

Chapter 9

Chemical Reactions in Aqueous Solutions



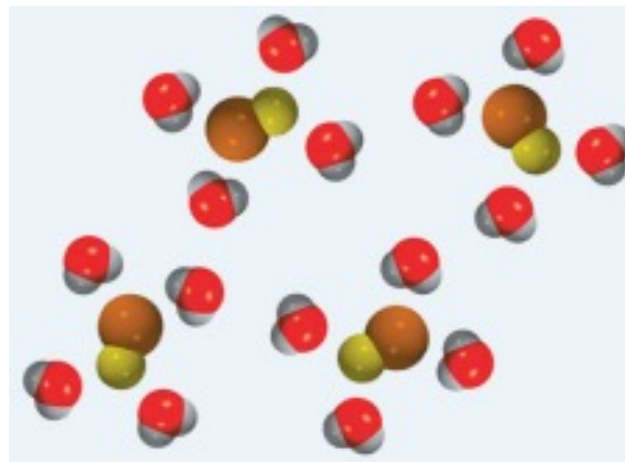
Solutions: Key Terms

Solution

- Homogenous mixture of 2 or more substances

Solvent:

- Component with largest amount
- Water, the “universal solvent”
 - (does not dissolve everything)

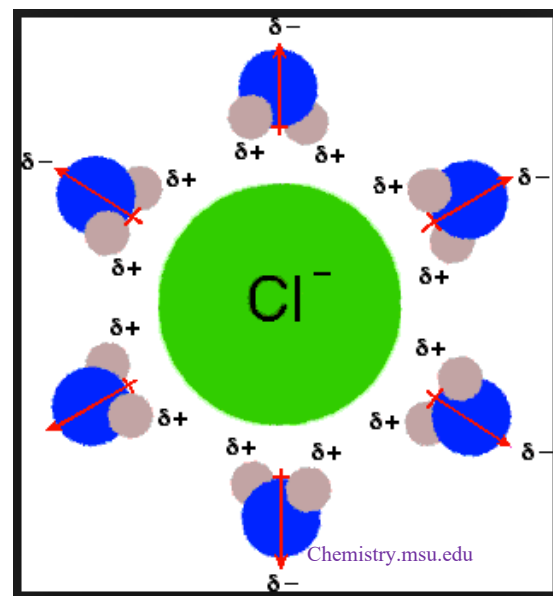


Solute:

- Components present in smaller amounts than the solvent

Solvation/dissolving:

- Solvent molecules surround & support solute molecules or ions
- Solvent is NOT part of chemical reactions



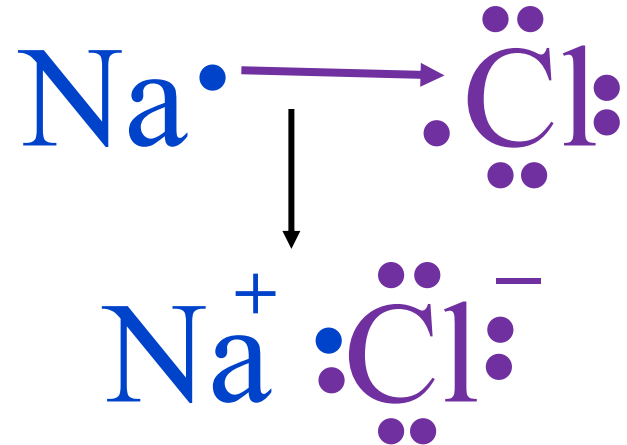
Solubility Depends on Bond Type

Electronegativity – measure of atom's attraction for electrons

- Electronegativity difference determines bonding type

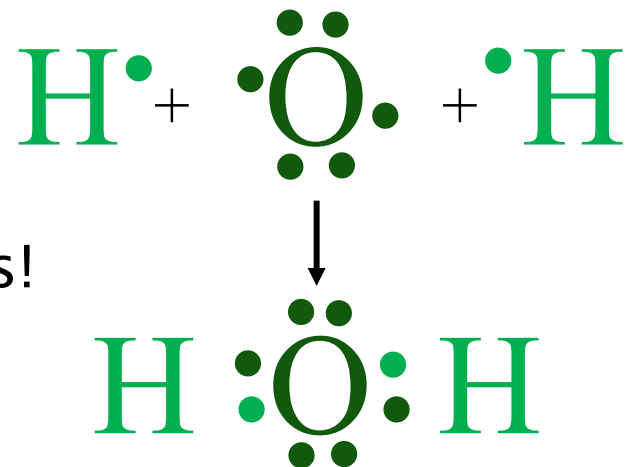
Ionic:

- Large electronegativity difference
- Metal + nonmetal
- Transfer of electrons
 - Involves ions – have charges!



Covalent:

- Moderate to small electroneg. diff.
- Often two nonmetals
- Electrons are shared
 - Atoms remain neutral – not ions!
- Two kinds, polar and nonpolar



Covalent Bonds: Nonpolar vs Polar

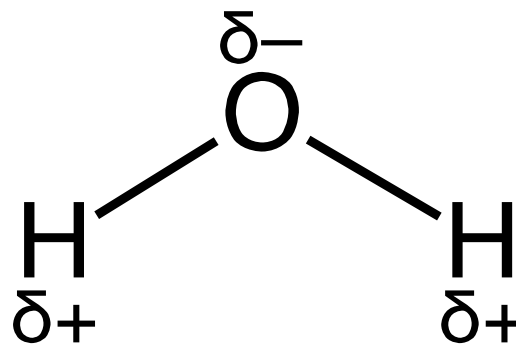
Nonpolar – electrons shared equally

- very small/no electroneg. difference
- no partial charges

Polar – electrons shared unequally

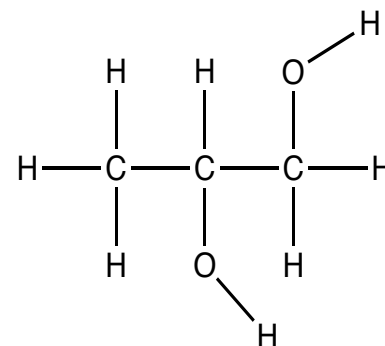
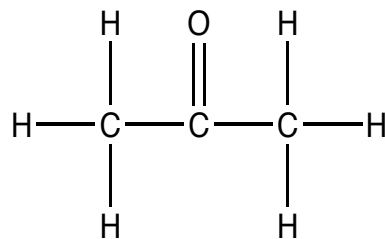
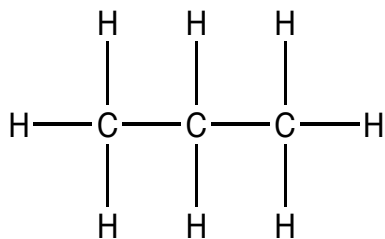
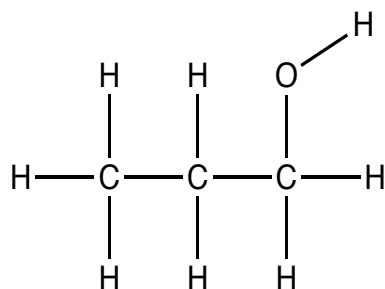
- moderate electroneg. difference
- **results in partially charged atoms (δ^+ or δ^-)**
- water is polar

Like Dissolves Like!



Rank the following in order of increasing water solubility.

Remember that water is polar & can hydrogen bond
Greater polarity & hydrogen bonding ability increase water solubility.



