Chapter 9

Chemical Reactions in Aqueous Solutions

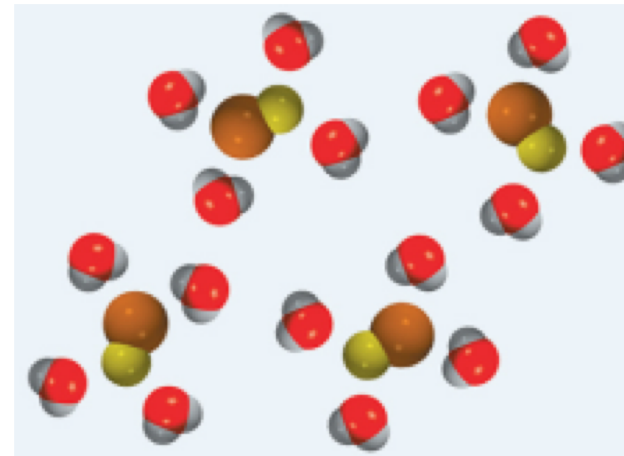
Solutions: Key Terms

Solution

- Homogenous mixture of 2 or more substances

Solvent:

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

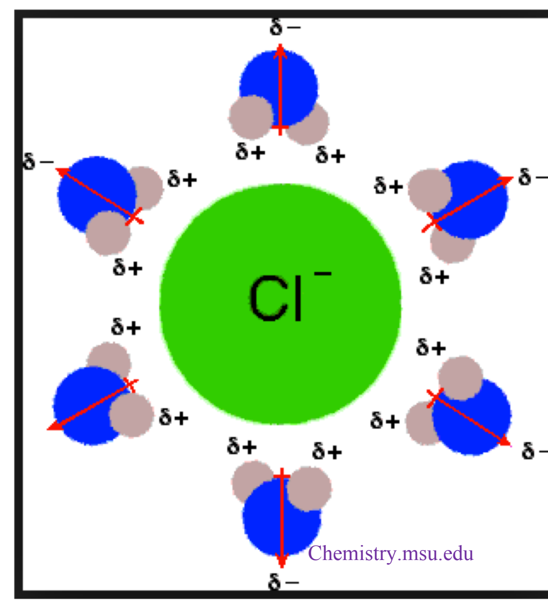


Solute:

- 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



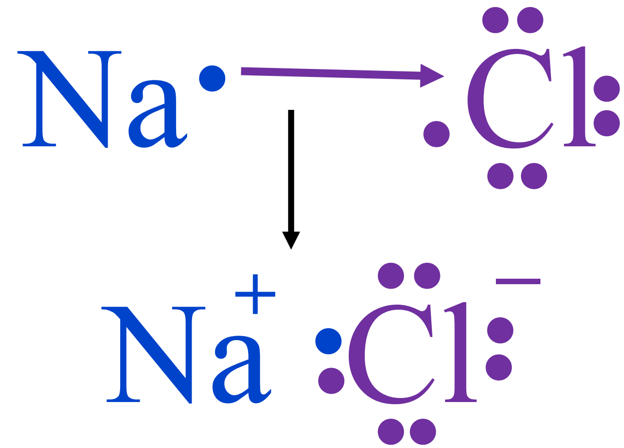
Solubility Depends on Bond Type

Electronegativity – measure of atom's attraction for electrons

- Electronegativity difference determines bonding type

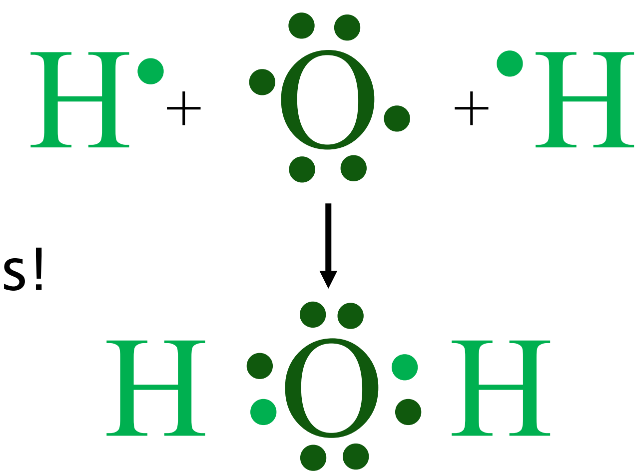
Ionic:

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



Covalent:

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

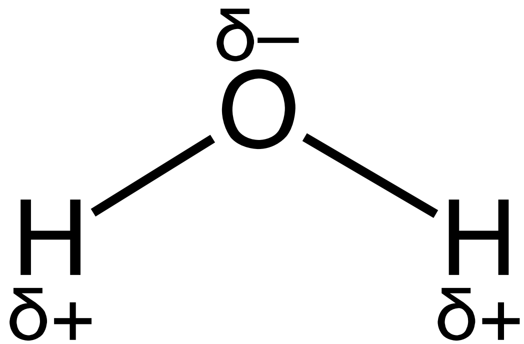


Covalent Bonds: Nonpolar vs Polar

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!



