

Ch 4: Aqueous Reactions and Solution Stoichiometry

4.1 General Properties of Aqueous Solutions

1. Electrolytic Properties

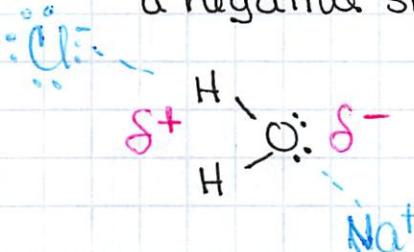
A. electrolyte - a substance whose aqueous solutions contain ions & can conduct an electric current.

B. nonelectrolyte - a substance that does NOT form ions in solution.

2. Ionic Compounds in water

A. Ionic solids dissociate into their component ions as they dissolve.

B. Water is a great (effective) solvent for ionic compounds because it's a polar molecule, it has a positive side & a negative side.



A cation (+) is attracted to the negative side of H_2O molecule, while an anion (-) is attracted to H_2O 's positive side

C. Ions become surrounded by H_2O molecules - solvated

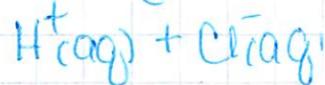
i) Solvation - process of dissolving, stabilizes ions in solution & prevents cations and anions from recombining

3. Molecular Compounds in water

A. When molecular compounds dissolve, solution consists of intact molecules dispersed thru the solution.

B. A few molecules have aqueous solutions that contain ions. Acids are examples.

Ex) HCl(g) dissolves to form hydrochloric acid, HCl(aq)
hydrogen
chloride
gas



4. Strong and Weak Electrolytes

A. Strong Electrolytes - solutes that exist in solution completely (or almost completely) as ions.

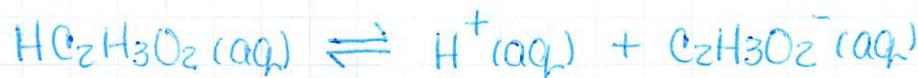
i) All soluble ionic compounds (i.e. NaCl) & a few molecular compounds (i.e. HCl) are strong electrolytes.

Ex) $\text{HCl(aq)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

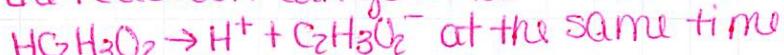
we use a full arrow b/c H^+ & Cl^- ions do not have a tendency to recombine into HCl .

B. Weak Electrolytes - solutes that exist in a solution mostly in the form of molecules with a small fraction in the form of ions

Ex) acetic acid



↳ half arrows in both directions mean the reaction can go in both directions.



$\text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^- \rightarrow \text{HC}_2\text{H}_3\text{O}_2^-$ - in the process of chemical equilibrium - relative amounts of each ion or molecule remains constant over time.

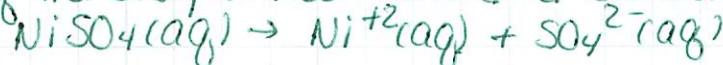
C. Do NOT confuse how much an electrolyte dissolves with its being strong or weak.

Ex) $\text{HC}_2\text{H}_3\text{O}_2$ - weak electrolyte
But it dissociates completely in H_2O

Ba(OH)_2 - strong electrolyte
But it's not very soluble in H_2O

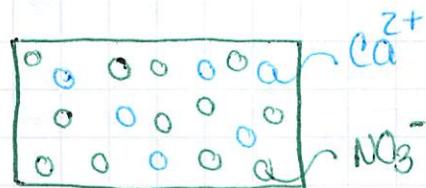
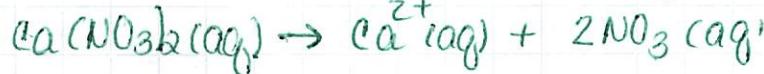
Ex) If you were to draw diagrams representing aqueous solutions of each of the following ionic compounds, how many anions would you show if the diagram contained 6 cations?