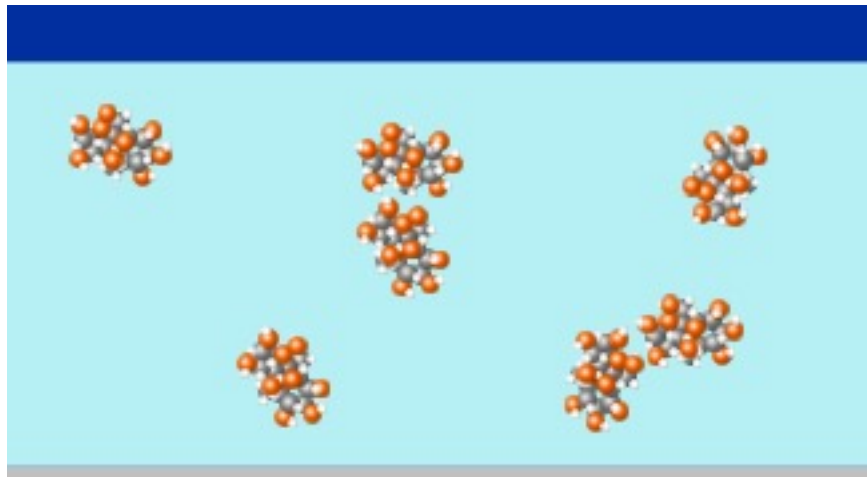
Dissolution vs Dissociation

Ionic & Covalent Compounds Behave Differently

Sugar vs Salt

Dissolution vs Dissociation

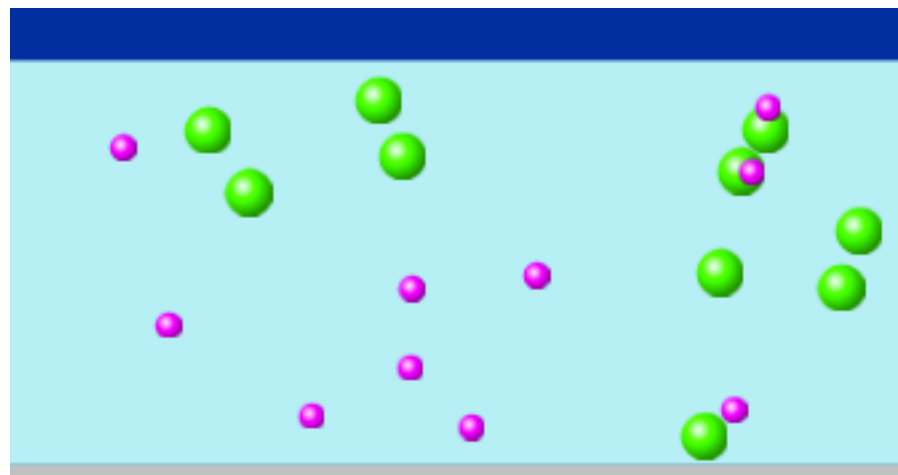
Covalent Molecule



Dissolved sugar:

- molecule remains together
- NOT dissociation!

Ionic Salt



Dissolved salt:

- ions separate
- dissociation!

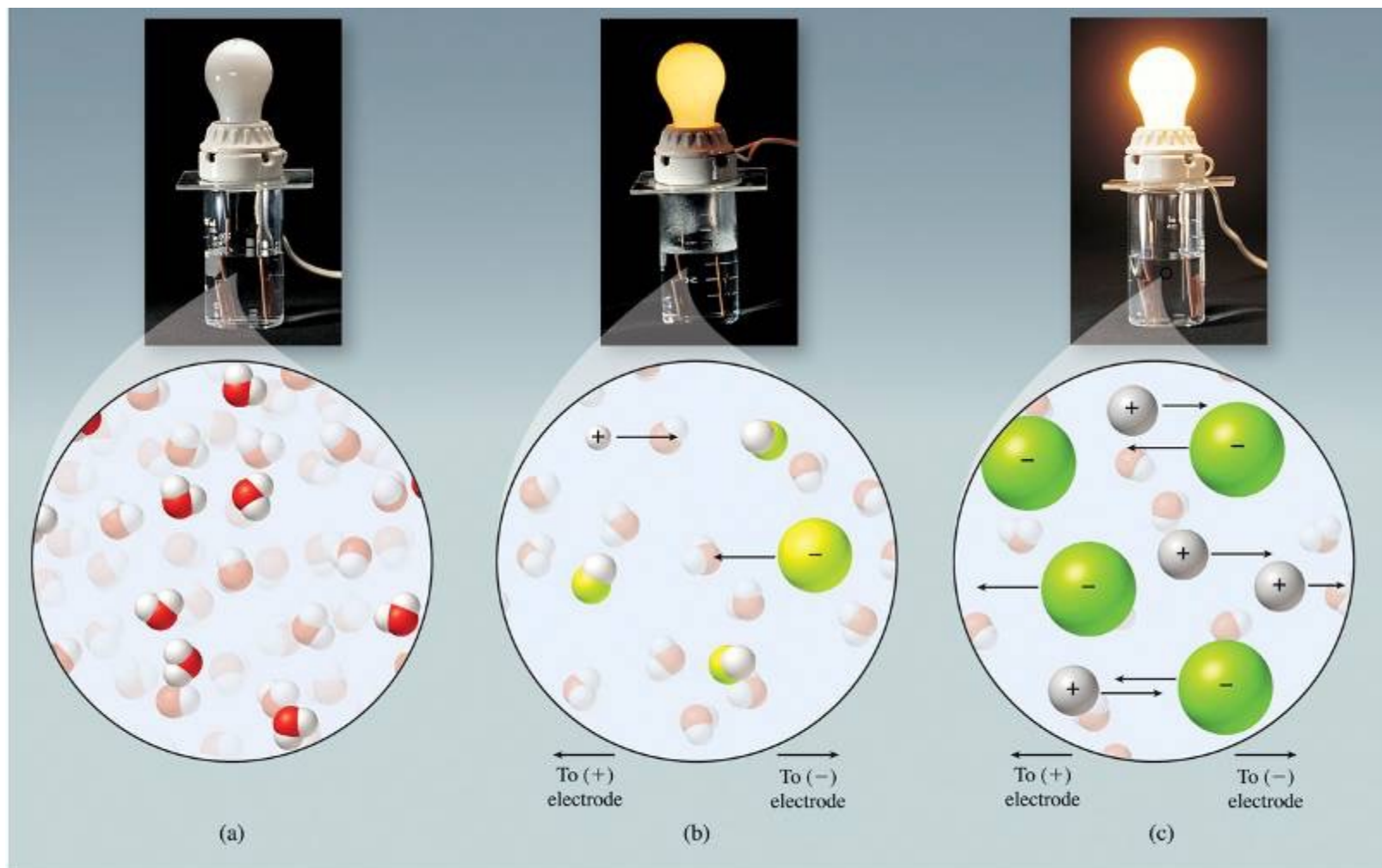
Extent of dissociation/ionization impacts many properties
– e.g. acid base strength, conductivity, freezing point

Conductivity of Electrolytes in Aqueous Solutions

Non-electrolyte
No ionization
Ex: sugar

Weak electrolyte
Some ionization
Ex: acetic acid

Strong electrolyte
Full ionization
Ex: NaCl



Concentration of Solutions: Molarity

Molarity (M) = moles solute/L solution

- Units: mol/L (molar, M)
- **Conversion factor between moles solute & volume of solution.**

How to prepare 2 liters of a 1.0M solution of NaCl:

1. Calculate mass of NaCl needed.

$$\frac{1\text{mol}_{\text{NaCl}}}{1\text{L}_{\text{NaCl}}} \times \frac{58.5\text{g}_{\text{NaCl}}}{1\text{mol}_{\text{NaCl}}} \times \frac{2\text{L}_{\text{NaCl}}}{1} = 117\text{g}_{\text{NaCl}}$$

2. Weigh out mass of NaCl.

3. Pour NaCl into volumetric flask.

4. Add water until the water reaches the 2L mark.



Molality

Molality (m) = moles solute/kg solvent

Units: mol/kg (molal, m)

Based on mass, not volume, therefore:

NOT TEMPERATURE DEPENDENT

How to prepare ~2 kg of a 1.0m solution of NaCl:

1. Calculate mass of NaCl needed.

$$\frac{1 \text{ mol}_{\text{NaCl}}}{\text{kg solv.}} \times \frac{58.5 \text{ g}_{\text{NaCl}}}{1 \text{ mol}_{\text{NaCl}}} \times 2 \text{ kg solv.} = 117 \text{ g}_{\text{NaCl}}$$

2. Weigh out mass of NaCl.

3. Place NaCl into container.

4. Tare (zero) the container. Add water until you obtain the desired mass of water.

Molarity Calculations:

1. What is the concentration, in moles/L, if 22.8 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is dissolved to make 500.0 mL of solution?

A: 0.155 M

2. How many grams of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) are needed to prepare 125 mL of a 1.83 M solution?

A: 67.3 g

3. What volume, in mL, of a 2.50 M solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) would contain 350.0 g of $\text{K}_2\text{Cr}_2\text{O}_7$?

A: 476 mL

Dilution Calculations

Water is added to a small amount of stock solution to make a less concentrated solution.

