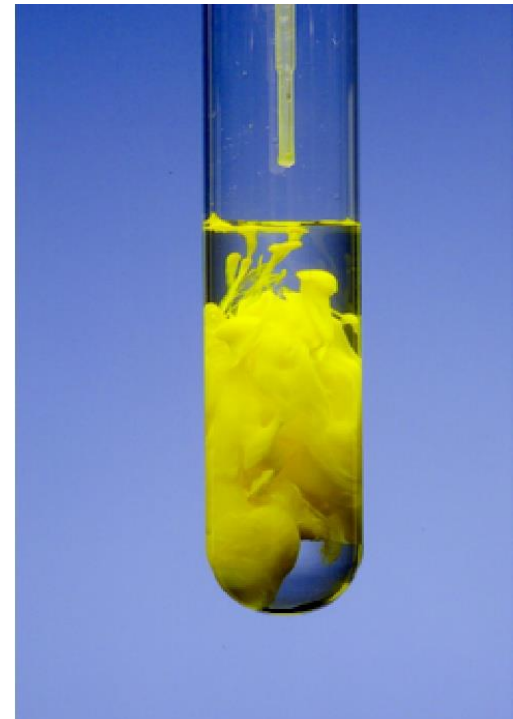
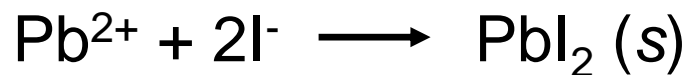
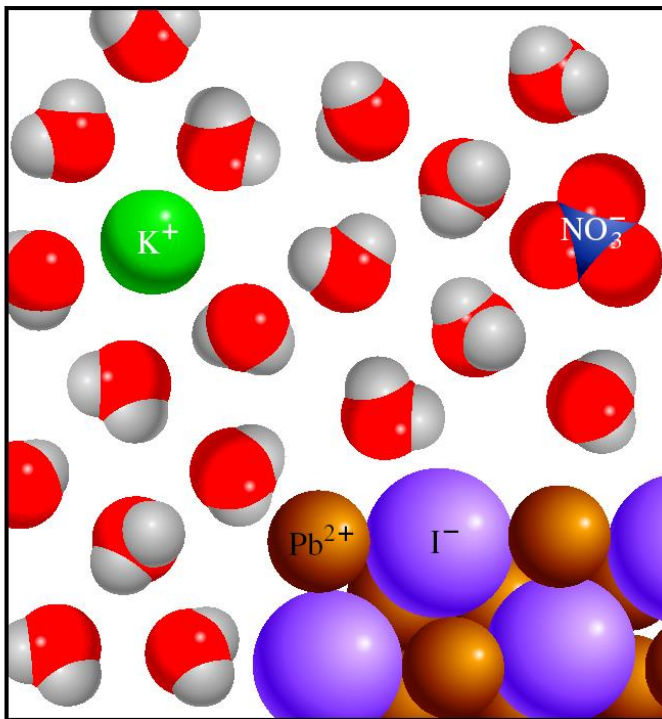
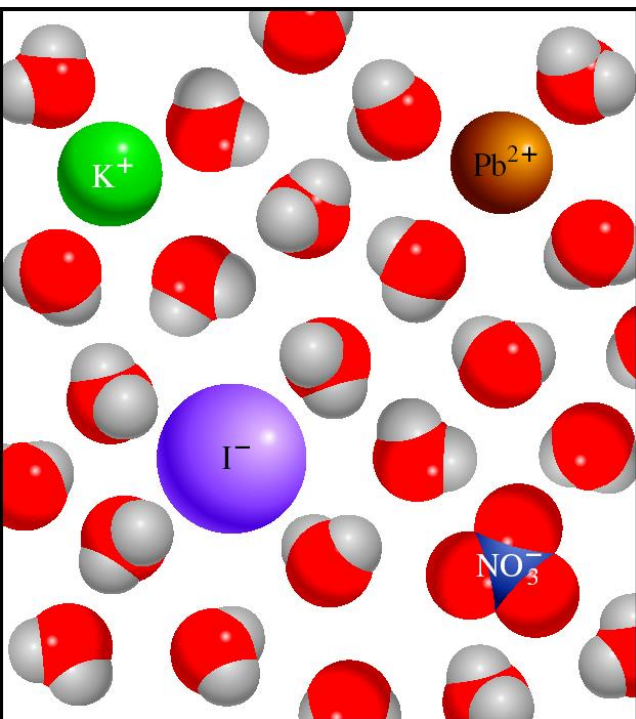
ionic equation



net ionic equation

Na⁺ and NO₃⁻ are ***spectator*** ions

Precipitation of Lead Iodide



Predicting Precipitation

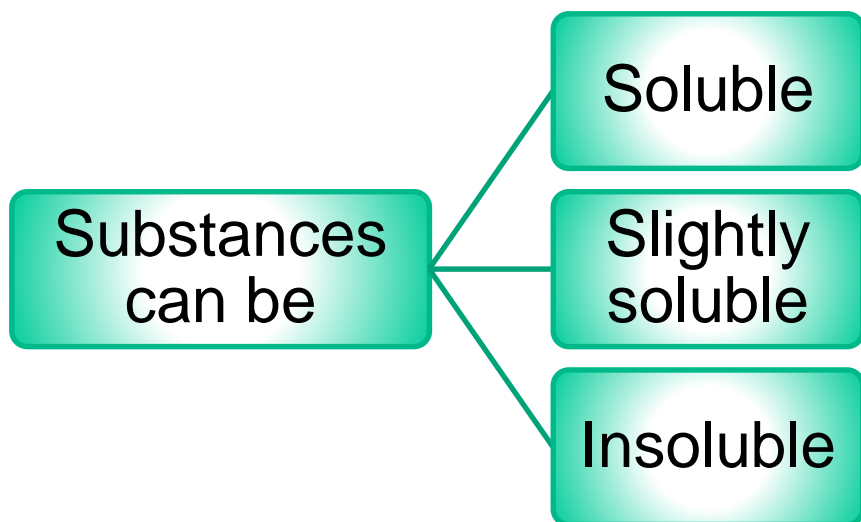
How can we predict whether a precipitate will form?



It depends on the **solubility** of the solute.



Solubility is the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature.



All ionic compounds are strong electrolytes, but not equally soluble.

Solubility Rules

TABLE 4.2 Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds

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^-)

Sulfates (SO_4^{2-})

Insoluble Exceptions

Halides of Ag^+ , Hg_2^{2+} , and Pb^{2+}

Sulfates of Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}

Insoluble Compounds

Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), sulfides (S^{2-})

Hydroxides (OH^-)

Soluble Exceptions

Compounds containing alkali metal ions and the ammonium ion

Compounds containing alkali metal ions and the Ba^{2+} ion



Identify each of the following species as a soluble or insoluble:

Silver sulfate, Ag_2SO_4 Insoluble

Calcium carbonate, CaCO_3 Insoluble

Sodium phosphate, Na_3PO_4 Soluble

Copper sulfide, CuS Insoluble

Calcium hydroxide, $\text{Ca}(\text{OH})_2$ Insoluble

Zinc nitrate, $\text{Zn}(\text{NO}_3)_2$ Soluble

Examples of Insoluble Compounds



CdS



PbS



Ni(OH)_2

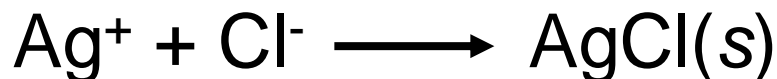
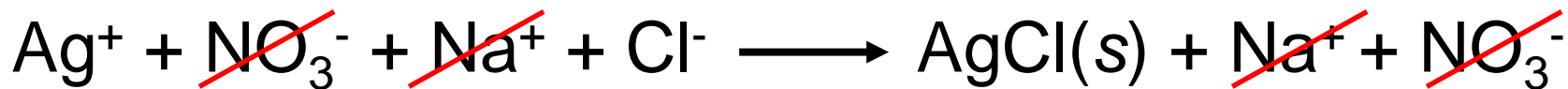
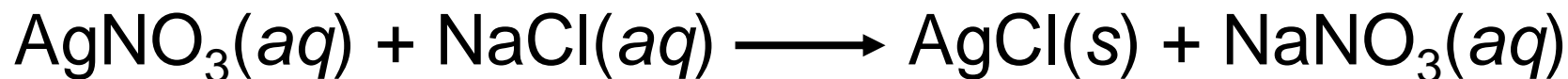