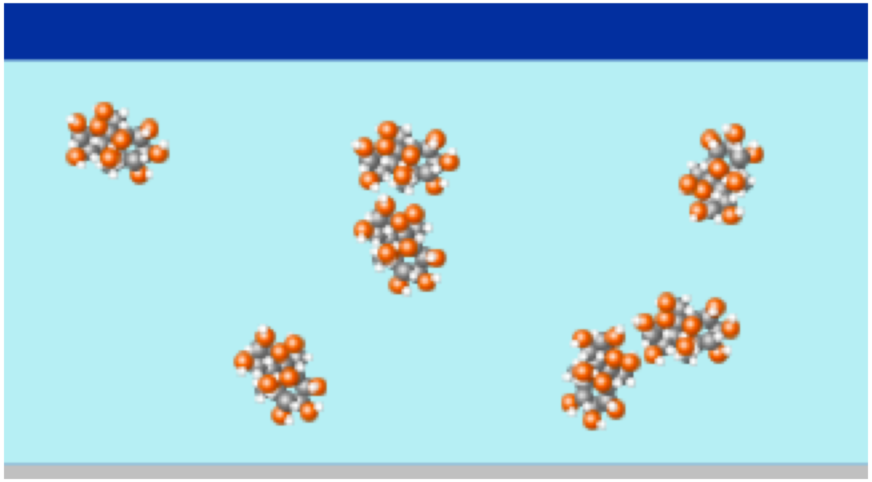
Dissolution vs Dissociation

Ionic & Covalent Compounds Behave Differently

Sugar vs Salt

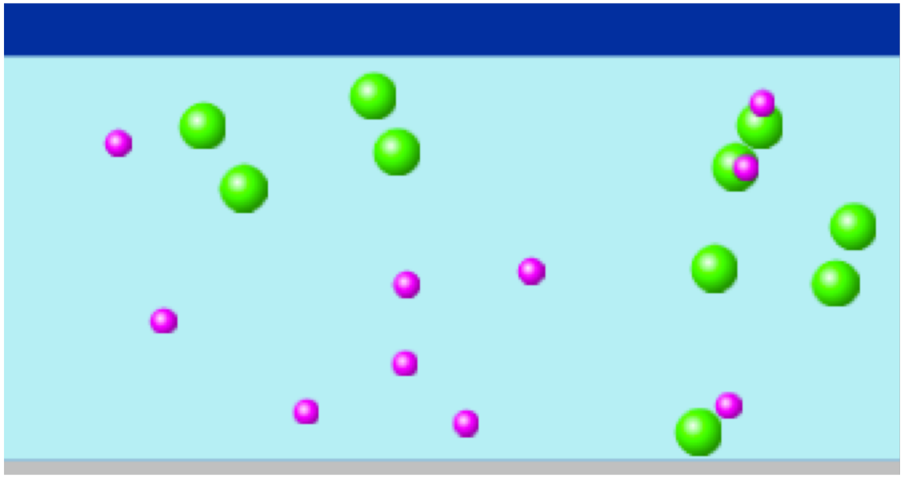
Dissolution vs Dissociation

Covalent Molecule



Dissolved sugar:
- molecule remains together
- NOT dissociation!

Ionic Salt

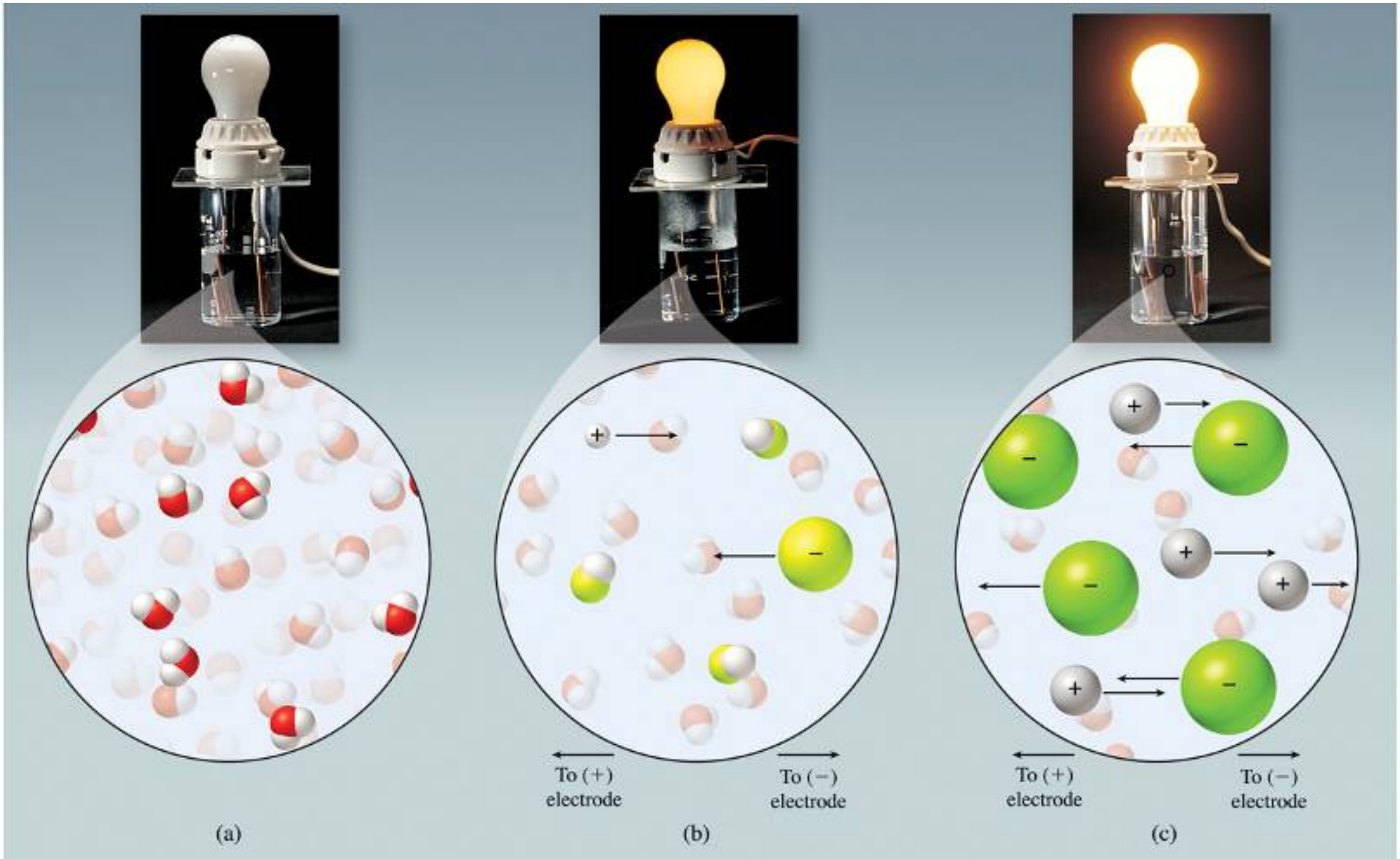


Dissolved salt:
- ions separate
- dissociation!

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

Conductivity of Electrolytes in Aqueous Solutions

Non-electrolyte	Weak electrolyte	Strong electrolyte
No ionization	Some ionization	Full ionization
Ex: sugar	Ex: acetic acid	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.

$$\frac{1mol_{NaCl}}{1L_{NaCl}} x \frac{58.5g_{NaCl}}{1mol_{NaCl}} x \frac{2L_{NaCl}}{1} = 117g_{NaCl}$$

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.

$$\frac{1 mol_{NaCl}}{\text{kg solv.}} \text{ x } \frac{58.5\ g_{NaCl}}{1 mol_{NaCl}} \text{ x } 2 \text{ kg solv.} = 117\ g_{NaCl}$$

2. Weigh out mass of NaCl.

3. Place NaCl into container.

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

Molarity Calculations:

1. What is the concentration, in moles/L, if 22.8 g of potassium dichromate ($K_2Cr_2O_7$) is dissolved to make 500.0 mL of solution?