Addition of solvent does not change the mass or moles of solute in a solution but does change the solution concentration.



$$M_1V_1 = M_2V_2$$

$$(\text{mol/L})(\text{L}) = (\text{mol/L})(\text{L})$$

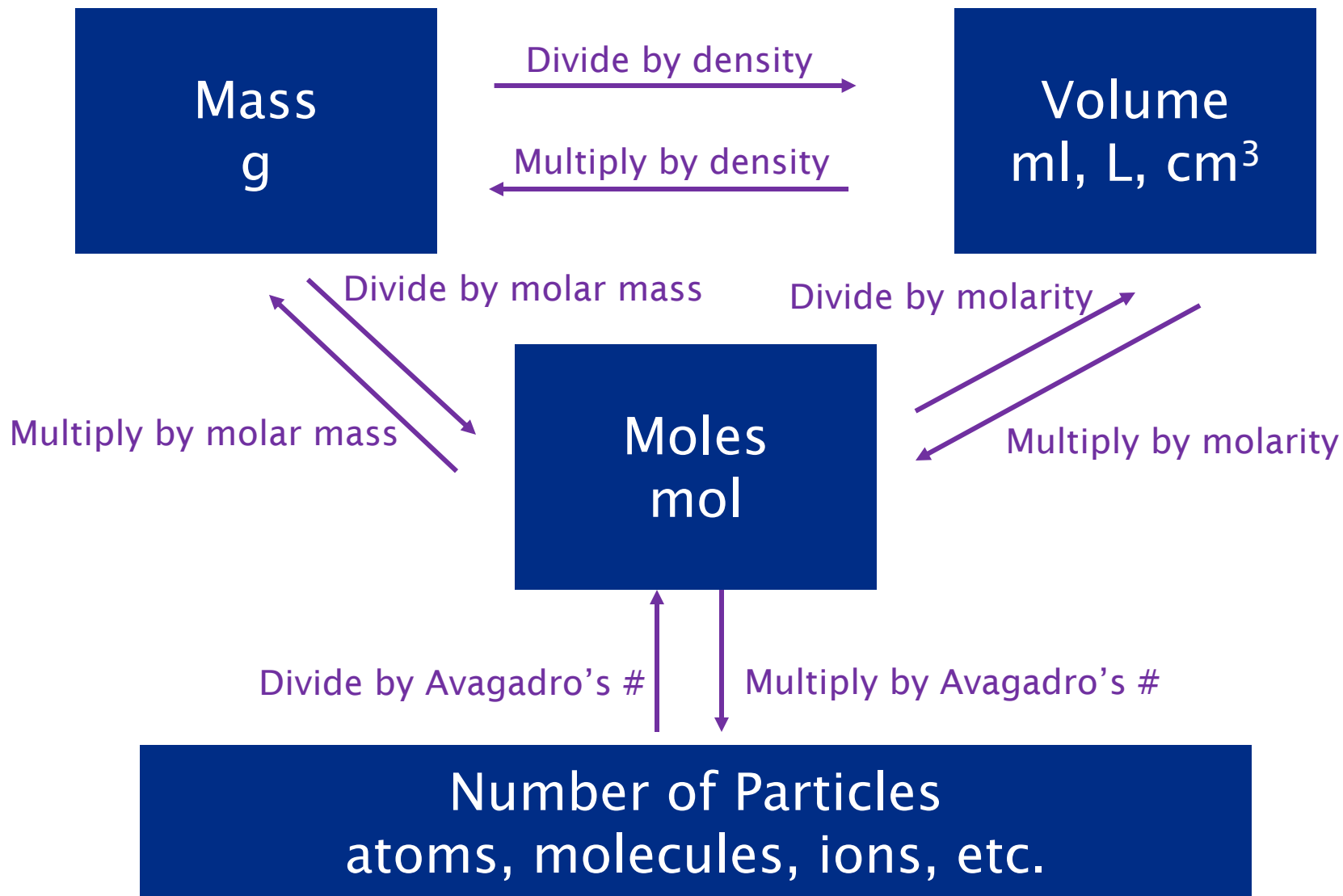


Calculate the volume of 1.0M stock solution needed to make 2000.0mL of a 0.12M solution of HCl.

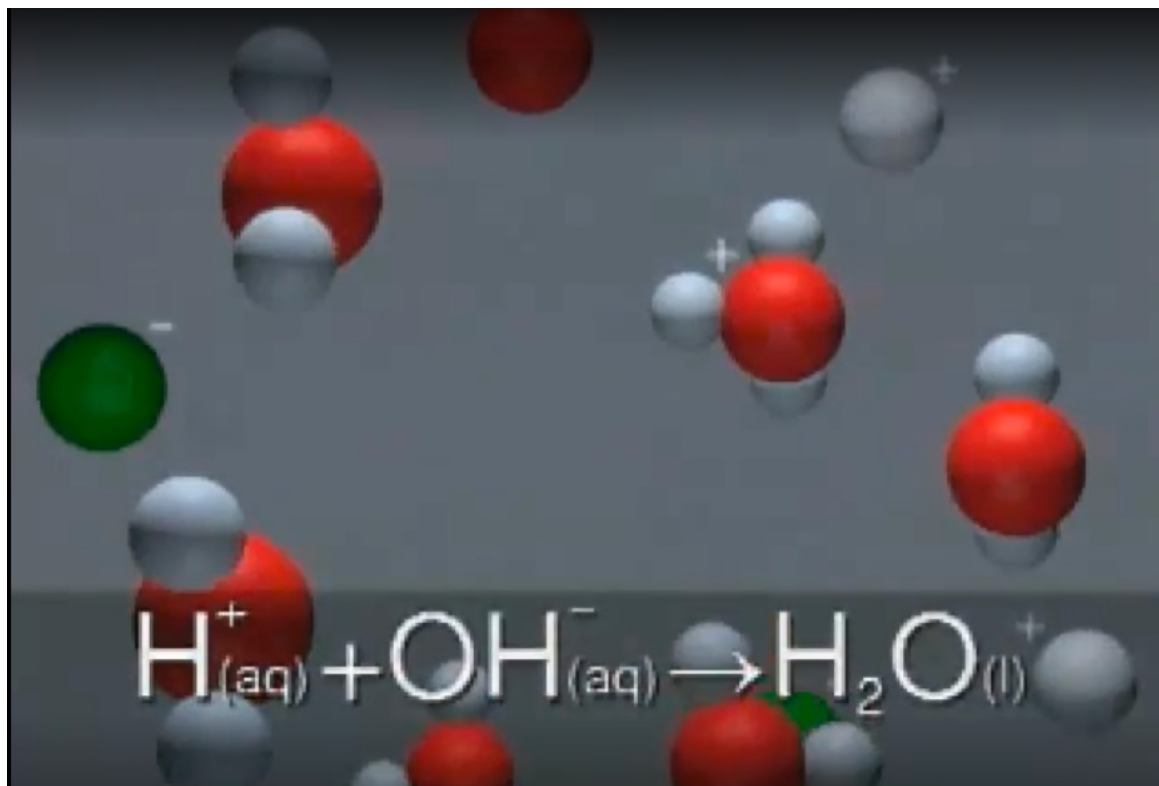
A: 240 mL

**This equation is ONLY for dilutions.
Never use this equation for titrations.**

Conversion Relationships



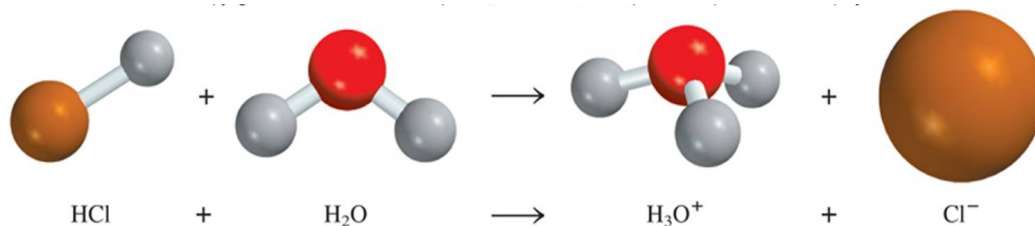
Acid–Base Reactions



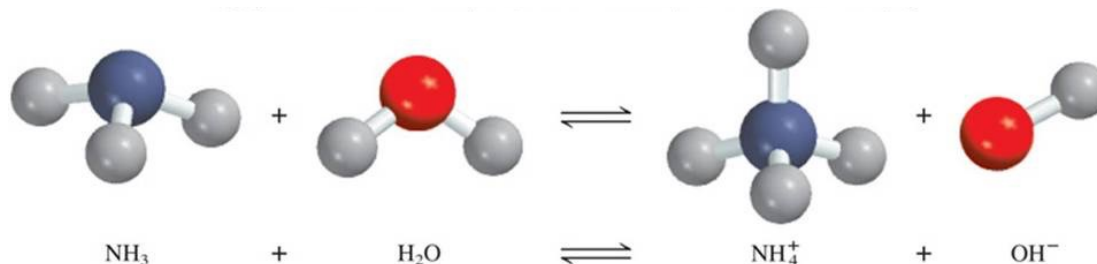
Acid–Base Reactions

Arrhenius Acids and Bases

Acid: Compound that ionizes in water to form a solution of H^+ ions (H_3O^+) and anions.