Al(OH)_3

Writing Net Ionic Equations

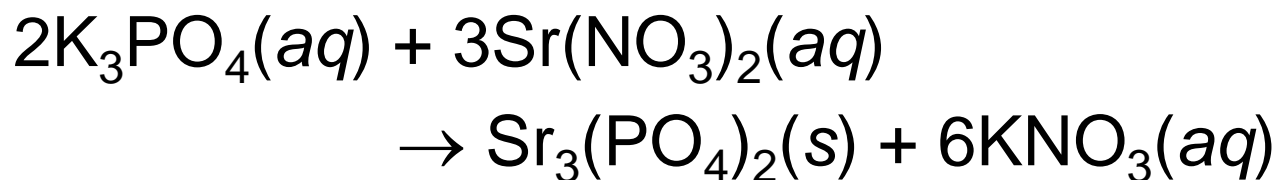
1. Write the balanced molecular equation.
2. Write the ionic equation showing the strong electrolytes completely dissociated into cations and anions.
3. Cancel the spectator ions on both sides of the ionic equation
4. Check that charges and number of atoms are balanced in the net ionic equation

Write the net ionic equation for the reaction of silver nitrate with sodium chloride.

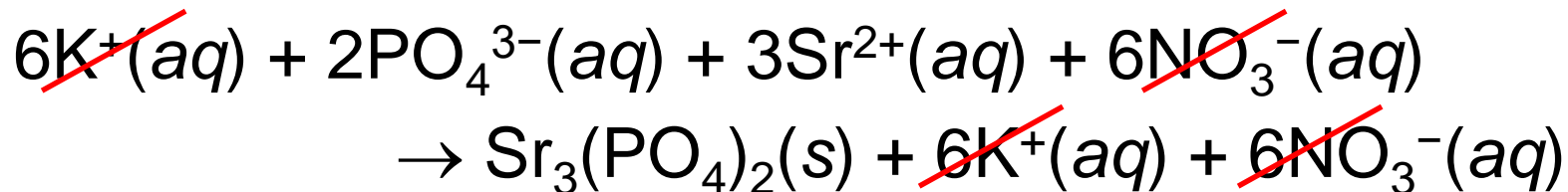




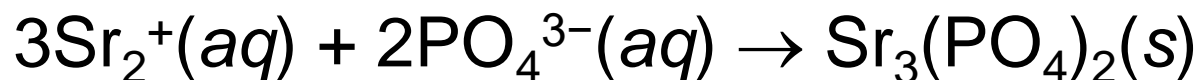
Predict what happens when a potassium phosphate K_3PO_4 solution is mixed with a strontium nitrate $\text{Sr}(\text{NO}_3)_2$ solution. Write the ionic and net ionic equation for the reaction.



Ionic:



Net ionic:



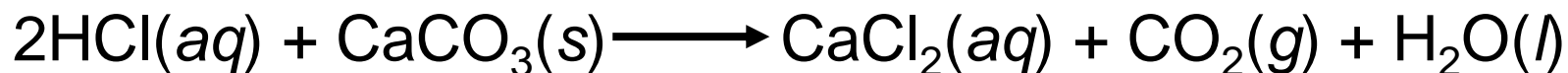
Acid-Base Reactions

Properties of Acids

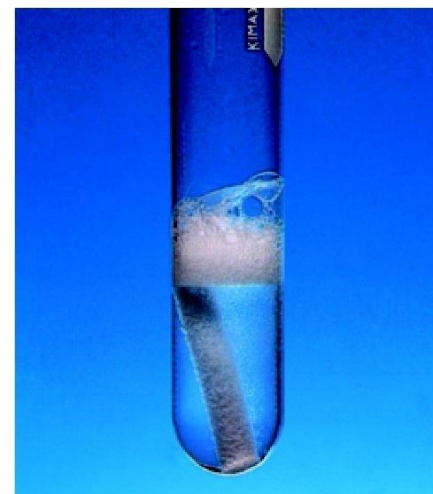
- Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.
- Cause color changes in plant dyes.
- React with certain metals to produce hydrogen gas.



- React with carbonates and bicarbonates to produce carbon dioxide gas



- Aqueous acid solutions conduct electricity.

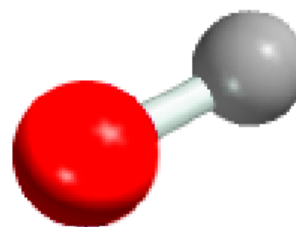
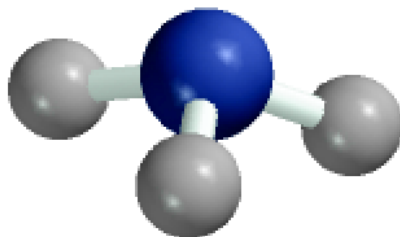


Acid-Base Reactions

Properties of Bases

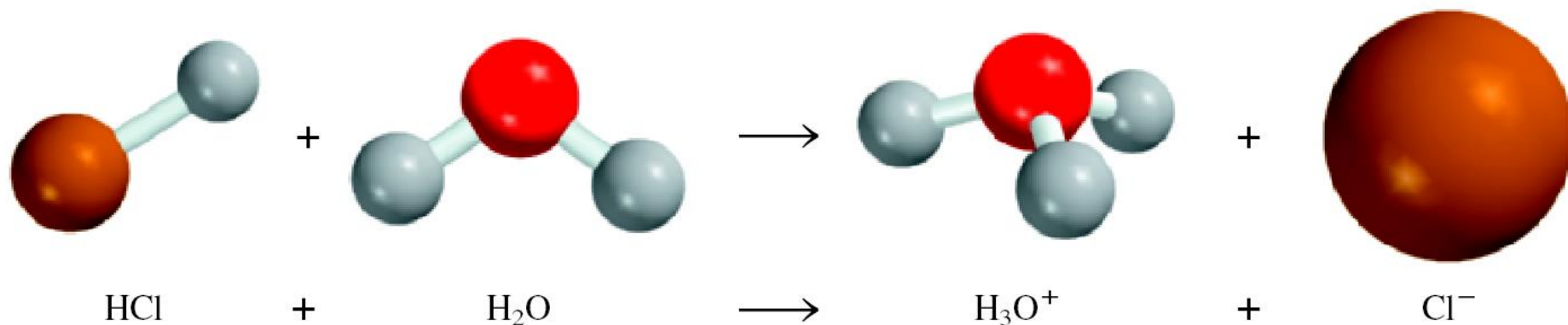
- Have a bitter taste.
- Feel slippery. Many soaps contain bases.
- Cause color changes in plant dyes.
- Aqueous base solutions conduct electricity.