A: 0.155 M

2. How many grams of potassium dichromate ($K_2Cr_2O_7$) are needed to prepare 125 mL of a 1.83 M solution?

A: 67.3 g

3. What volume of a 2.50 M solution of potassium dichromate ($K_2Cr_2O_7$) would contain 350.0 g of $K_2Cr_2O_7$?

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.

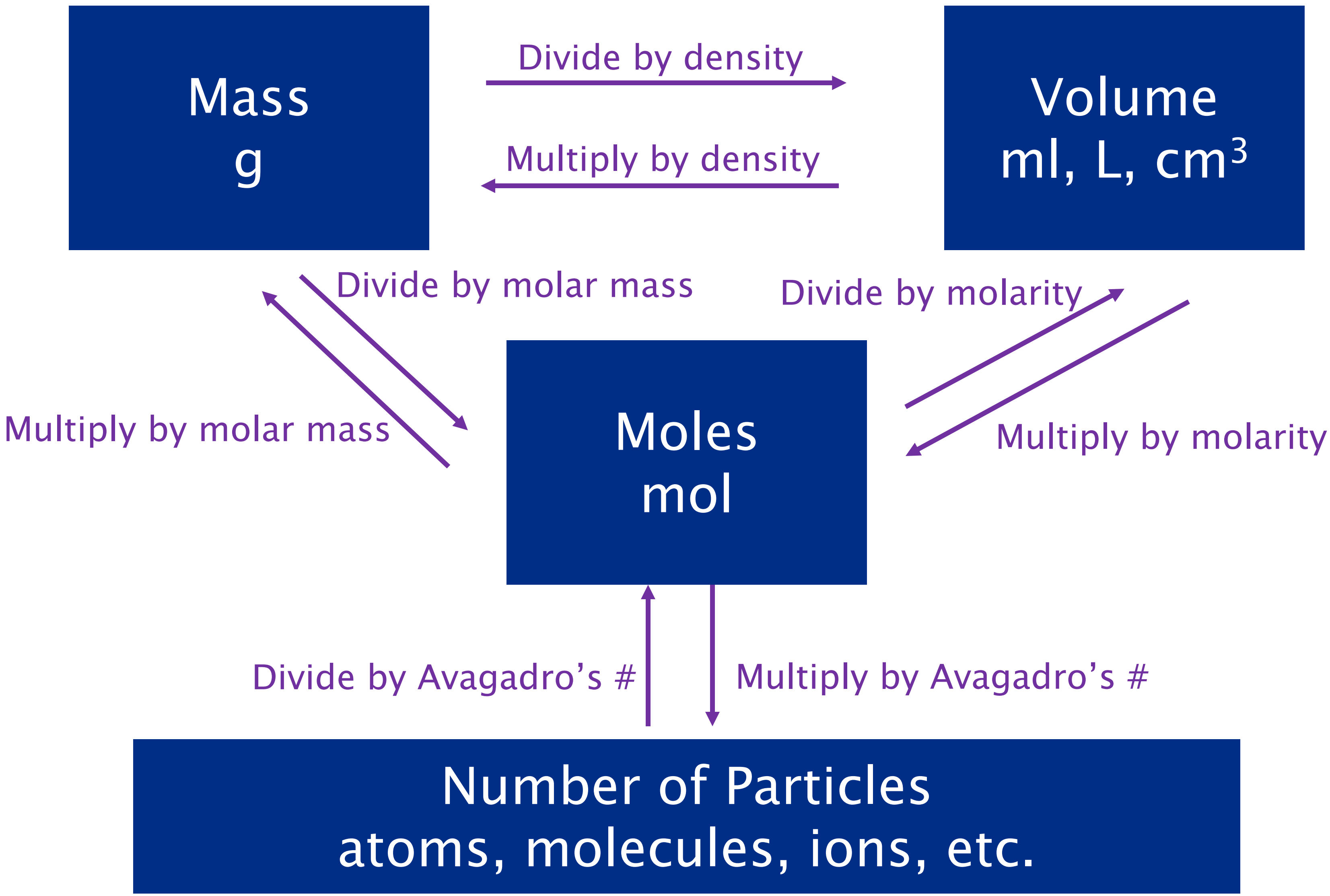
$$M_1V_1 = M_2V_2$$

$$(mol/L)(L) = (mol/L)(L)$$

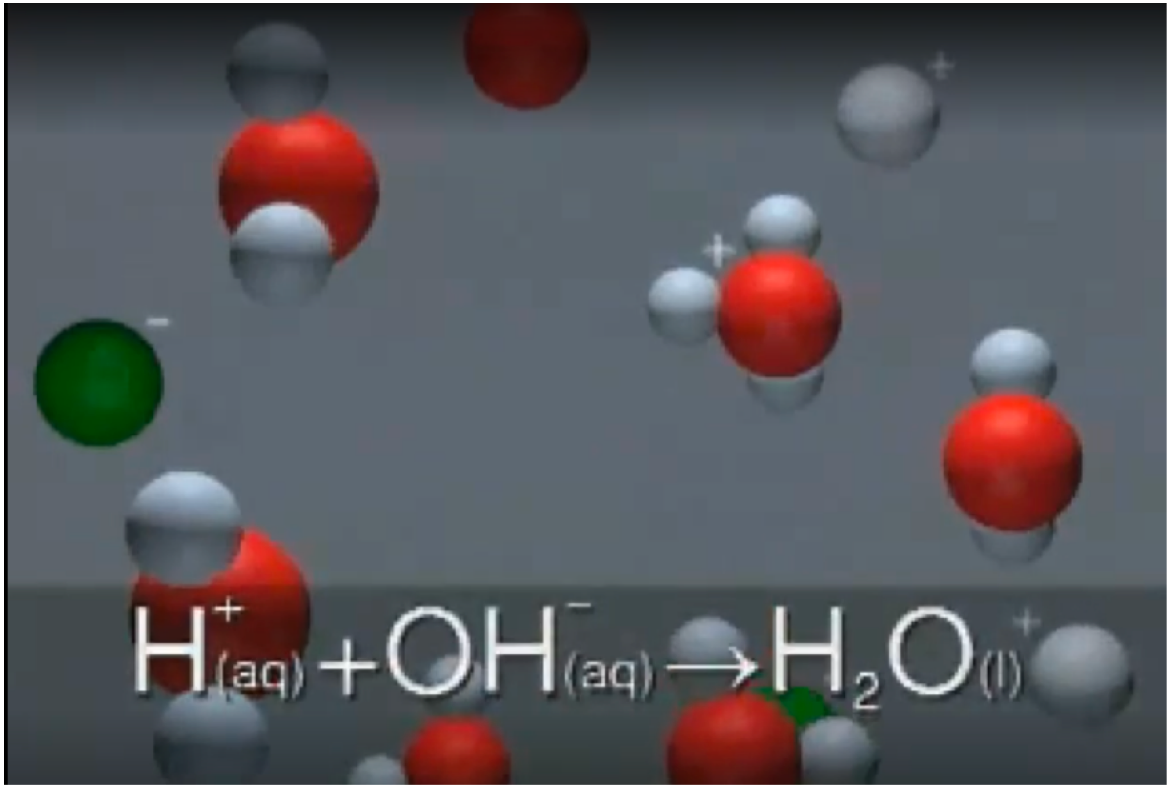
Calculate the volume of 1.0M stock solution needed to make 2000.0mL of a 0.12M solution of HCl.