Base: Compound that ionizes in water to form a solution of OH^- ions and cations



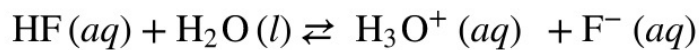
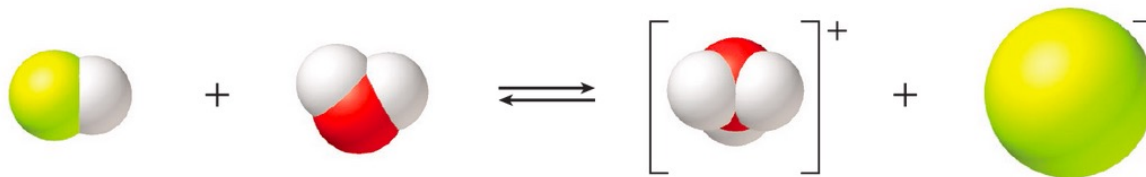
Neutralization: Reaction between Arrhenius acid & base
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ & cation + anion \rightarrow salt

Acid–Base Reactions

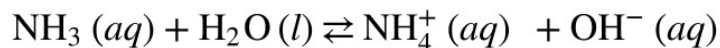
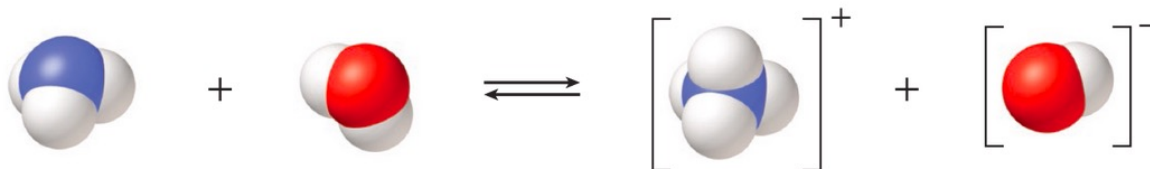
Brønsted Acids and Bases

A hydrogen atom that has lost its electron is often referred to as a **proton** (because that is all that is left).

Acid: Proton donor



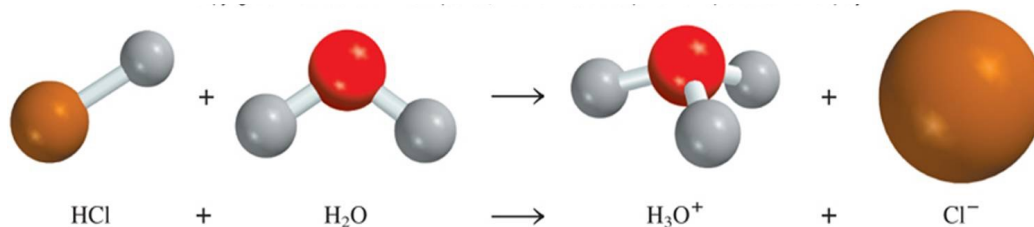
Base: proton acceptor



Strength of Acids and Bases

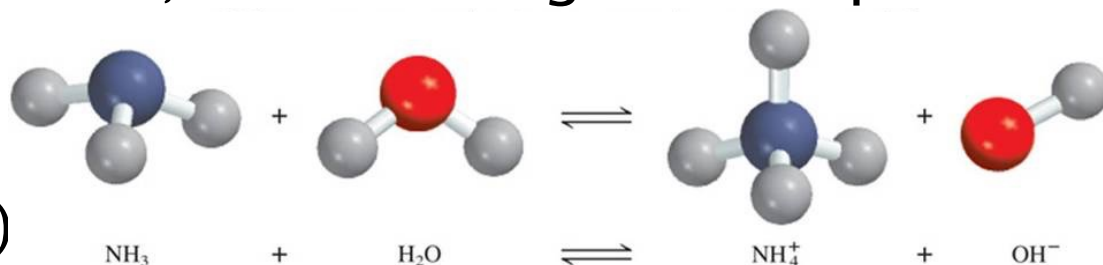
Strong acids and bases

- Completely ionized in water to give either H_3O^+ or OH^-
- Good conductors of electricity.
- Directional arrow (\rightarrow) indicates dissociation is complete



Weak acids and bases

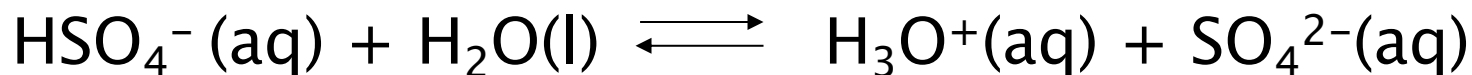
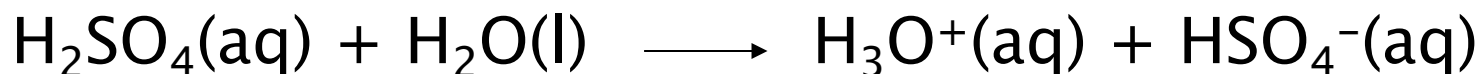
- Partial ionization in water, most of original compound remains
- Poor conductors
- Double arrow (\leftrightarrow , \rightleftharpoons) indicates dissociation is incomplete



Polyprotic Acids

Acids that have more than one ionizable proton

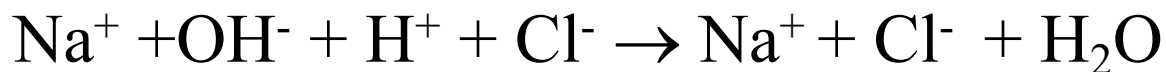
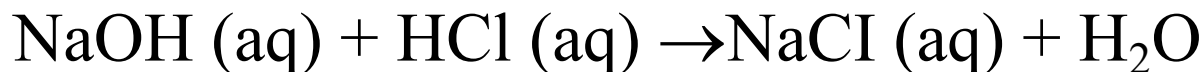
- Monoprotic – one ionizable proton
- Diprotic – two ionizable protons
- Polyprotic – multiple ionizable protons
- Ionize in successive steps



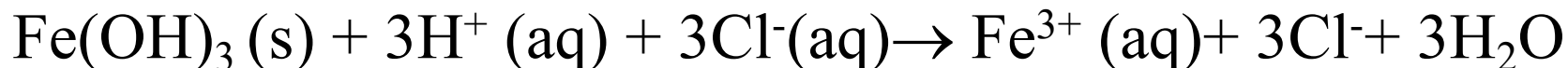
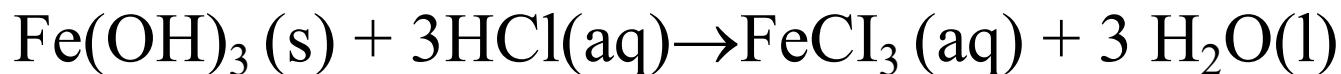
- In this case, the first proton dissociates completely
 - strong
- The second proton is only partially removed
 - weak

Acid-Base Neutralizations

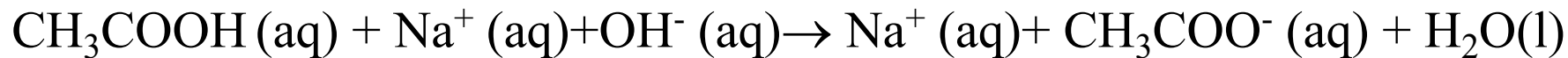
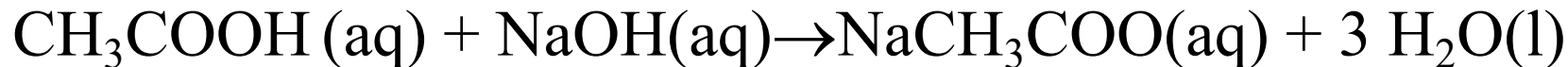
Strong acid with strong base



Solid (weak) base with strong acid



Weak acid with strong base



Common Acids and Bases

Strong Acids

HCl, HI, HBr

HNO₃

H₂SO₄

HClO₄

Weak Acids

HF, HNO₂, H₃PO₄

Acetic acid (CH₃COOHH)

Organic acids tend to be weak

Strong Bases

NaOH, KOH,
LiOH

Ba(OH)₂

Weak Bases

Other hydroxides
(don't dissolve)

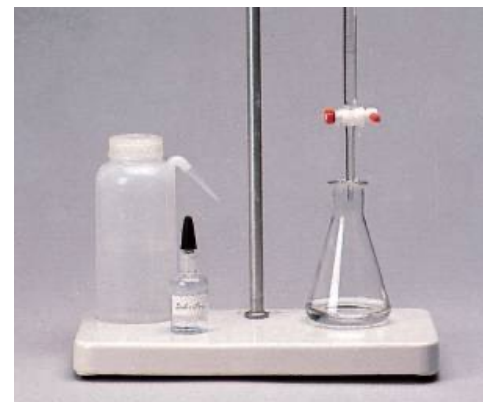
Ammonia: NH₃

REMEMBER: FULL IONIZATION = STRONG

Simple Acid–Base Titration

Used to determine acid/base [concentration]

1. To determine [acid], use known basic soln
To determine [base], use known acidic soln
2. React solution of known concentration
w/ measured volume of unknown solution
3. Add known solution dropwise until
endpoint of reaction
 - Ratio of reactants equals that in balanced equation.
 - **For acid/base: moles H^+ = moles OH^-**
 - Use an indicator to determine endpoint
4. Record volume of known solution needed
to reach endpoint
5. Calculate molarity of unknown solution based on initial
volume of unknown soln & molarity & volume needed for
known soln.