a) NiSO_4



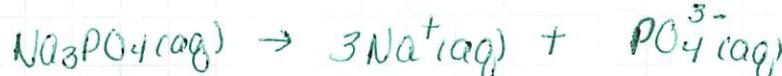
1 Ni^{2+} for every 1 SO_4^{2-}

b) $\text{Ca(NO}_3)_2$

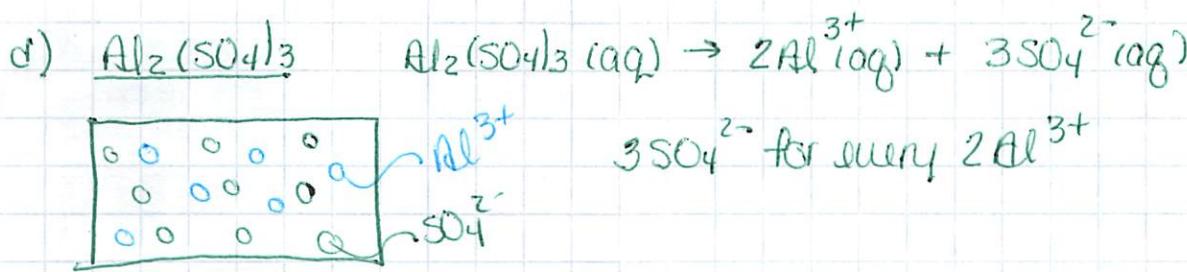


2 NO_3^- for every 1 Ca^{2+}

c) Na_3PO_4



1 PO_4^{3-} for every 3 Na^+



4.2 Precipitation Reactions - reactions that result in an insoluble product (the other product remains in solution)

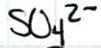
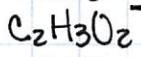
1. precipitate - an insoluble solid formed by a reaction in solution
Ex) $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{KI}(\text{aq}) \rightarrow \text{PbI}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$

2. Solubility Guidelines for Ionic Compounds

- A. solubility - amount of the substance that can be dissolved in a given amount of solvent at a given temperature
 - i) insoluble - a substance is considered insoluble if it has a solubility less than .01 mol/L.

Soluble Ionic Compounds

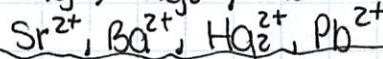
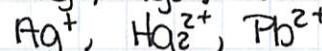
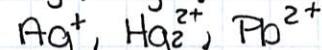
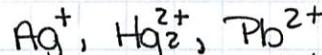
Compounds containing: NO_3^-



Important Exceptions

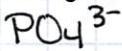
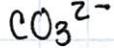
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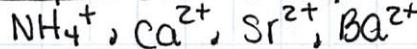


Insoluble Ionic Compounds

Compounds containing: S^{2-}



Important Exceptions



NH_4^+ , alkali metal cations

NH_4^+ , alkali metal cations

$\text{NH}_4^+, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$, alkali metal cations

- In order to predict if a precipitate will form, consider

- 1) the ions present in the reactants

- 2) the possible combinations of the cations & anions

- 3) the table above to determine if any combinations are insoluble.

Ex) Will a precipitate form when $\text{Mg}(\text{NO}_3)_2$ & NaOH react.

Ions



Possible Products:



Soluble?

NO

Yes

Ans:

YES



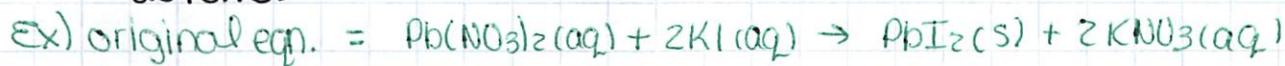
Ex) What compound precipitates when solutions of $\text{Fe}_2(\text{SO}_4)_3$ & LiOH mix? Write a balanced equation for the reaction.

| Ions | Possible Products | Soluble? |
|--------------------|--------------------------|----------|
| Fe^{3+} | $\text{Fe}(\text{OH})_3$ | no |
| SO_4^{2-} | Li_2SO_4 | |
| Li^+ | | yes |
| OH^- | | |



3. Ionic Equations

A. complete ionic equation - all strong electrolytes are shown as ions.



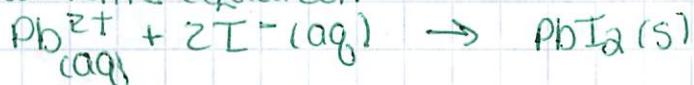
complete ionic eqn.