A: 240 mL

Conversion Relationships



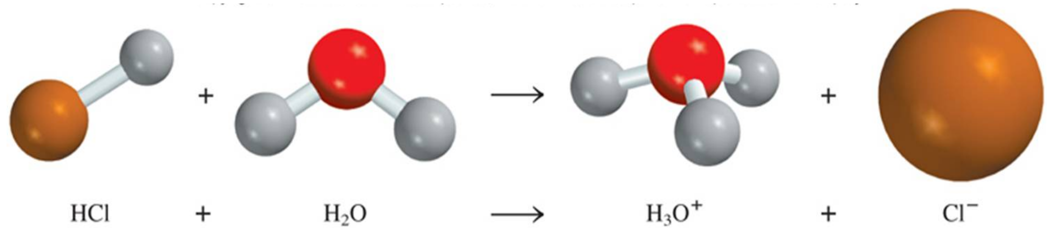
Acid–Base Reactions



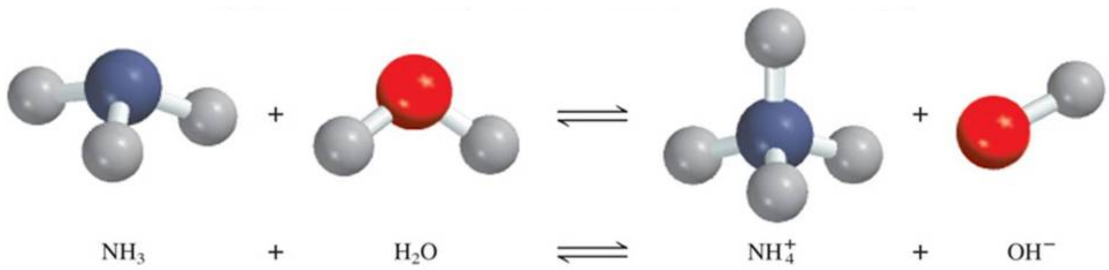
Acid–Base Reactions

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

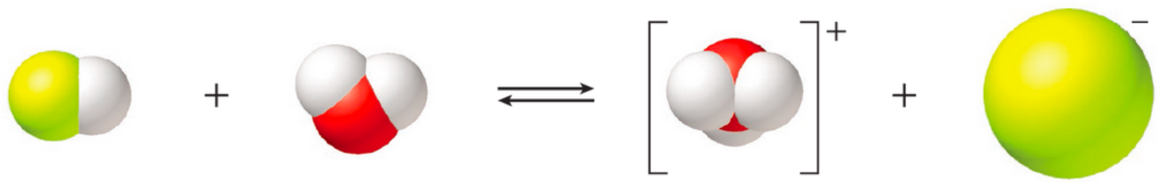
$H^+ + OH^- \rightarrow H_2O$ & cation + anion $\rightarrow$ salt

Acid–Base Reactions

Brønsted Acids and Bases

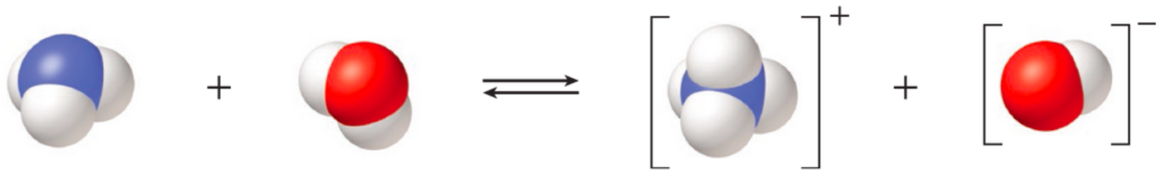
A hydrogen atom that has lost its electron is often referred to as a **proton.**

Acid: Proton donor



$$HF\,(aq) + H_2O\,(l) \rightleftarrows H_3O^+\,(aq) + F^-\,(aq)$$

Base: proton acceptor

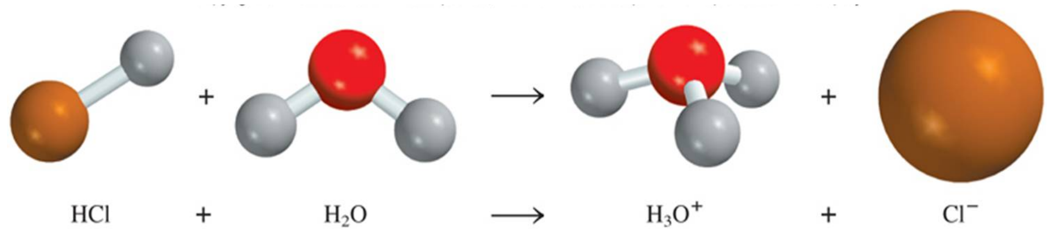


$$NH_3\,(aq) + H_2O\,(l) \rightleftarrows NH_4^+\,(aq) + OH^-\,(aq)$$

Strength of Acids and Bases

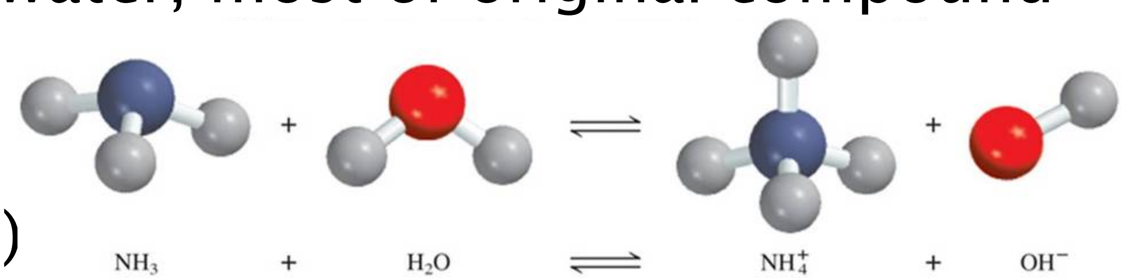
Strong acids and bases

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



Weak acids and bases

- Partial ionization in water, most of original compound remains
- Poor conductors
- Double arrow (↔, ⇄) 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

$$H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

- 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

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

$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$

Net ionic equation: $OH^- + H^+ \rightarrow H_2O$

Solid (weak) base with strong acid

$Fe(OH)_3\ (s) + 3HCl(aq) \rightarrow FeCl_3\ (aq) + 3\ H_2O(l)$

$Fe(OH)_3\ (s) + 3H^+\ (aq) + 3Cl^-(aq) \rightarrow Fe^{3+}\ (aq) + 3Cl^- + 3H_2O$