Simple Acid–Base Titration

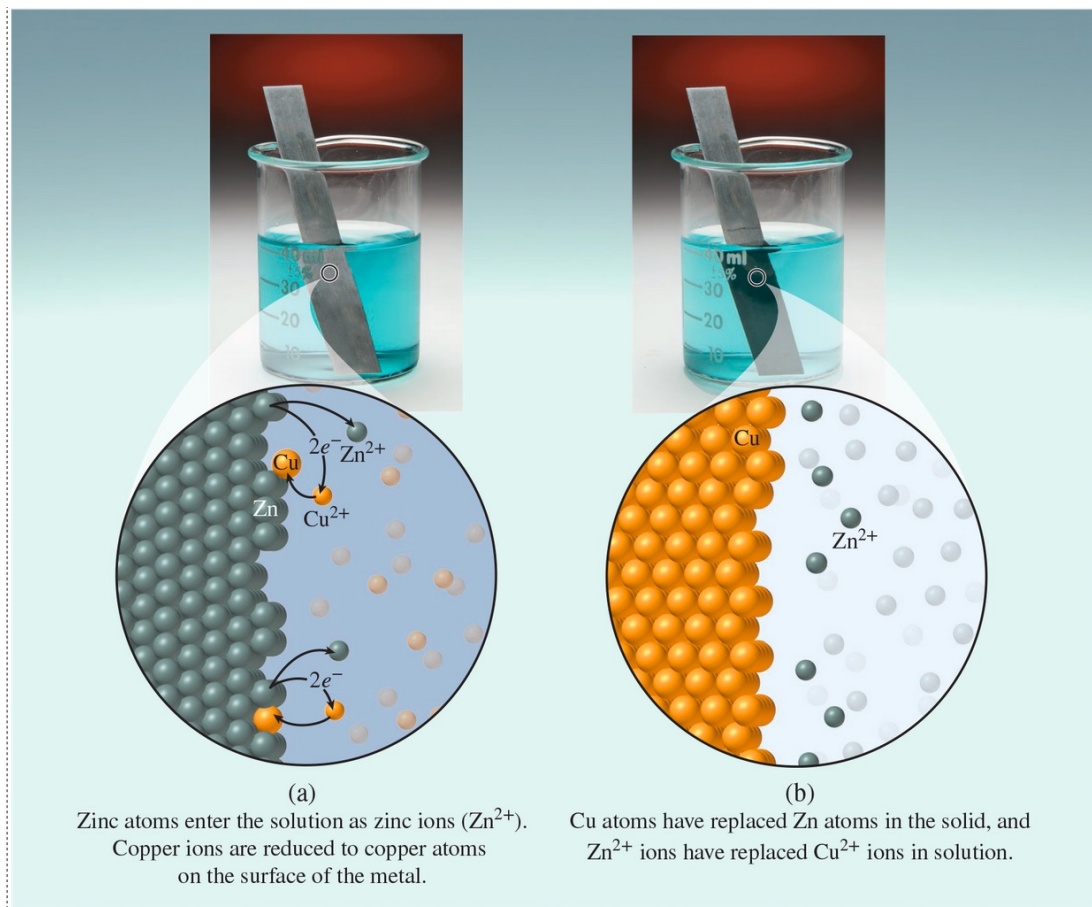
25.00–mL of 0.200 M (H_2SO_4) is titrated with 12.32 ml of a NaOH solution. What is the molarity of the NaOH solution?

- 1) Write the balanced equation
- 2) Determine # moles used of known solution (H_2SO_4)
- 3) Use balanced equation to get moles of unknown (NaOH)
- 4) Divide by volume of unknown to get molarity

$$M_{\text{NaOH}} = 0.812\text{M}$$

24

Redox Reactions



Oxidation–Reduction Reactions

Oxidation–reduction reactions (REDOX reactions):

- Occur when electrons are transferred from one reactant to another during a chemical reaction.
 - There is a change in oxidation number for both substances

Oxidation State/oxidation number: Theoretical charge on atom

Oxidation – the process where the oxidation number increases.
– Electrons are **lost** from the substance

Reduction – the process where the oxidation number decreases.
– Electrons are **gained** by the substance

Oxidation and reduction always accompany each other;
Neither can occur alone

LEO the lion says GER



LEO

Lose
Electrons
Oxidation

GER

Gain
Electrons
Reduction



OIL RIG

Oxidation
Is
Loss

Reduction
Is
Gain

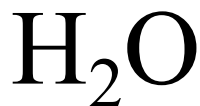
Oxidation Number Rules

The rule earlier in the list always takes precedence.

- 1.) Overall Ox # for a compound is zero
- 2.) Ox # = 0 for an element (not in a compound)
Ox # = ionic charge for an ion
- 3.) Ox # = +1 for 1A elements & H (note: if w/metal H is -1)
- 4.) Ox # = +2 for 2A elements
- 5.) Ox # = -2 for oxygen (usually)
- 6.) Ox # = -1 for 7A elements (If both elements are in 7A, the one higher in the list is -1)
- 7.) Ox # = -2 for 6A elements other than oxygen
- 8.) Ox # = -3 for 5A elements (very shaky!!!)

Determining Oxidation Numbers

Determine the oxidation number of each element in:



If compound contains polyatomic ions, separate into ions before determining Ox. state of each element.



Is it REDOX?

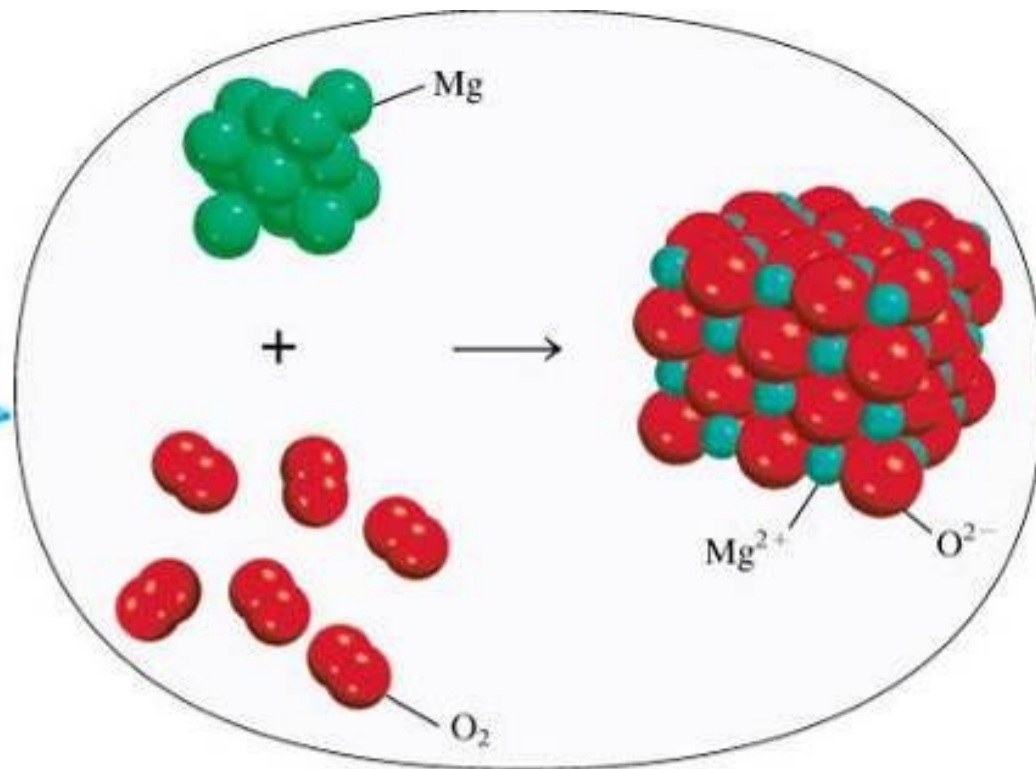


Redox Reaction: Half-reactions

Oxidation half-reaction: $\text{Mg (s)} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$

Reduction half-reaction: $1/2\text{O}_2(\text{g}) + 2\text{e}^- \rightarrow \text{O}^{2-}$

Sum of half-reactions: $\text{Mg (s)} + 1/2\text{O}_2(\text{g}) \rightarrow \text{MgO(s)}$



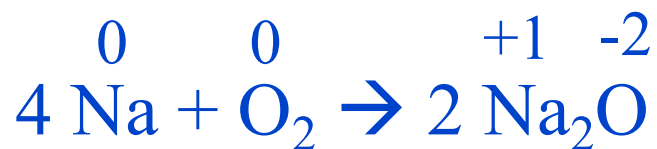
Oxidizing and Reducing Agents

Oxidizing agent: reactant that promotes oxidation

- Oxidation = loss of electrons
- Oxidizing agent takes e^- from other species \rightarrow is reduced!
- Characteristic of nonmetals: ex: fluorine, oxygen.
- High electron affinity: easily gains electrons