Examples:

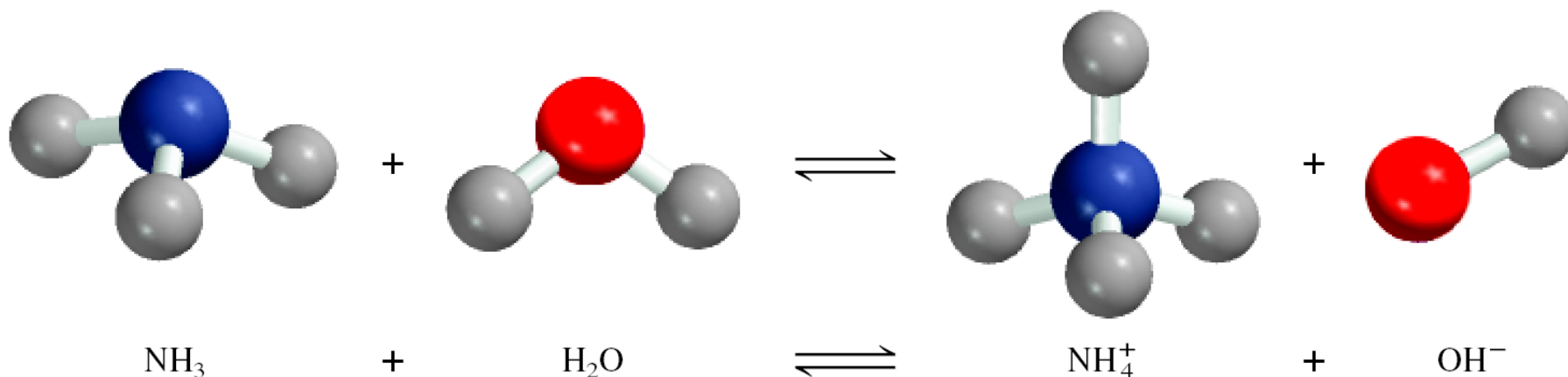


Arrhenius Acid & Base

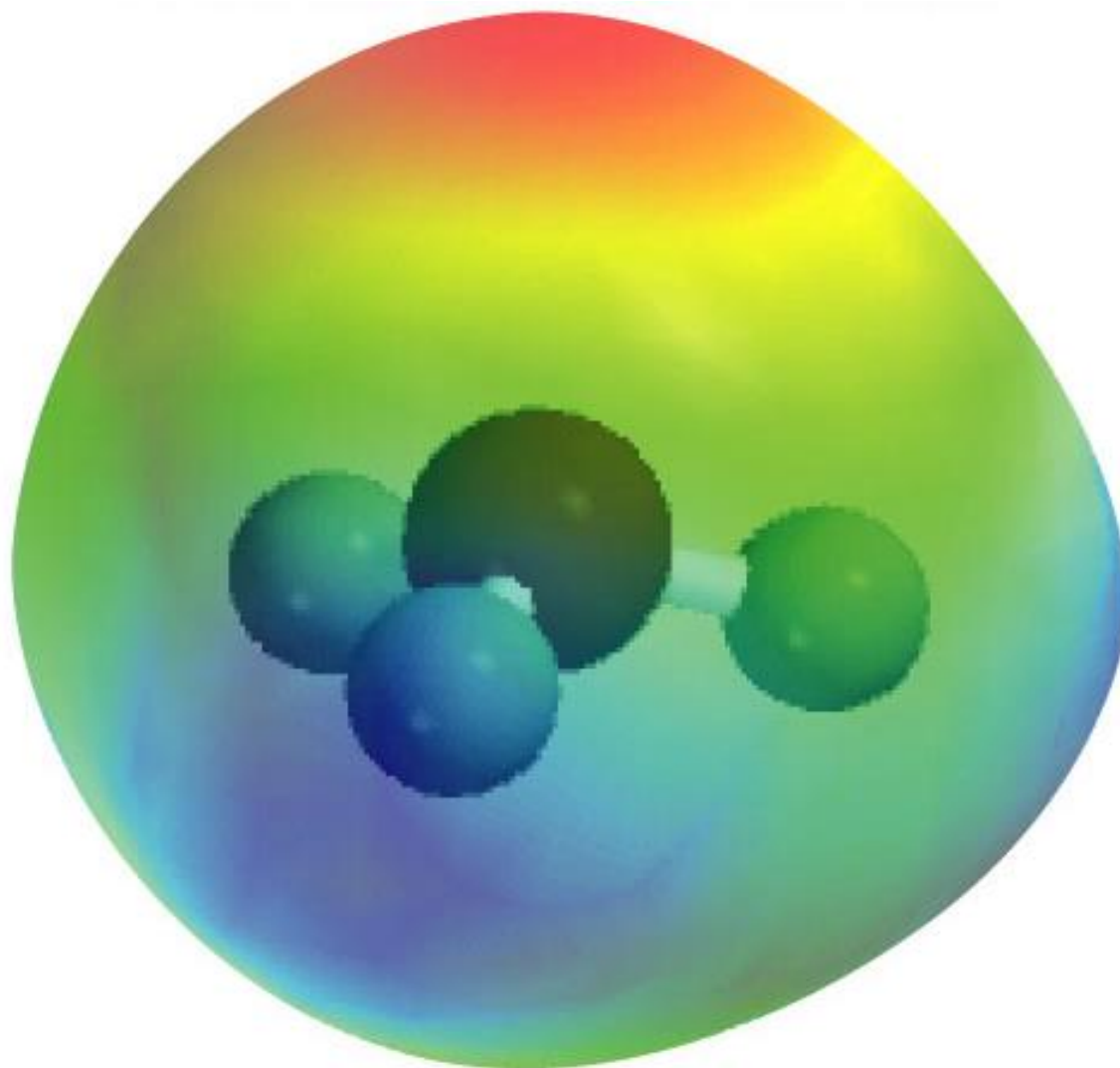
Arrhenius acid is a substance that produces H^+ (H_3O^+) in water.



Arrhenius base is a substance that produces OH^- in water.



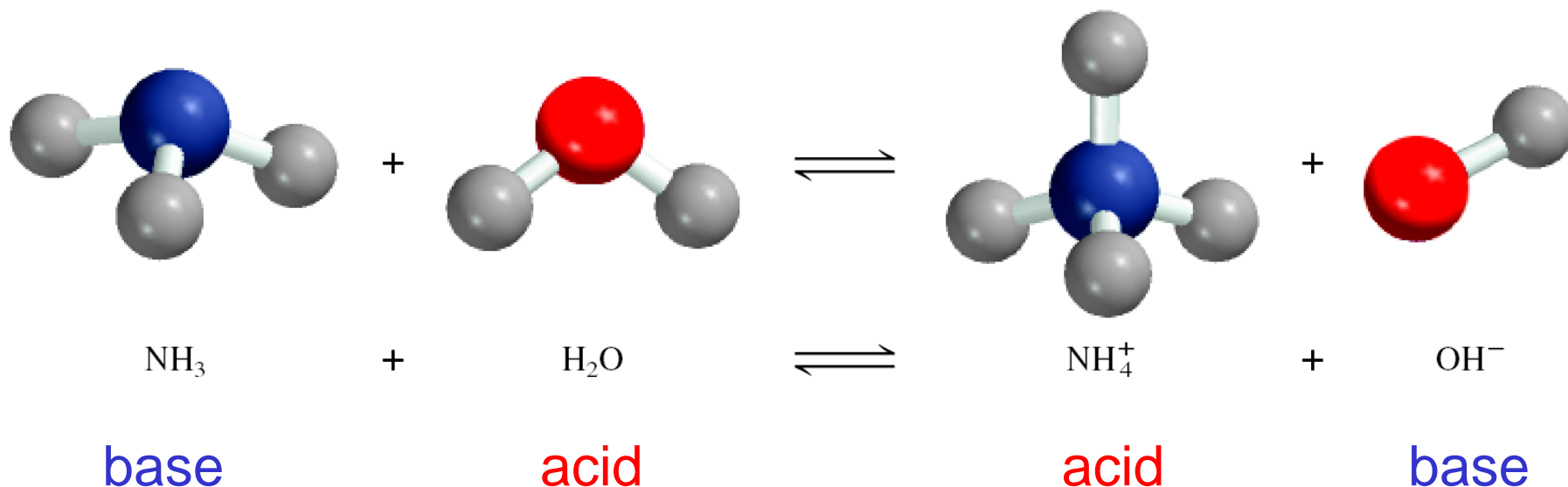
Hydronium ion, hydrated proton, H_3O^+



Brønsted Acid & Base

A **Brønsted acid** is a proton donor.

A **Brønsted base** is a proton acceptor.



A Brønsted acid must contain **at least one** ionizable proton!