Net ionic equation: $Fe(OH)_3\ (s) + 3H^+ \rightarrow Fe^{3+} + 3H_2O$

Weak acid with strong base

$CH_3COOH\ (aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + 3\ H_2O(l)$

$CH_3COOH\ (aq) + Na^+\ (aq) + OH^-\ (aq) \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq) + H_2O(l)$

Net ionic equation: $CH_3COOH\ (aq) + OH^-\ (aq) \rightarrow CH_3COO^-\ (aq) + H_2O(l)$

Common Acids and Bases

Strong Acids	Weak Acids
HCl, HI, HBr	HF, HNO_2, H_3PO_4
HNO_3	Acetic acid ($CH_3COO\underline{H}$)
H_2SO_4	Organic acids tend to be weak
$HClO_4$	

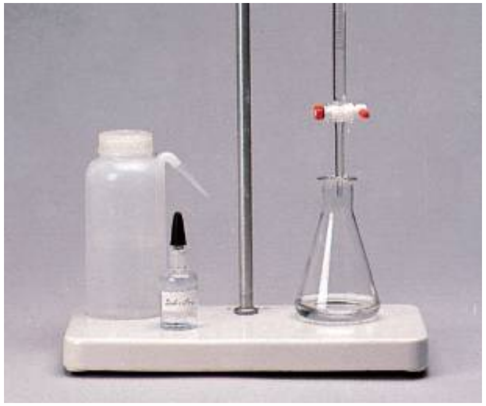
Strong Bases	Weak Bases
NaOH, KOH, LiOH	Other hydroxides (don't dissolve)
$Ba(OH)_2$	Ammonia: NH_3

REMEMBER: FULL IONIZATION = STRONG

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.

Acid-BaseTitration

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

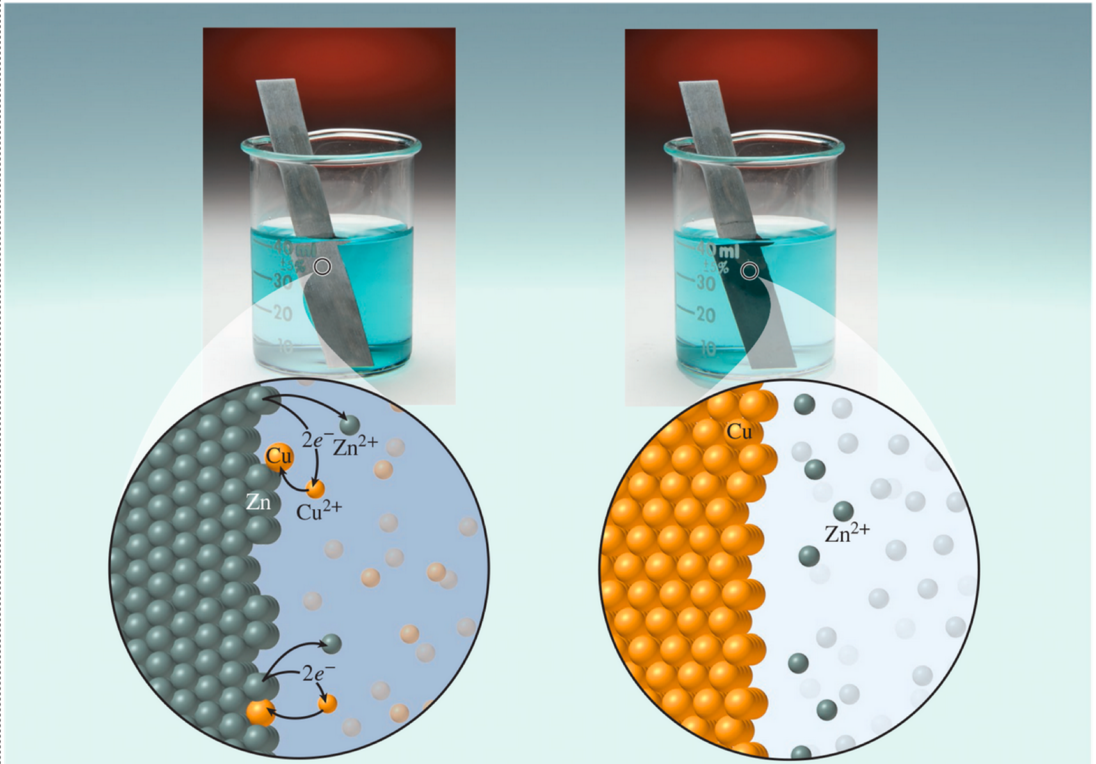
2) Determine # moles used of known solution (H_2SO_4)

3) Use balanced equation to get moles of unknown (NaOH)

4) Divide by volume of unknown to get molarity

M_{NaOH} = 0.812M

Redox Reactions



(a)
Zinc atoms enter the solution as zinc ions (Zn^{2+}). Copper ions are reduced to copper atoms on the surface of the metal.

(b)
Cu atoms have replaced Zn atoms in the solid, and Zn^{2+} ions have replaced Cu^{2+} ions in solution.