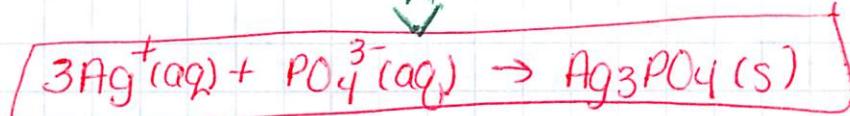
K^+ & NO_3^- are called spectator ions - appear the same on both sides of the reaction.

B. net ionic equation - only includes the ions involved directly in the reaction (no spectator ions)

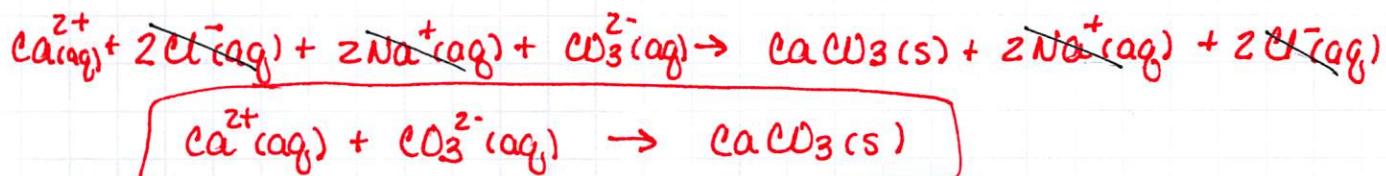
net ionic equation =



Ex) Write the net ionic equation for the precipitation reaction between silver nitrate & potassium phosphate solutions.



Ex) Write the net ionic equation for the precipitation reaction that occurs when solutions of calcium chloride and sodium carbonate occurs.



4.3 Acid - Base Reactions

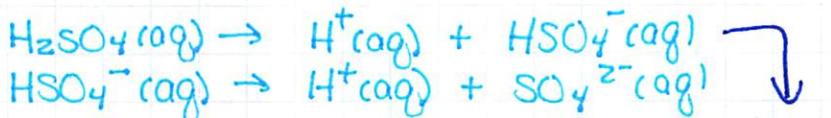
1. Acids - substances that ionize in aqueous solutions to form hydrogen ions, therefore increasing the concentration of $\text{H}^+(\text{aq})$ ions.

A. monoprotic acids - can ionize to give off one H^+

Ex) HF and HNO_3

B. diprotic acids - give off 2H^+ , occurs in 2 steps

Ex) H_2SO_4

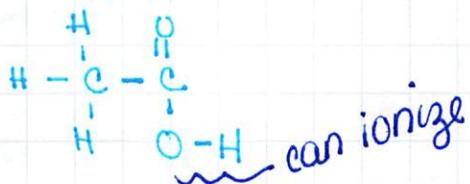


only the 1st ionization is complete

c. exceptions

Ex) $\text{HC}_2\text{H}_3\text{O}_2 \rightarrow$ is monoprotic even though it has 4 H's.