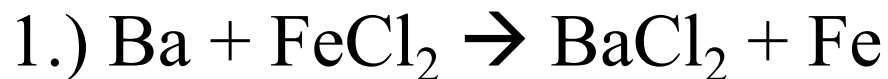
Reducing agent: reactant that promotes reduction

- Reduction = gain in electrons
- Reducing agent loses e^- \rightarrow is oxidized!
- Characteristic of an active metal, such as sodium.
- Low ionization energy: easily loses electrons



Na oxidized; is reducing agent
O reduced; is oxidizing agent

Writing Half Reactions & Determining Oxidizing & Reducing Agents



oxidation:

reduction:



oxidation:

reduction:

Balancing Simple Redox Reactions Using Charge

Balance the following redox reaction:



Process:

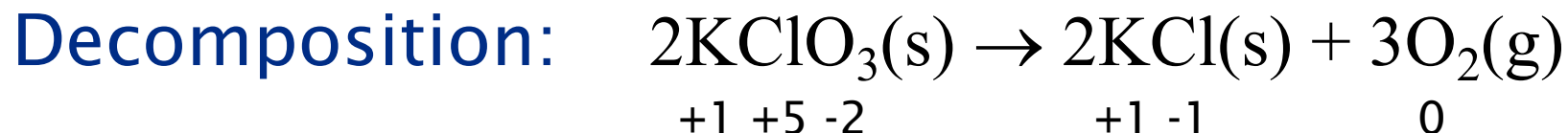
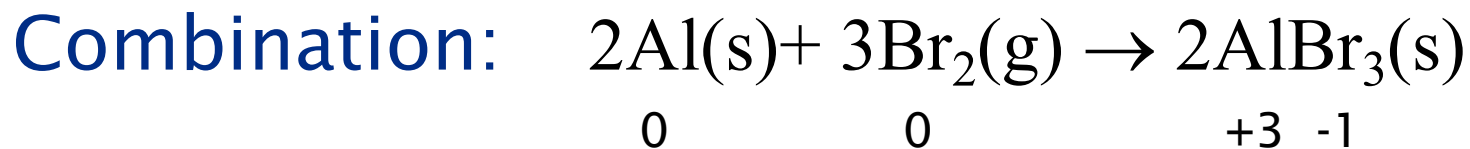
1. Write out the half-reactions
2. Add coefficients to get an equal number electrons in products & reactants
3. Add the two half-reactions and cancel the electrons



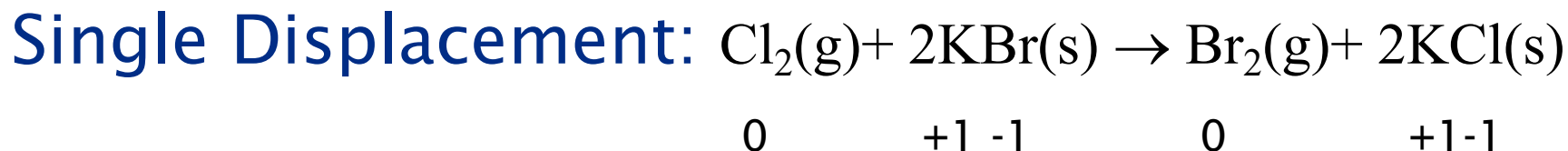
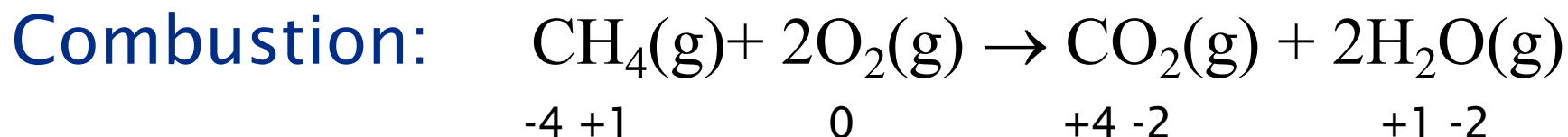
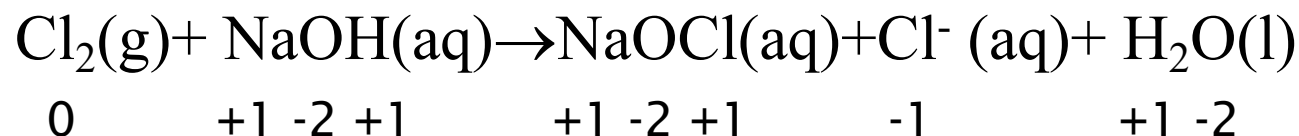
Elemental Oxidation Numbers

1 1A																18 8A	
1 H +1 -1																2 He	
2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	
3 Li +1	4 Be +2											5 B +3	6 C +4 -4	7 N +5 +4 +3 +2 +1 -3	8 O +2 -1 -2	9 F -1	10 Ne
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 +2 +1 -1	18 Ar
		3 3B	4 4B	5 5B	6 6B	7 7B	8	9	10	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

Types of Redox Reactions



Disproportionation (e.g. bleach production):



No need to memorize – you can always just figure out the oxidation numbers!

Redox Titration

Determine the concentration (M) of a potassium permanganate (KMnO_4) solution if 25.32 mLs are needed to react completely with 7.24 g $\text{Na}_2\text{C}_2\text{O}_4$ (s).

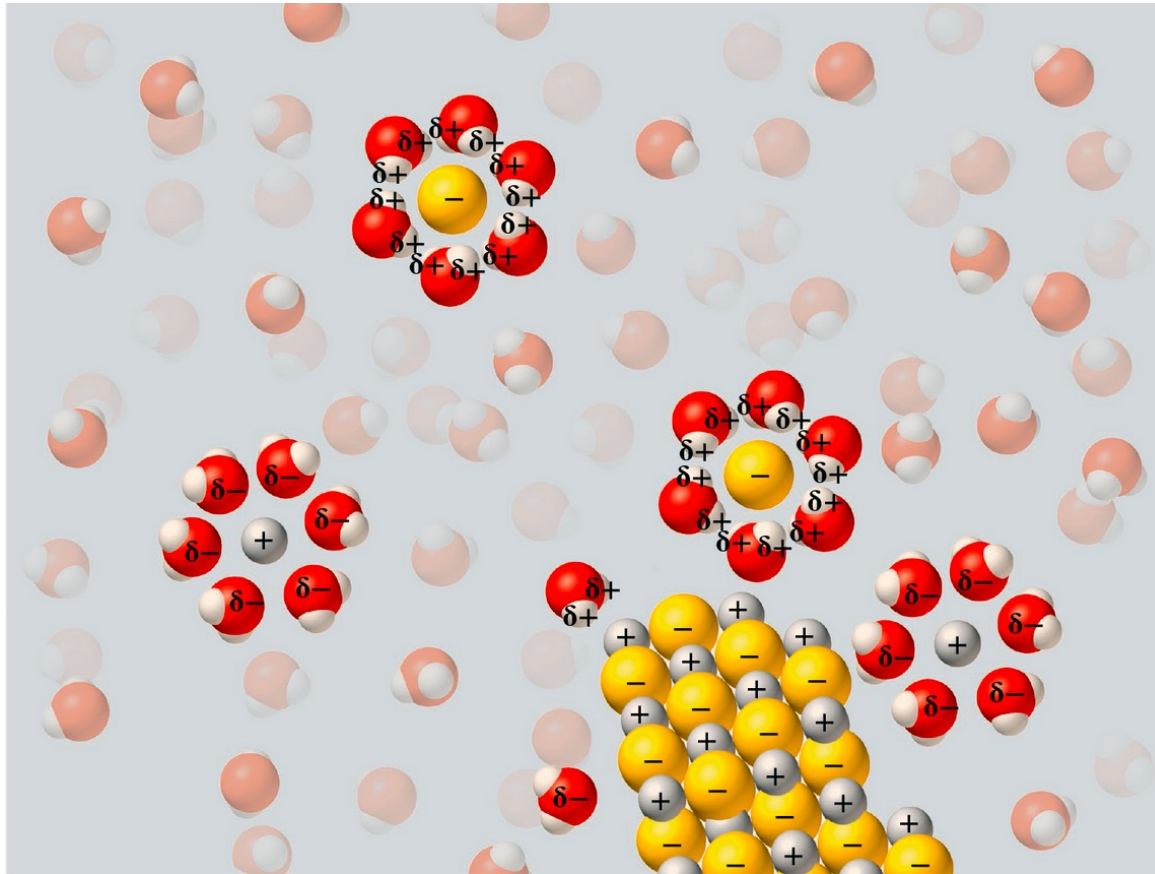


1.) Determine amount in moles of KMnO_4 . (Stoichiometry!)