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 IA 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:

NH_3

CO_3^{2-}

H_2O

H_2O_2

NH_4^+

NO_3^-

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

ex: NH_4NO_3

Is it REDOX?

$$Zn\,(s) + 2\,H_2O\,(g) \rightarrow H_2\,(g) + Zn(OH)_2$$

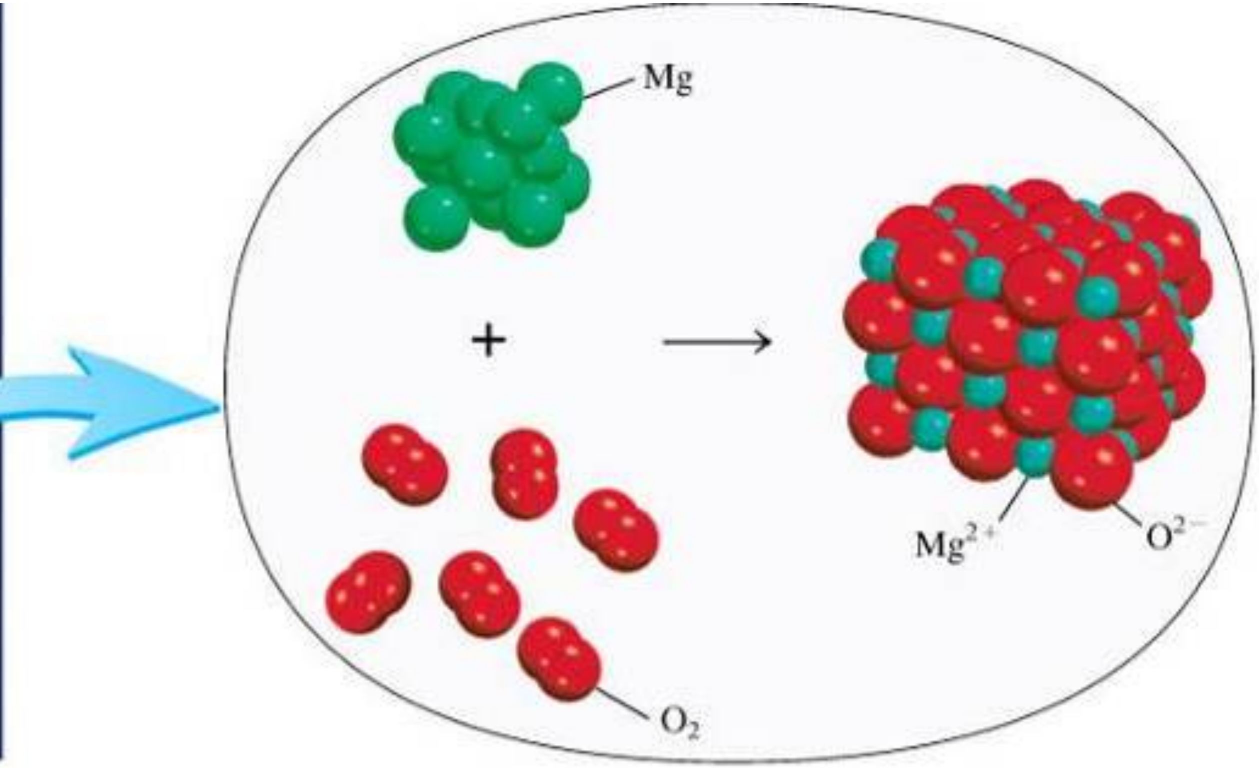
$$ZnCl_2\,(aq) + 2\,NaBr\,(aq) \rightarrow 2\,NaCl\,(aq) + ZnBr_2\,(aq)$$

Redox Reaction: Half-reactions

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

Reduction half-reaction: $1/2O_2(g) + \mathbf{2e^-} \rightarrow O^{2-}$

Sum of half-reactions: $Mg(s) + 1/2O_2(g) \rightarrow MgO(s)$



Oxidizing and Reducing Agents

Oxidizing agent: reactant that promotes oxidation

- Oxidation = loss of electrons
- Oxidizing agent takes e^- from other species → 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^- → is oxidized!
- Characteristic of an active metal, such as sodium.
- Low ionization energy: easily loses electrons

$$4\ \overset{0}{Na} + \overset{0}{O_2} \rightarrow 2\ \overset{+1}{Na_2}\overset{-2}{O}$$

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

Writing Half Reactions & Determining Oxidizing & Reducing Agents

1.) $Ba + FeCl_2 \rightarrow BaCl_2 + Fe$

oxidation:

reduction:

2.) $F_2 + 2\,NaCl \rightarrow Cl_2 + 2\,NaF$

oxidation:

reduction:

Balancing Simple Redox Reactions Using Charge

Balance the following redox reaction:
$Fe^{3+}(aq) + Cu(s) \rightarrow Fe(s) + Cu^{2+}(aq)$

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

$2Fe^{3+}(aq) + 3Cu(s) \rightarrow 2Fe(s) + 3Cu^{2+}(aq)$

Elemental Oxidation Numbers

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** +1 −1																	2 **He**
3 **Li** +1	4 **Be** +2											5 **B** +3	6 **C** +4 +2 −4	7 **N** +5 +4 +3 +2 +1 −3	8 **O** +2 $-\frac{1}{2}$ −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 +1 −1	18 **Ar**
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

Combination: $2Al(s) + 3Br_2(g) \rightarrow 2AlBr_3(s)$

0 0 +3 -1

Decomposition: $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

+1 +5 -2 +1 -1 0

Disproportionation (e.g. bleach production):

$Cl_2(g) + NaOH(aq) \rightarrow NaOCl(aq) + Cl^-(aq) + H_2O(l)$

0 +1 -2 +1 +1 -2 +1 -1 +1 -2

Combustion: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

-4 +1 0 +4 -2 +1 -2

Single Displacement: $Cl_2(g) + 2KBr(s) \rightarrow Br_2(g) + 2KCl(s)$

0 +1 -1 0 +1 -1

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 $Na_2C_2O_4$ (s).

$$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \rightarrow 10CO_2 + 8H_2O + 2MnSO_4 + 5Na_2SO_4 + K_2SO_4$$