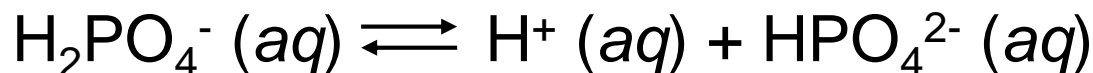
Identify each of the following as a Brønsted acid, base, or both. (a) HI, (b) CH_3COO^- , (c) H_2PO_4^- , (d) HSO_4^-



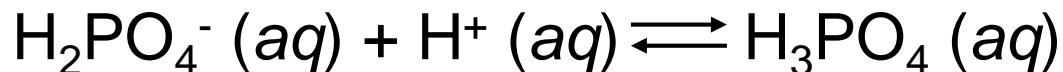
Brønsted acid



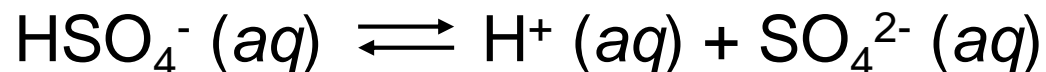
Brønsted base



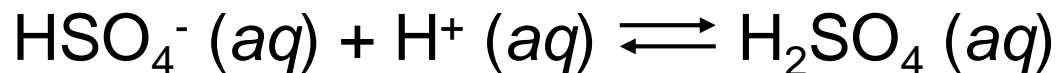
Brønsted acid



Brønsted base



Brønsted acid



Brønsted base

Mono-, Di- & Triprotic Acids

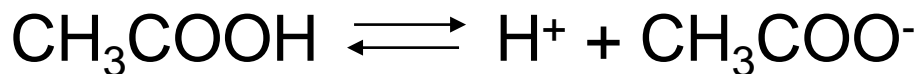
Monoprotic acids



Strong electrolyte, strong acid



Strong electrolyte, strong acid

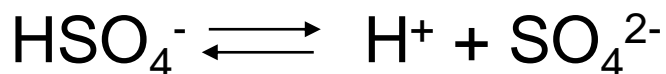


Weak electrolyte, weak acid

Diprotic acids

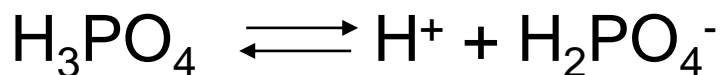


Strong electrolyte, strong acid

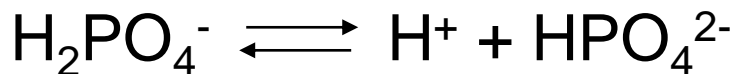


Weak electrolyte, weak acid

Triprotic acids



Weak electrolyte, weak acid



Weak electrolyte, weak acid



Weak electrolyte, weak acid

TABLE 4.3**Some Common Strong and Weak Acids****Strong Acids**

Hydrochloric acid HCl

Hydrobromic acid HBr

Hydroiodic acid HI

Nitric acid HNO_3

Sulfuric acid H_2SO_4

Perchloric acid HClO_4

Weak Acids

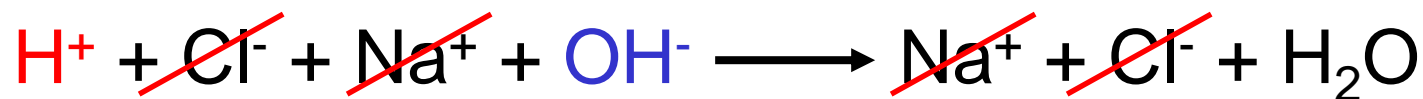
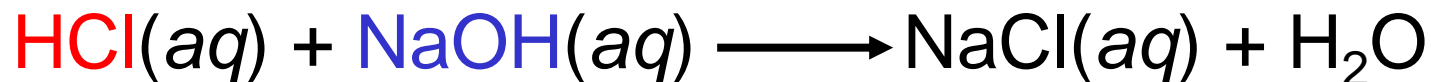
Hydrofluoric acid HF

Nitrous acid HNO_2

Phosphoric acid H_3PO_4

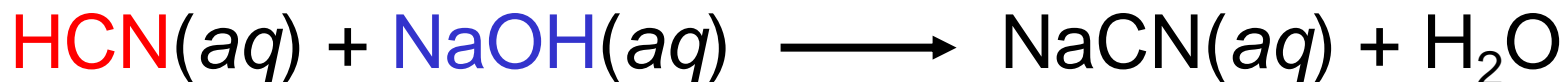
Acetic acid CH_3COOH

Neutralization Reaction

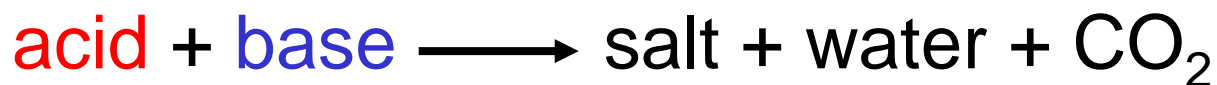


Neutralization Reaction Involving a Weak Electrolyte

weak acid + base \longrightarrow salt + water

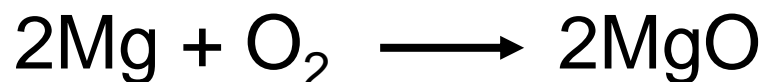
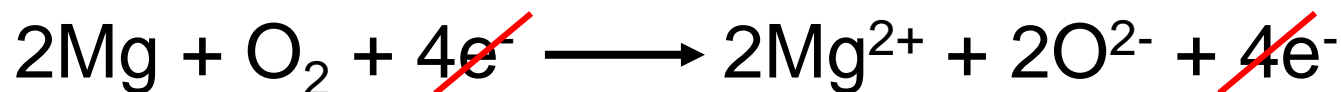
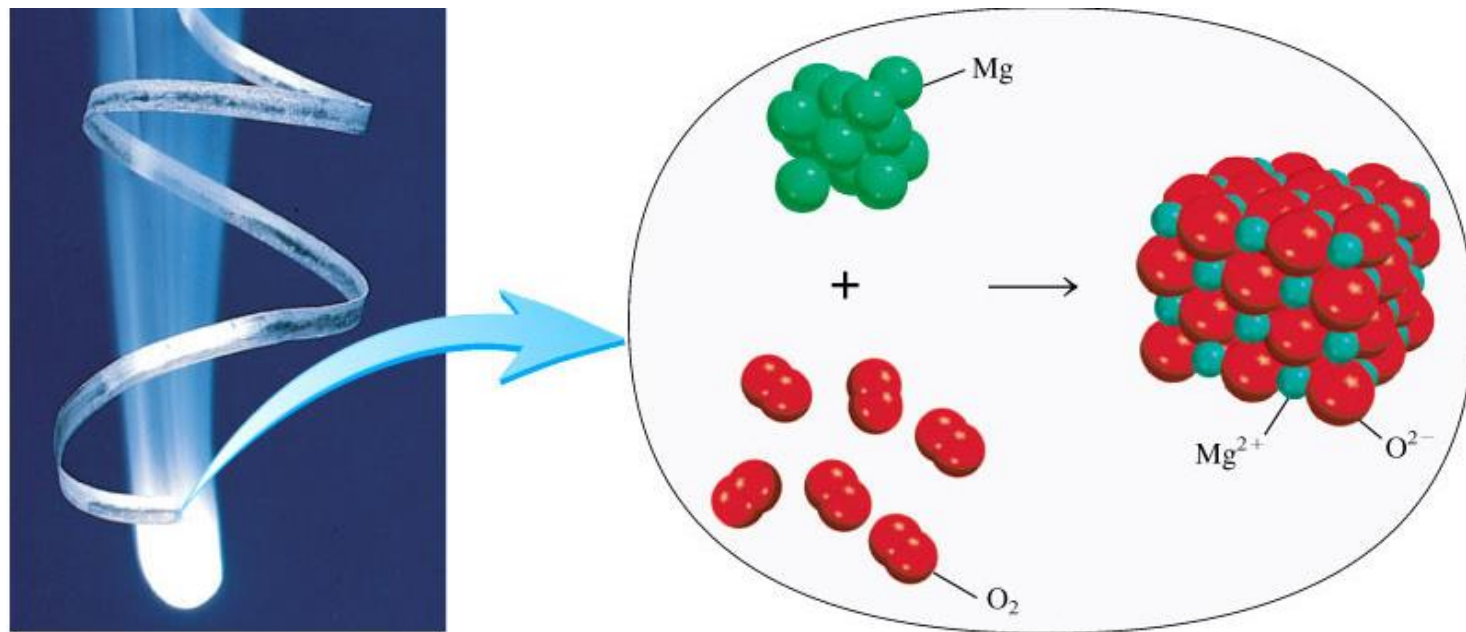