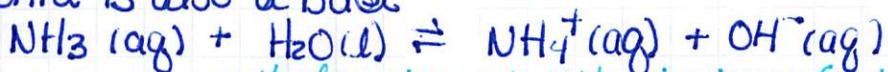
Only the H bonded to the oxygen can ionize. The other 3 H's are bonded to C and C-H bonds do not break in H_2O



2. Bases - substances that accept (react with) H^+ ions. Produce hydroxide (OH^-) ions when they dissolve in water.

Ex) Ionic hydroxide compounds such as NaOH , KOH , & Ca(OH)_2

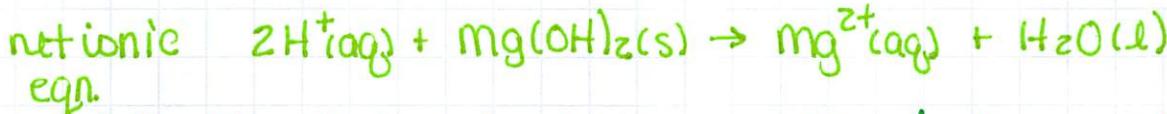
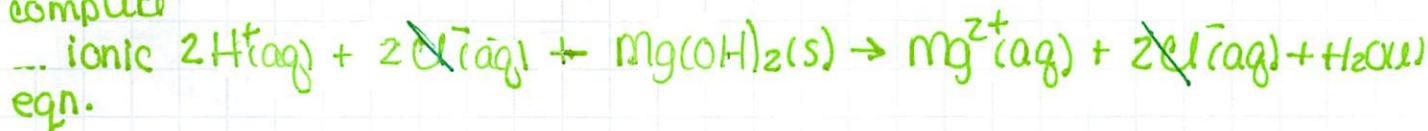
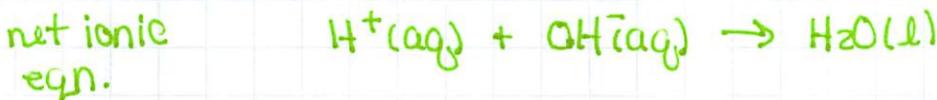
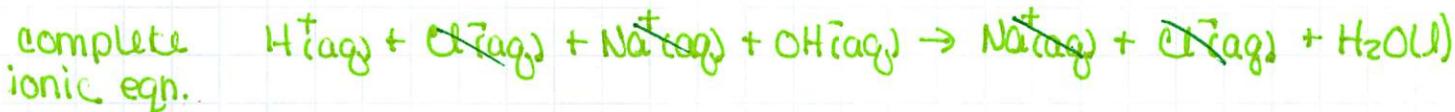
Ex) ammonia is also a base



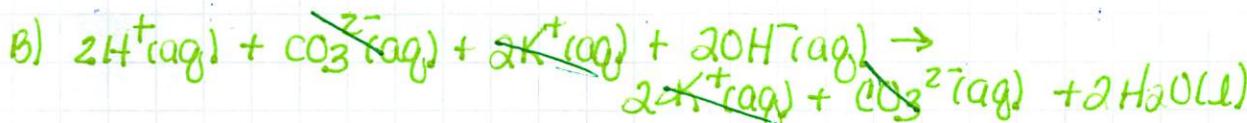
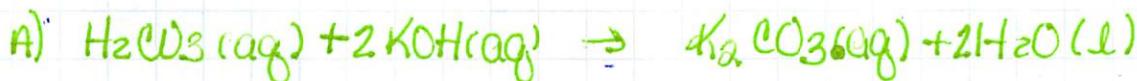
only a small fraction of NH_3 ionizes ($\sim 1\%$) so it's a weak electrolyte.

5. Neutralization Reactions and Salts

- A. Neutralization Reaction - a reaction between an acid and a base, producing a salt and water
- B. Salt - any ionic compound whose cation comes from a base & whose anion comes from an acid
- Ex) HCl + NaOH

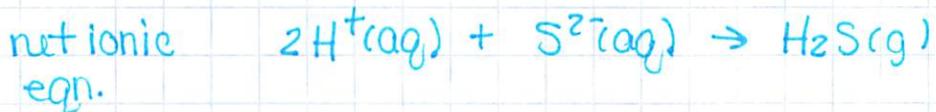


Ex) A) write a balanced molecular equation for the reaction between carbonic acid and potassium hydroxide. B) write the net ionic equation.