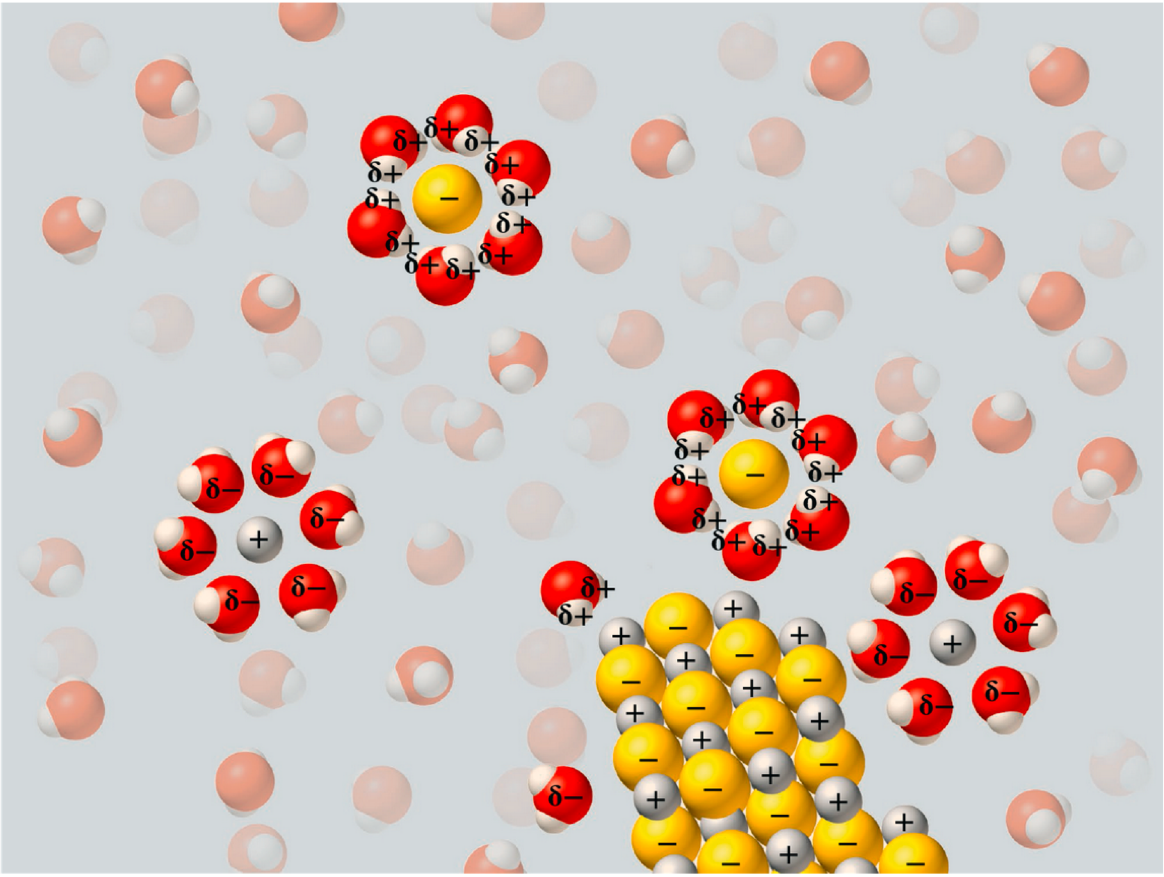
$Na_2C_2O_4 = 133.9992 g/mol$

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

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

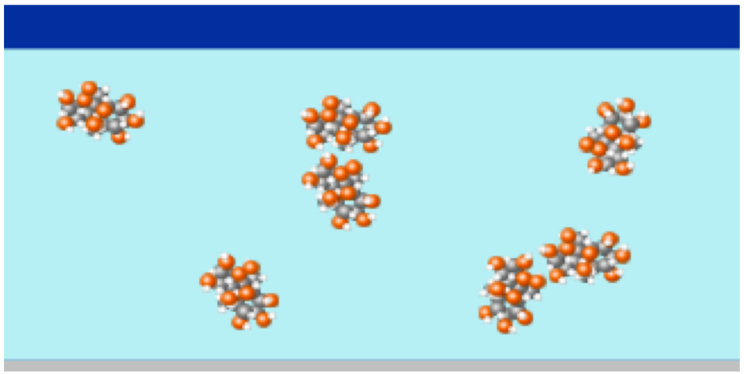
A: 0.854 M $KMnO_4$

Ion Concentration & Ionic Equations



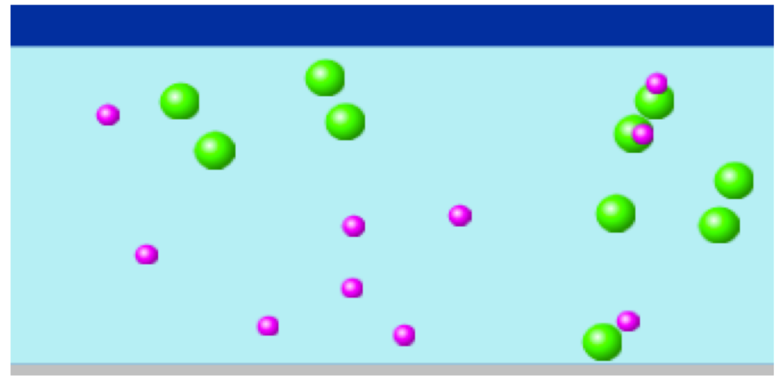
Total Ion Concentration Can Be Higher Than Concentration of Compound in Solution

Covalent Molecule



Concentration:
7 molecules/jar

Ionic Salt, ex. NaCl



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

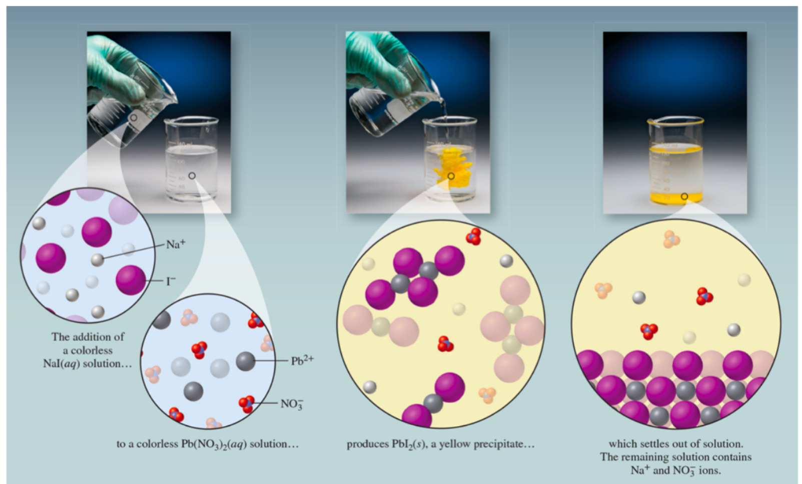
A: 6.53×10^{-3} M

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



$$Pb(NO_3)_2\ (aq) + 2KI\ (aq) \rightarrow PbI_2\ (s) + 2KNO_3\ (aq)$$

$$Pb^{2+}\ (aq) + 2NO_3^-\ (aq) + 2K^+\ (aq) + 2I^-\ (aq) \rightarrow PbI_2\ (s) + 2K^+\ (aq) + 2NO_3^-\ (aq)$$

Net ionic equation: $Pb^{2+}\ (aq) + 2I^-\ (aq) \rightarrow PbI_2\ (s)$

Writing Net Ionic Equations

$$Na_2CO_3\ (aq) + PbCl_2\ (aq) \rightarrow 2\ NaCl\ (aq) + PbCO_3\ (s)$$

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)

$$Pb^{2+}\ (aq) + CO_3^{2-}\ (aq) \rightarrow PbCO_3\ (s)$$

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

$FeCl_3$ (aq) + Na_2CO_3 (aq) → ?