Neutralization Reaction Producing a Gas



Oxidation-Reduction Reactions

(electron transfer reactions)



Oxidation-Reduction Reactions

(electron transfer reactions)



OILRIG

Oxidation

Is

Loss of e^-

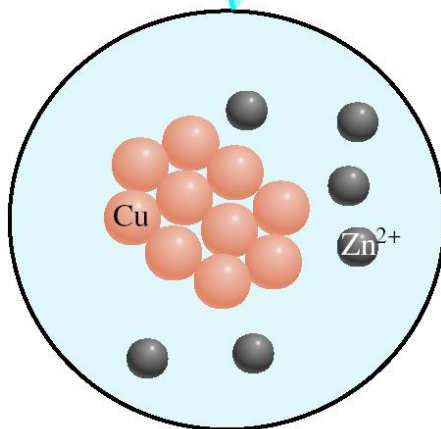
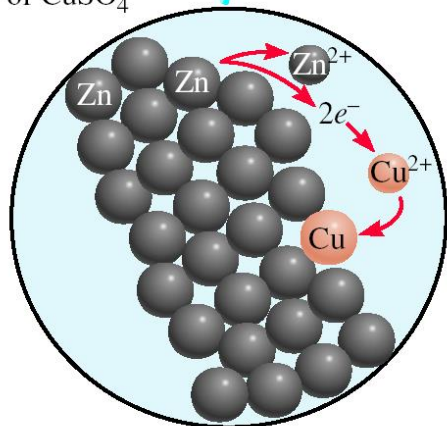
Reduction

Is

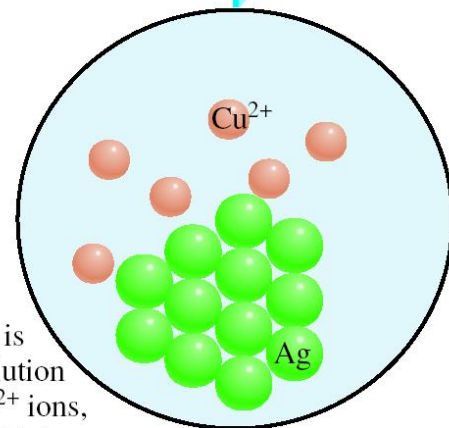
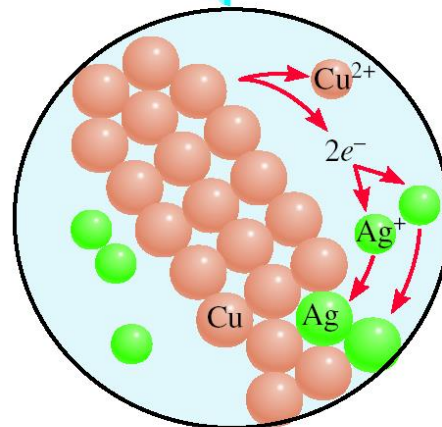
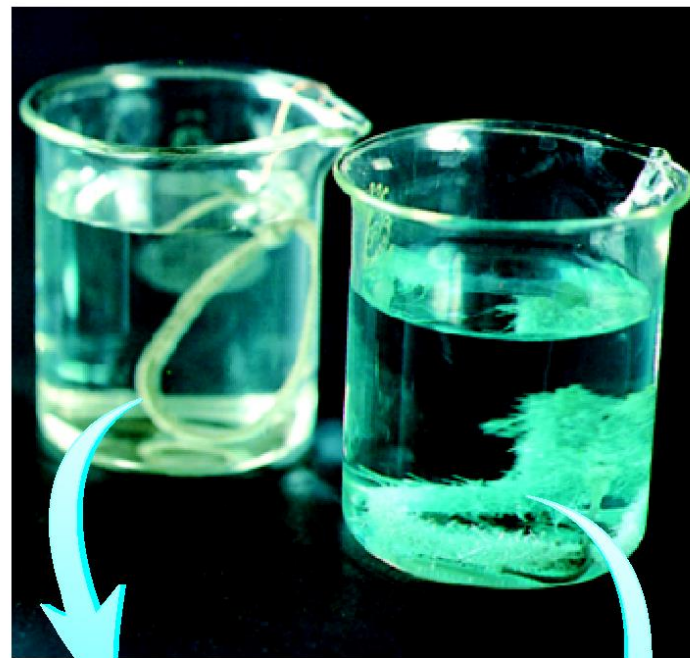
Gain of e^-



The Zn bar is in aqueous solution of CuSO_4



Cu^{2+} ions are converted to Cu atoms.
Zn atoms enter the solution as Zn^{2+} ions.



When a piece of copper wire is placed in an aqueous AgNO_3 solution Cu atoms enter the solution as Cu^{2+} ions, and Ag^+ ions are converted to solid Ag.

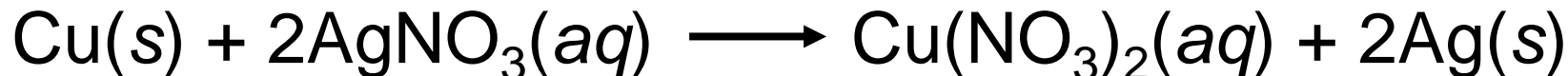
- Zinc bar reacts with copper(II) sulfate to form copper metal. Write the redox reaction, half-reactions & identify the oxidizing agent, reducing agent.



$\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$ Zn is oxidized Zn is the **reducing agent**

$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$ Cu²⁺ is reduced Cu²⁺ is the **oxidizing agent**

- Copper wire reacts with silver nitrate to form silver metal. Write the redox reaction, half-reactions & identify the oxidizing agent, reducing agent.



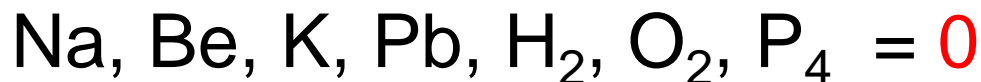
$\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$ Cu is oxidized Cu is the **reducing agent**

$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$ Ag⁺ is reduced Ag⁺ is the **oxidizing agent**

Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.



2. In monatomic ions, the oxidation number is equal to the charge on the ion.



3. The oxidation number of oxygen is **usually** -2 . In H_2O_2 and O_2^{2-} it is -1 .

4. The oxidation number of hydrogen is **+1** *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is **-1**.
5. Group IA metals are **+1**, IIA metals are **+2** and fluorine is always **-1**.
6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.
7. Oxidation numbers do not have to be integers.
Oxidation number of oxygen in the superoxide ion, O_2^- , is **$-\frac{1}{2}$** .

What are the oxidation numbers of all the elements in HCO_3^- ?



$$\text{O} = \textbf{-2} \quad \text{H} = \textbf{+1}$$

$$3\text{x}(\textbf{-2}) + \textbf{1} + \textbf{?} = \textbf{-1}$$

$$\text{C} = \textbf{+4}$$

The Oxidation Numbers of Elements in their Compounds

1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A											
1 H +1 -1												5 B +3	6 C +4 +2 -4	7 N +5 +4 +3 +2 +1 -3	8 O +2 +1 -2	9 F -1	10 Ne											
2 2A	3 Li +1	4 Be +2												11 Na +1	12 Mg +2	13 Al +3	14 Si +4 -4	15 P +5 +3 -3	16 S +6 +4 +2 -2	17 Cl +7 +6 +5 +4 +3 +1 -1	18 Ar							
	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	19 K +1	20 Ca +2	21 Sc +3	22 Ti +4 +3 +2	23 V +5 +4 +3 +2	24 Cr +6 +5 +4 +3 +2	25 Mn +7 +6 +4 +3 +2	26 Fe +3 +2	27 Co +3 +2	28 Ni +2	29 Cu +2 +1	30 Zn +2	31 Ga +3	32 Ge +4 -4	33 As +5 +3 -3	34 Se +6 +4 -2	35 Br +5 +3 +1 -1	36 Kr +4 +2
	37 Rb +1	38 Sr +2	39 Y +3	40 Zr +4	41 Nb +5 +4	42 Mo +6 +4 +3	43 Tc +7 +6 +4	44 Ru +8 +6 +4 +3	45 Rh +4 +3 +2	46 Pd +4 +2	47 Ag +1	48 Cd +2	49 In +3	50 Sn +4 +2	51 Sb +5 +3 -3	52 Te +6 +4 -2	53 I +7 +5 +1 -1	54 Xe +6 +4 +2										
	55 Cs +1	56 Ba +2	57 La +3	72 Hf +4	73 Ta +5	74 W +6 +4	75 Re +7 +6 +4	76 Os +8 +4	77 Ir +4 +3	78 Pt +4 +2	79 Au +3 +1	80 Hg +2 +1	81 Tl +3 +1	82 Pb +4 +2	83 Bi +5 +3	84 Po +2	85 At -1	86 Rn										