2.) Determine concentration of KMnO_4 . (Molarity!)

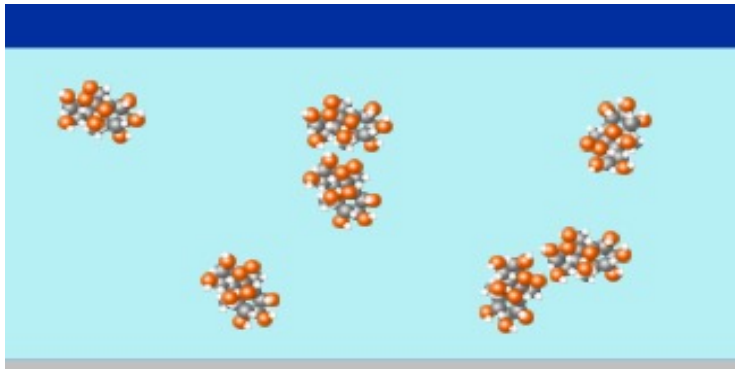
A: 0.854 M KMnO_4

Ion Concentration & Ionic Equations



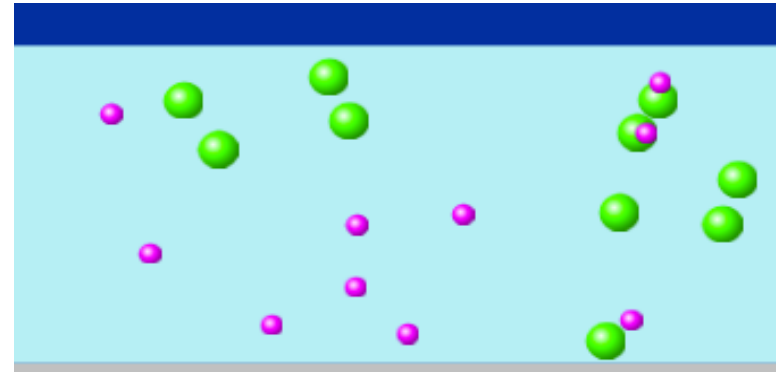
Total Ion Concentration Can Be Higher Than Concentration of Compound in Solution

Covalent Molecule



Concentration:
7 molecules/jar

Ionic Salt, ex. NaCl



Concentration:
10 NaCl units/jar
 $10 \text{ Na}^+ + 10 \text{ Cl}^- = 20 \text{ ions/jar}$

Calculating Ion Concentrations in Solution

What are the concentrations of aluminum ion, sulfate ion & nitrate ion in a solution that is 1.2 M aluminum sulfate and 1.0 M aluminum nitrate?

A: 3.6 M SO_4^{2-} ; 3.0 M NO_3^- ;
3.4 M Al^{3+}

1. Write down how the salts dissociate in water.
2. Multiply concentration of each material by the number of ions it puts into the solution.
3. Add up ions if there is more than 1 source.

Mathematical Solubility Problems

What is the molarity of a sodium phosphate solution if adding AgNO_3 (aq) to 75.0 mL produces 0.205 g Ag_3PO_4 (s)?

1. Produce the balanced chemical equation.
2. Determine the amount of Ag_3PO_4 (s) in moles.
MM = 418.5754 g/mol
3. Use moles of Ag_3PO_4 (s) to determine the moles Na_3PO_4 .
4. Calculate the molarity (mol/L) of Na_3PO_4 .

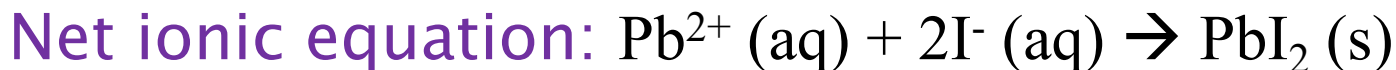
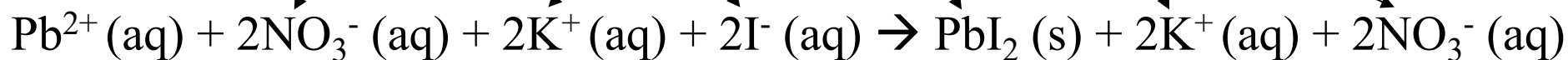
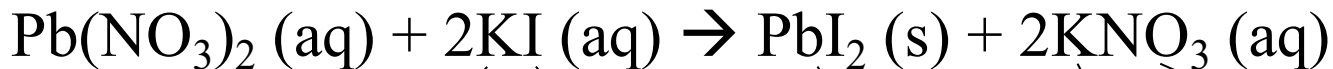
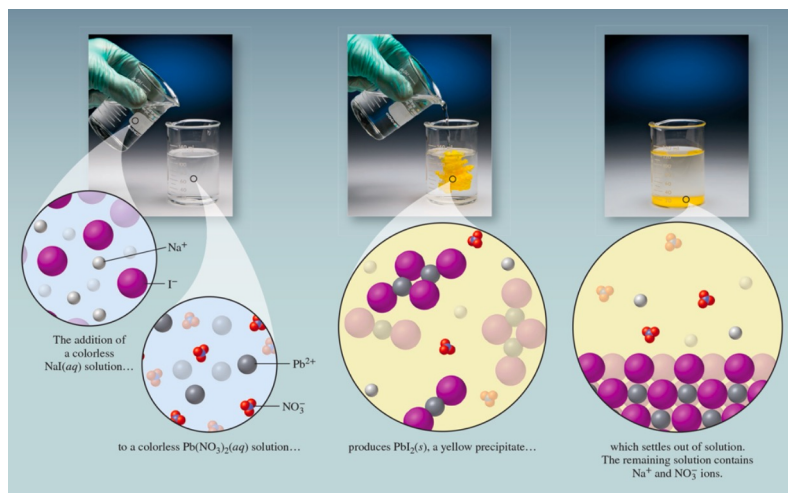
A: $6.53 \times 10^{-3} \text{ M}$ ⁴¹

Types of Ionic Reactions: Precipitation Reactions

Precipitation: Ions in solution combine to form an insoluble solid salt

Precipitate: Solid salt that is formed

Spectator Ions: Ions that do not react in solution; they remain as ions



Writing Net Ionic Equations



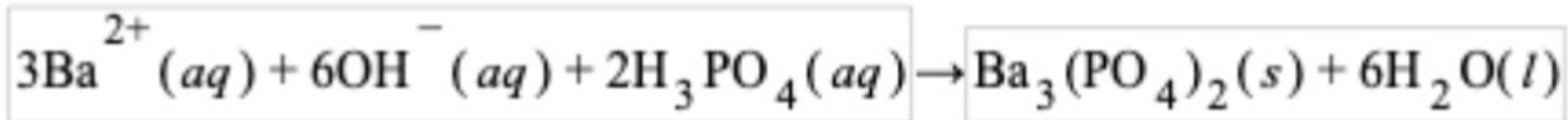
Steps:

1. Write ions (all ions = total ionic equation)
2. Cross off species that are the same on both sides
3. Write net ionic equations using only species that have changed (changed: aq on one side, s, l, or g on the other)



A note for the homework:

Weak acids are written as undissociated in total & net ionic equations.



For exams, you will not need to write net ionic equations for weak acid dissociation this semester because weak acids are covered in depth in CHM 112.

Solubility Rules for ions

Solubility rules classify compounds into those that are usually **soluble** and those that are usually **insoluble**.

Soluble

Ammonium (NH_4^+)

Hydrogen (H^+)

Alkali metals (group 1A)

Nitrate (NO_3^-)

Perchlorate (ClO_4^-) & Chlorate (ClO_3^-)

Acetate (CH_3COO^-)

**Always
soluble**

**Usually
Soluble**

Halides (F^- , Cl^- , Br^- , & I^-)

Exceptions (insoluble if with):
 Pb^{2+} , Hg_2^{2+} , Ag^+

Sulfate (SO_4^{2-})

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

**Sparingly
Soluble
(Insoluble)**

Sulfide (S^{2-})

Hydroxide (OH^-)

Oxide (O^{2-})

Carbonate (CO_3^{2-})

Phosphate (PO_4^{3-})

Chromate (CrO_4^{2-})

Exceptions:
**soluble if with any of
the cations listed in the
always soluble box**

Determining Products of Precipitation Reactions



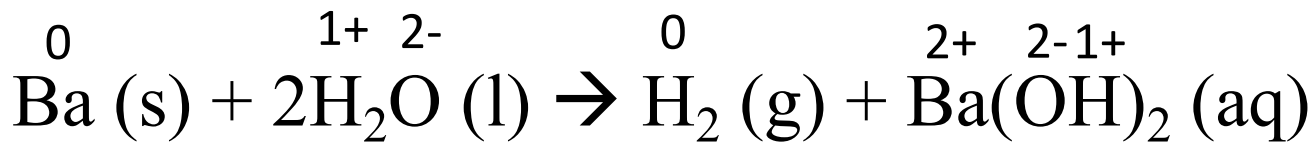
1. Divide reactant compounds into cations & anions
2. Match cation from one salt with anion from other salt
Note: Always keep the metal on the left in salts!
3. Balance charges in salts to generate formulas
4. Write balanced equation
5. Use solubility rules to predict solubility of products