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

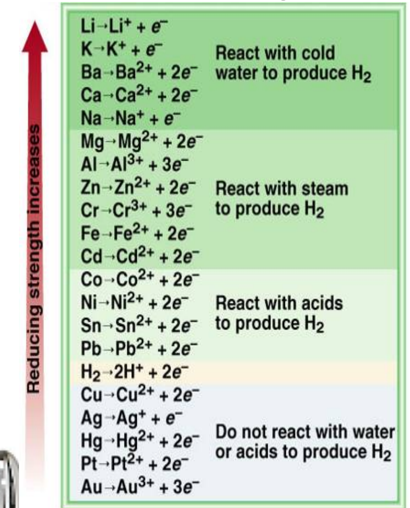
5. Use solubility rules to predict solubility of products

2 $FeCl_3$ (aq) + 3 Na_2CO_3 (aq) → 6 NaCl (aq) + $Fe_2(CO_3)_3$ (s)

Single Displacement Reactions

$A + BC \rightarrow AB + C$

Relative Activites with Water & Acid



Hydrogen Displacement

0 1+ 2- 0 2+ 2- 1+

$$Ba\ (s) + 2H_2O\ (l) \rightarrow H_2\ (g) + Ba(OH)_2\ (aq)$$

Metal Displacement

0 1+ 1- 0 2+ 1-

$$Cu\ (s) + 2AgCl\ (aq) \rightarrow 2Ag\ (s) + CuCl_2\ (aq)$$

Silver Plating

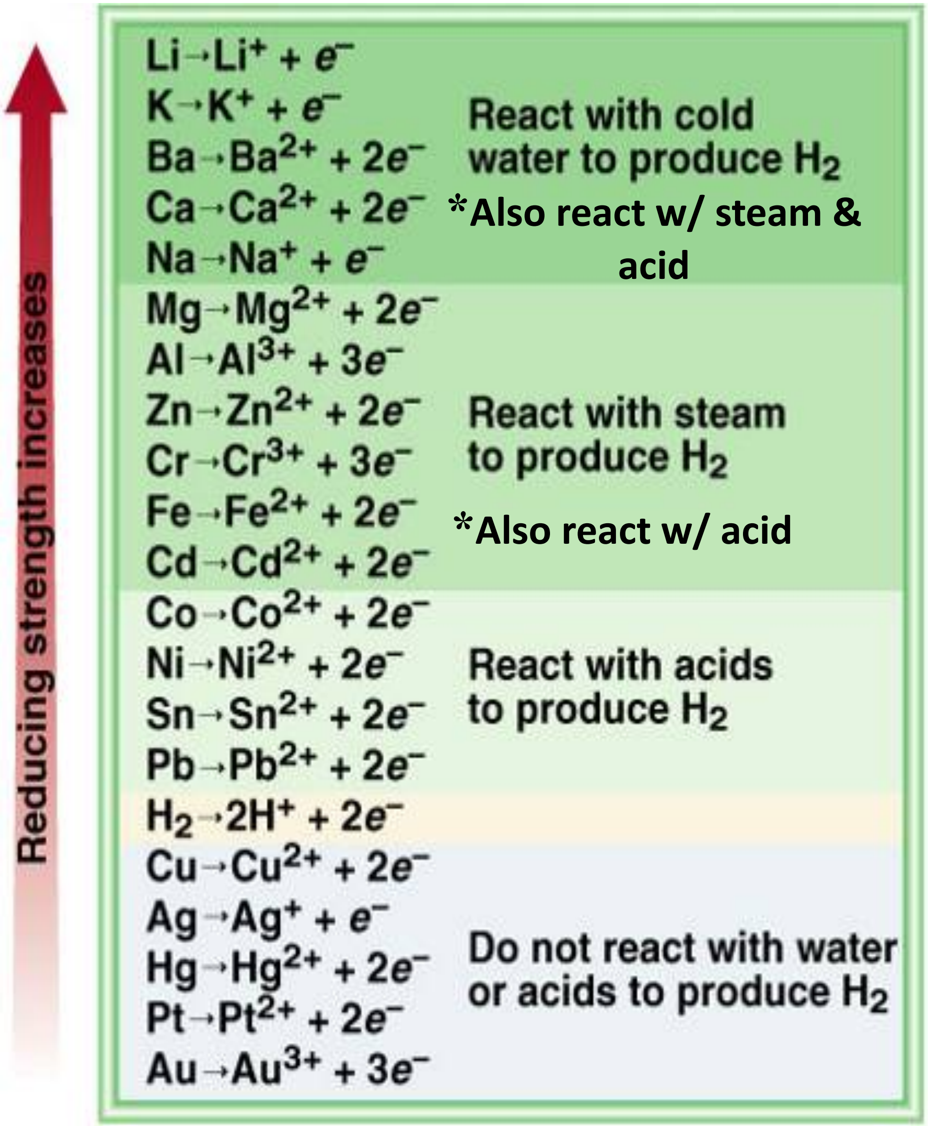
Halogen Displacement: $F_2 > Cl_2 > Br_2 > I_2$

0 1+ 1- 0 1+ 1-

$$Cl_2\ (g) + 2KBr\ (s) \rightarrow Br_2\ (g) + 2KCl\ (s)$$

Production of Bromine Gas

Activity Series



Reactivity of 2 metals

Higher metal replaces lower metal

Higher metal becomes cation

Lower metal will be free metal

$$Pb(s) + 2CuF(aq) \rightarrow PbF_2(aq) + Cu(s)$$

$$Cu(s) + PbF_2(aq) \rightarrow NR$$

Reactivity with water

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

$$Mg(s) + 2H_2O(g) \rightarrow Mg(OH)_2(aq) + H_2(g)$$

$$Fe(s) + H_2O(l) \longrightarrow NR$$

Reactivity with acid

$$Pb(s) + 2HCl(aq) \rightarrow PbCl_2(aq) + H_2(g)$$

$$Pt(s) + 2HCl(aq) \rightarrow NR$$

Determining Products of Single Displacement Reactions

1.) $Ba + CrCl_3 \rightarrow$

2.) $Ag + CrCl_3 \rightarrow$

3.) $F_2 + CrBr_3 \rightarrow$

4.) $Zn + HCl \rightarrow$

5.) $Zn + H_2O$ (g) $\rightarrow$

6.) $Zn + H_2O$ (l) $\rightarrow$

Must Know These Diatomic Molecules:

H_2, F_2, Cl_2, Br_2, I_2, N_2, 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.

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

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

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

3. Filter, dry, & weigh precipitate.

   1.0882g AgCl(s) recovered

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

A: 47.54%Cl