What are the oxidation numbers of all the elements in each of these compounds?



$$\text{Na} = +1 \quad \text{O} = -2$$

$$3x(-2) + 1 + ? = 0$$

$$\text{I} = +5$$



$$\text{F} = -1$$

$$7x(-1) + ? = 0$$

$$\text{I} = +7$$



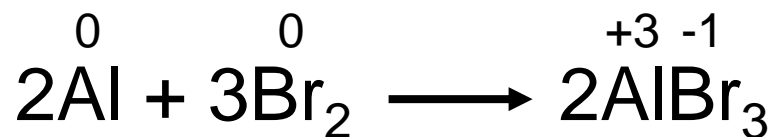
$$\text{O} = -2 \quad \text{K} = +1$$

$$7x(-2) + 2x(+1) + 2x(?) = 0$$

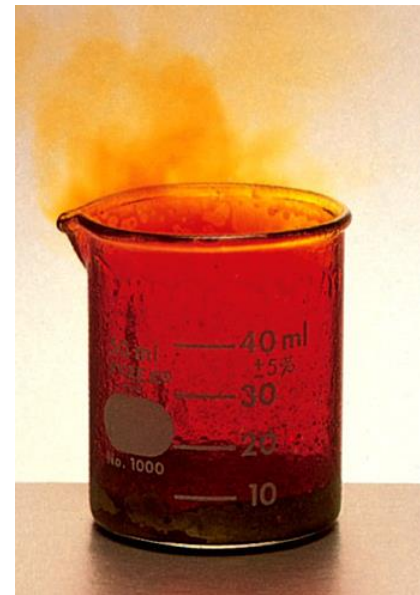
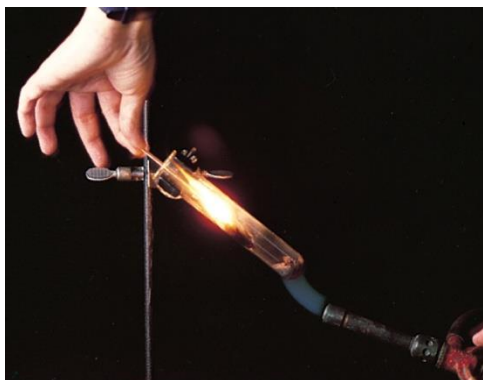
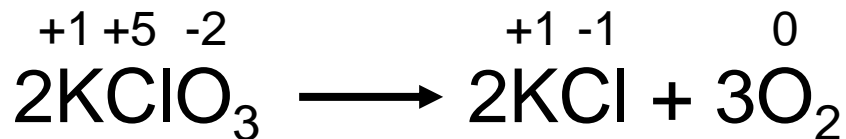
$$\text{Cr} = +6$$

Types of Oxidation-Reduction Reactions

Combination Reaction

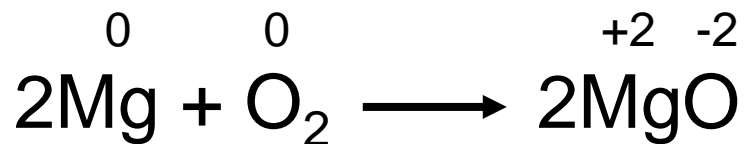
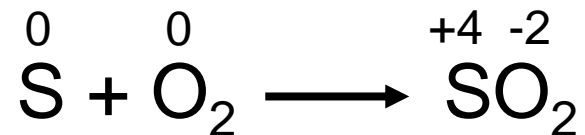
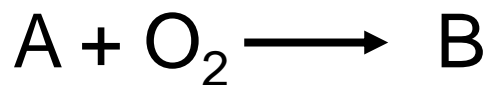


Decomposition Reaction



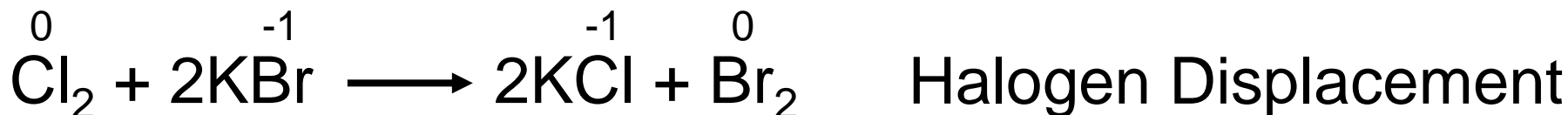
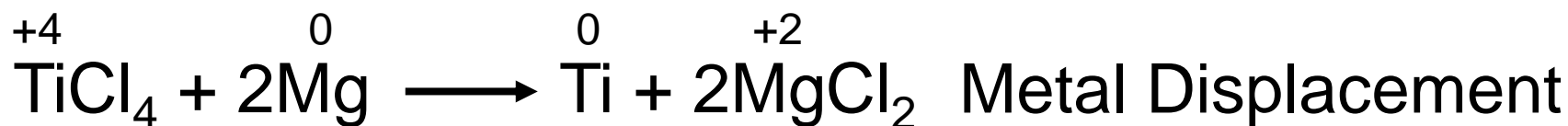
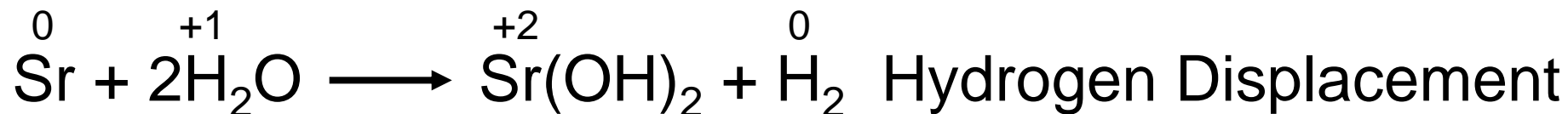
Types of Oxidation-Reduction Reactions

Combustion Reaction




Types of Oxidation-Reduction Reactions

Displacement Reaction



The Activity Series for Metals



$\text{Li} \rightarrow \text{Li}^+ + e^-$	
$\text{K} \rightarrow \text{K}^+ + e^-$	
$\text{Ba} \rightarrow \text{Ba}^{2+} + 2e^-$	React with cold water to produce H_2
$\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$	
$\text{Na} \rightarrow \text{Na}^+ + e^-$	
$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	
$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$	
$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$	React with steam to produce H_2
$\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$	
$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	
$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$	
$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$	
$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$	React with acids to produce H_2
$\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^-$	
$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$	
$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$	
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$	
$\text{Ag} \rightarrow \text{Ag}^+ + e^-$	
$\text{Hg} \rightarrow \text{Hg}^{2+} + 2e^-$	Do not react with water or acids to produce H_2
$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$	
$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$	