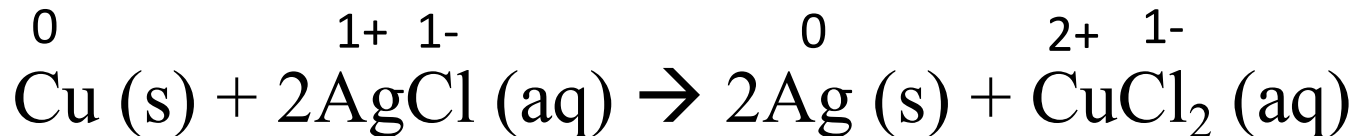
Single Displacement Reactions



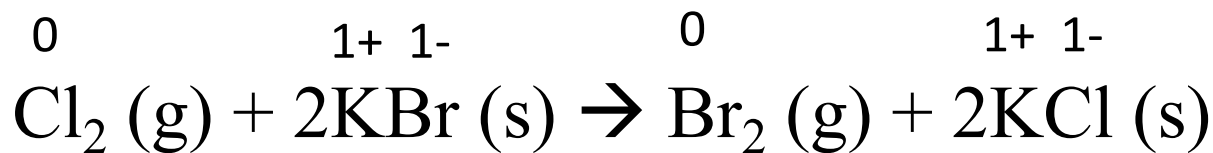
Hydrogen Displacement



Metal Displacement



Halogen Displacement: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$



Relative Activities
with Water & Acid

Reducing strength increases ↑

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

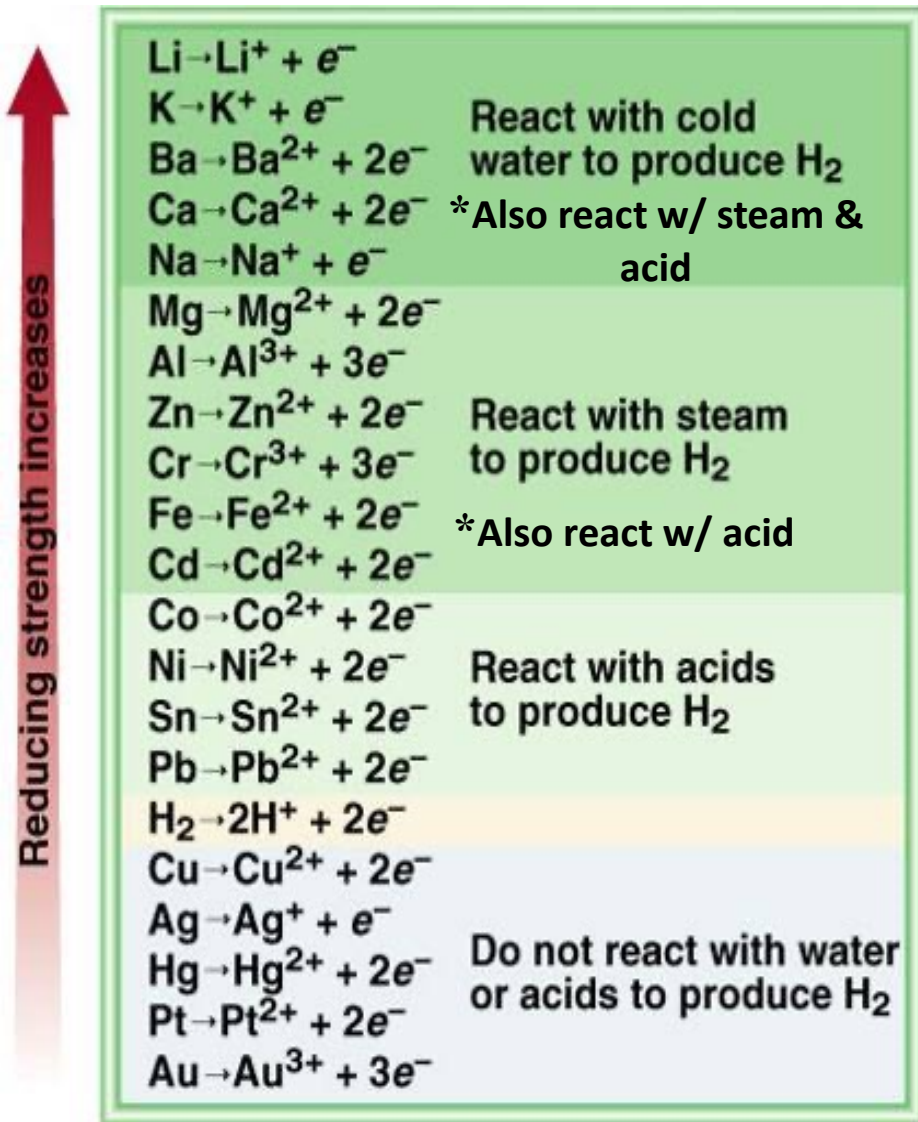


Silver
Plating



Production of
Bromine Gas

Activity Series

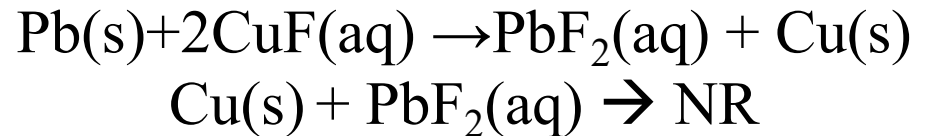


$\text{Li} \rightarrow \text{Li}^+ + e^-$	
$\text{K} \rightarrow \text{K}^+ + e^-$	React with cold water to produce H_2
$\text{Ba} \rightarrow \text{Ba}^{2+} + 2e^-$	
$\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$	*Also react w/ steam & acid
$\text{Na} \rightarrow \text{Na}^+ + e^-$	
$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	
$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$	
$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$	React with steam to produce H_2
$\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$	
$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	*Also react w/ acid
$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$	
$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$	
$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$	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
$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$	
$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$	

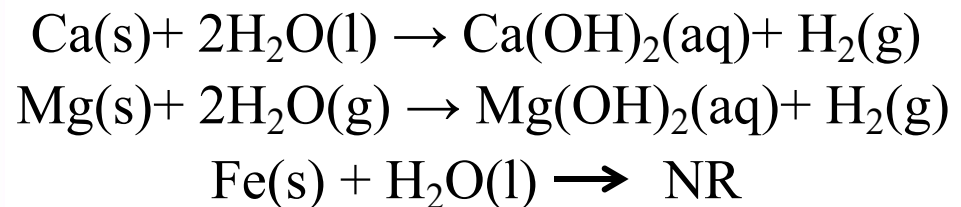
Reactivity of 2 metals

Higher metal replaces lower metal

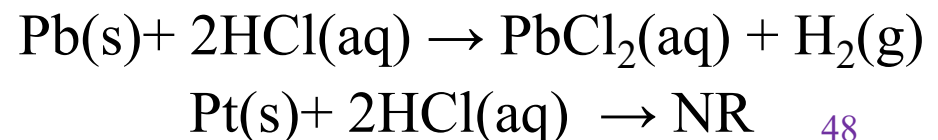
Higher metal becomes cation
Lower metal will be free metal



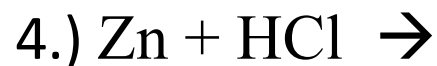
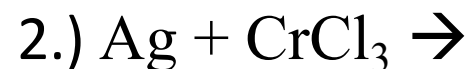
Reactivity with water



Reactivity with acid



Determining Products of Single Displacement Reactions



Must Know These Diatomic Molecules:

$\text{H}_2, \text{F}_2, \text{Cl}_2, \text{Br}_2, \text{I}_2, \text{N}_2, \text{O}_2$

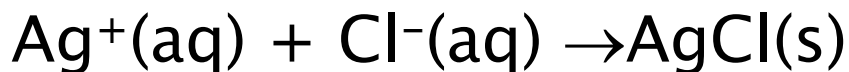
Solution Based Experiments: Gravimetric Analysis

What is the mass % Cl in a sample of unknown composition?

1. Dissolve known mass of an unknown sample in water.

$0.5662\text{g } M_xCl_y \text{ dissolved in water} \rightarrow xM^+ + yCl^-$

2. React unknown with Ag^+ to form a precipitate.



3. Filter, dry, & weigh precipitate.

$1.0882\text{g } AgCl(s) \text{ recovered}$

4. Use stoichiometry to determine moles and mass of chlorine, then determine %Cl.



A: 47.54%Cl