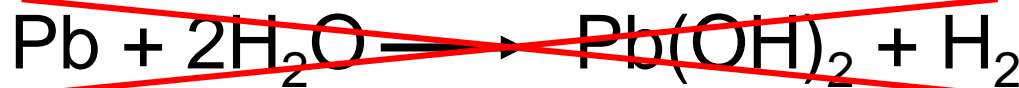
Hydrogen Displacement Reaction



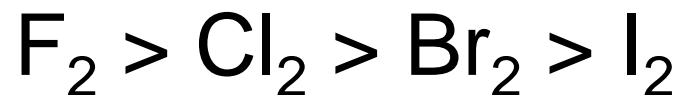
M is metal

BC is acid or H_2O

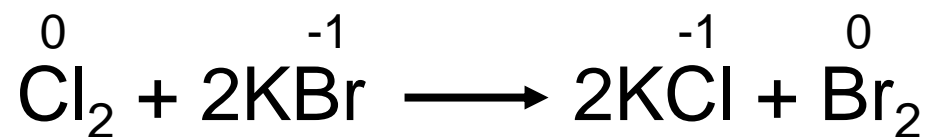
B is H_2



The Activity Series for Halogens



Halogen Displacement Reaction

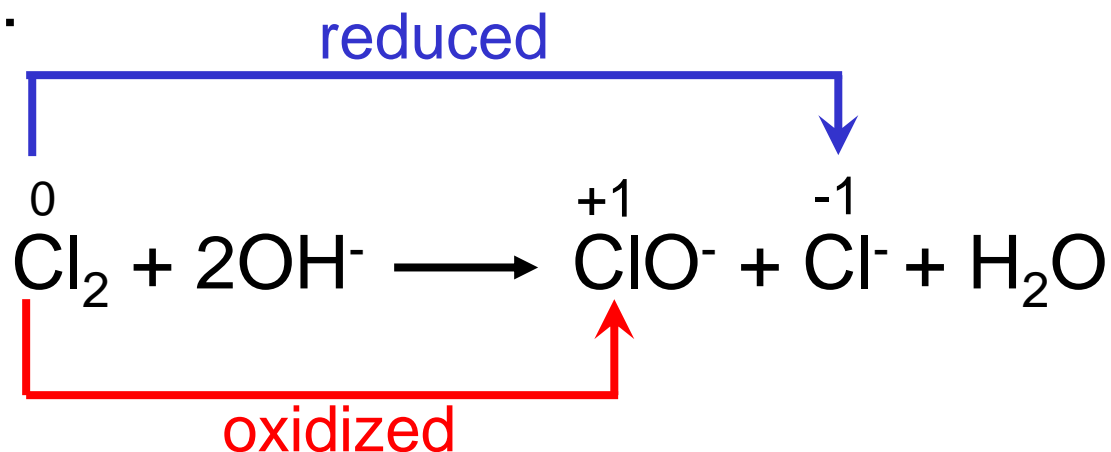


Types of Oxidation-Reduction Reactions

Disproportionation Reaction

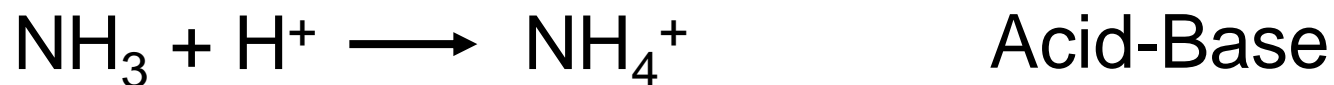
The same element is simultaneously oxidized and reduced.

Example:

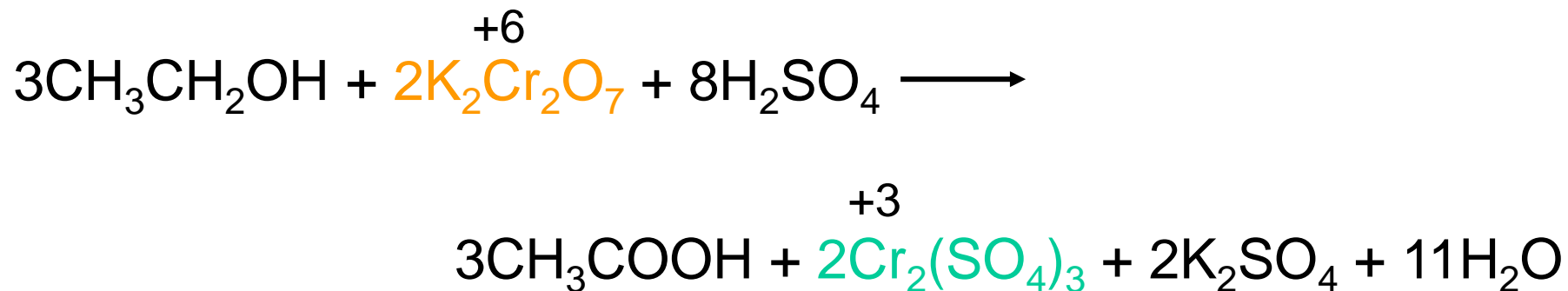




Classify each of the following reactions.



Chemistry in Action: Breath Analyzer



Solution Stoichiometry

The **concentration** of a solution is the amount of solute present in a given quantity of solvent or solution.

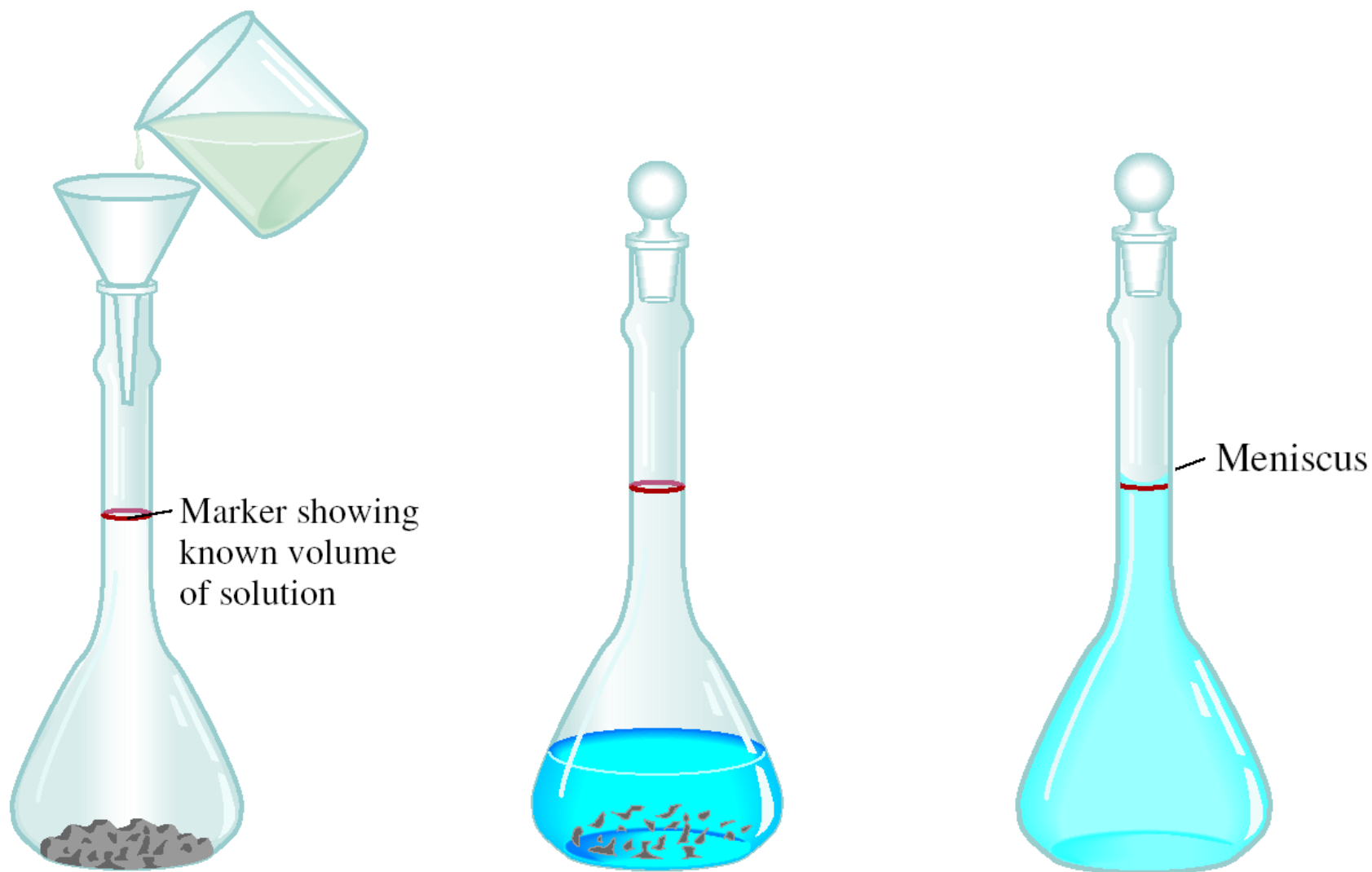
$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

What mass of KI is required to make 500.0 mL of a 2.80 M KI solution?

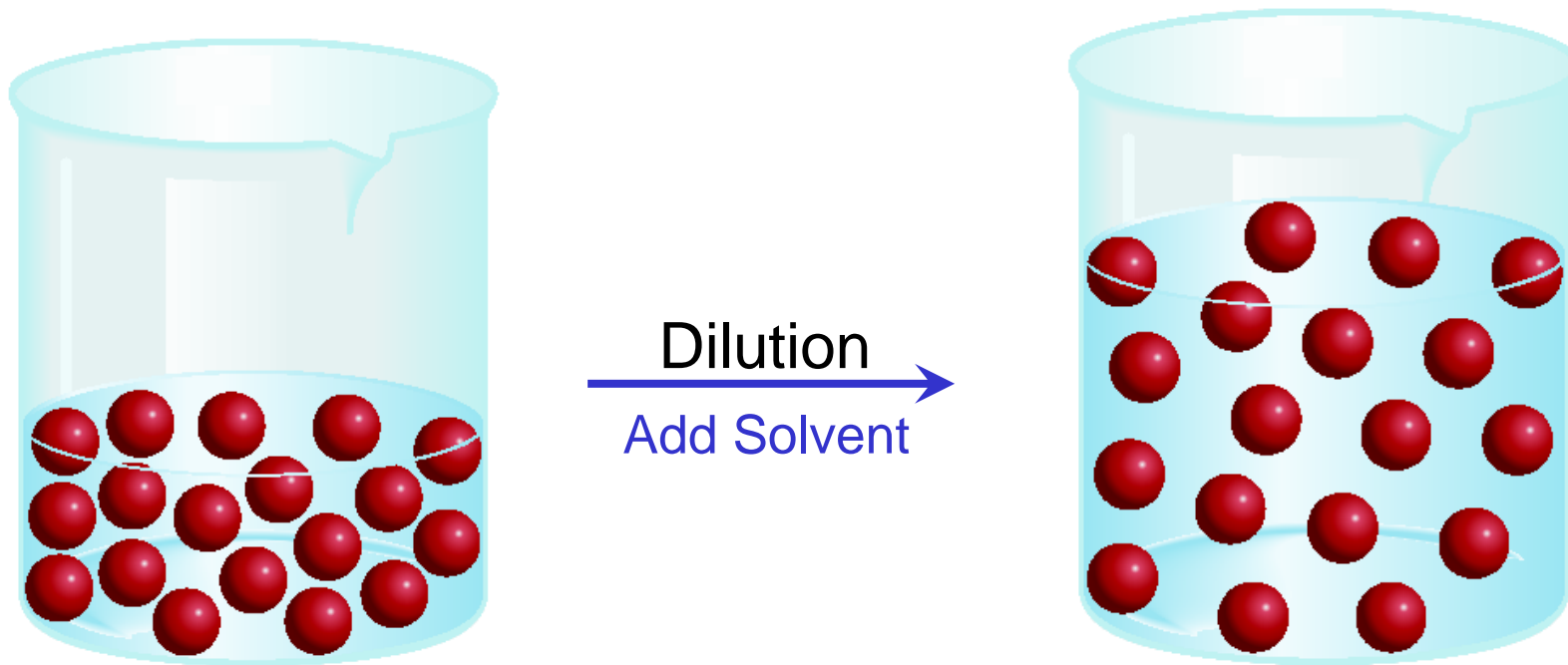
volume of KI solution $\xrightarrow{M \text{ KI}}$ moles KI $\xrightarrow{M \text{ KI}}$ grams KI

$$500.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{2.80 \text{ mol KI}}{1 \text{ L soln}} \times \frac{166 \text{ g KI}}{1 \text{ mol KI}} = 232 \text{ g KI}$$

Preparing a Solution of Known Concentration



Dilution is the procedure for preparing a less concentrated solution from a more concentrated solution.



Moles of solute
before dilution (i)

=

Moles of solute
after dilution (f)

$$M_i V_i$$

=

$$M_f V_f$$

How would you prepare 60.0 mL of 0.200 M HNO_3 from a stock solution of 4.00 M HNO_3 ?

$$M_i V_i = M_f V_f$$

$$M_i = 4.00 \text{ M} \quad M_f = 0.200 \text{ M} \quad V_f = 0.0600 \text{ L} \quad V_i = ? \text{ L}$$

$$V_i = \frac{M_f V_f}{M_i} = \frac{0.200 \text{ M} \times 0.0600 \text{ L}}{4.00 \text{ M}} = 0.00300 \text{ L} = 3.00 \text{ mL}$$

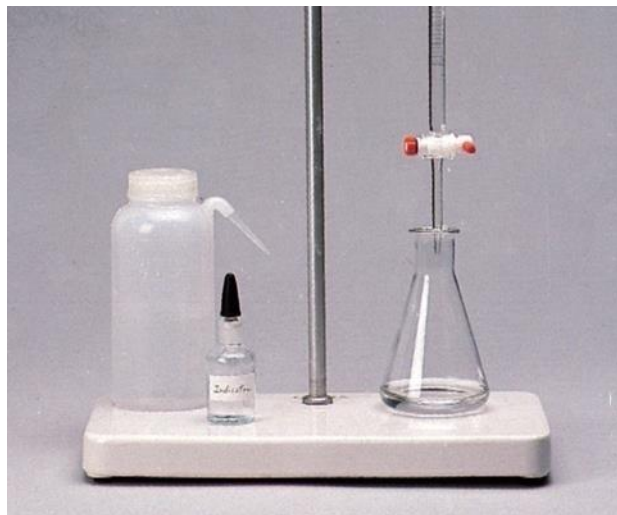
Dilute 3.00 mL of acid with water to a total volume of 60.0 mL.

Titration

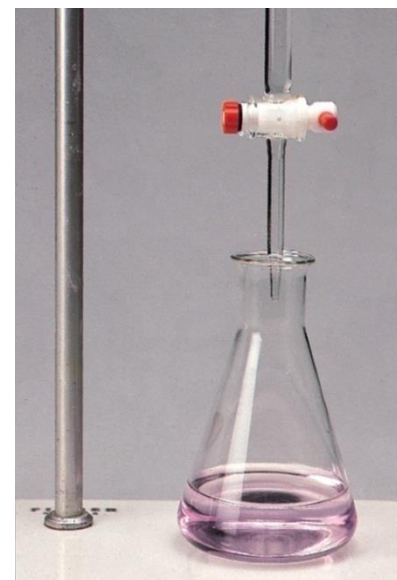
In a **titration** a solution of accurately known concentration is added gradually to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Equivalence point – the point at which the reaction is complete

Indicator – substance that changes color at (or near) the equivalence point



Slowly add base
to unknown acid
UNTIL
the indicator
changes color



What volume of a 1.420 M NaOH solution is required to titrate 25.00 mL of a 4.50 M H₂SO₄ solution?

WRITE THE CHEMICAL EQUATION!



volume acid $\xrightarrow[\text{acid}]{M}$ moles reqd $\xrightarrow[\text{coef.}]{\text{rxn}}$ moles base $\xrightarrow[\text{base}]{M}$ volume base

$$25.00 \text{ mL} \times \frac{4.50 \text{ mol H}_2\text{SO}_4}{1000 \text{ mL soln}} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_4} \times \frac{1000 \text{ mL soln}}{1.420 \text{ mol NaOH}} = 158 \text{ mL}$$