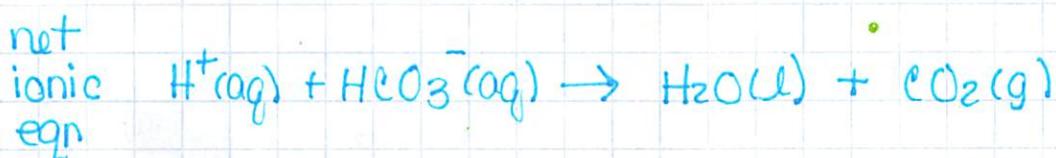
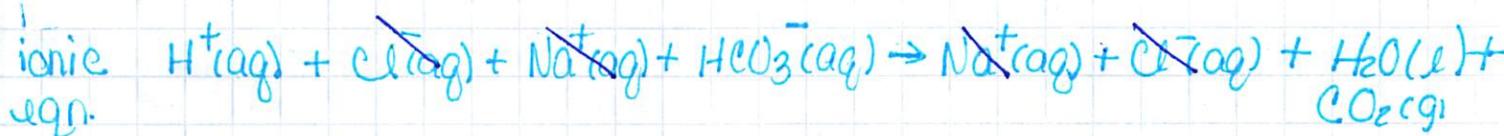
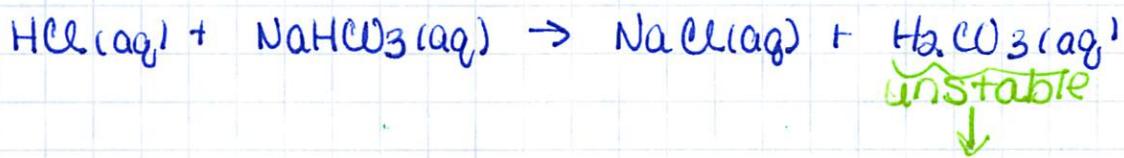


6. Acid-Base Reactions w/ Gas Formation - Bases w/ sulfide (S^{2-}) ions & carbonate (CO_3^{2-}) ions react w/ acids to form gases that have low solubility in water

Ex) reaction of HCl & Na_2S

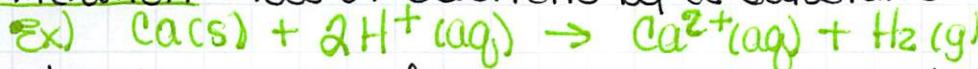


Ex) reaction of HCl & $NaHCO_3$



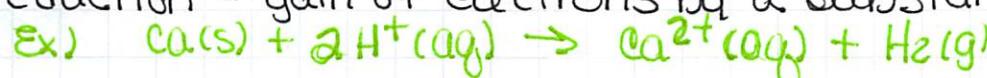
4.4. Oxidation-Reduction (redox) Reactions - when electrons are transferred between reactants

1. oxidation - loss of electrons by a substance



Ca is oxidized
 $\text{Ca}^0 \rightarrow \text{Ca}^{2+}$

2. reduction - gain of electrons by a substance



H is reduced
 $\text{H}^+ \rightarrow \text{H}_2$

3. Oxidation Numbers - actual charge of a monatomic ion

A. Rules for assigning oxidation numbers

1) Atoms in their elemental form \rightarrow ox. # is zero!

2) Any monatomic ion, ox. # is equal to its charge

3) Nonmetals usually have negative ox. # (but they are sometimes positive)

a) oxygen's ox. # is usually -2

i) exception is peroxide (O_2^{2-}) - ox. # is -1 .

b) hydrogen

i) ox. # is $+1$ when bonded to nonmetals

ii) ox. # is -1 when bonded to metals

c) fluorine's ox. # is always -1

i) other halogens are -1 in most binary compounds, but when combined w/oxygen in a polyatomic anion, they become positive.

4) Sum of ox. #'s in a neutral compound is zero

5) Sum of ox. #'s in a polyatomic ion is the charge of the ion.

Ex) Determine the oxidation state (st) for:

a) P in P_2O_5 $2(x) + 5(-2) = 0$

$$\text{P}_2\text{O}_5 \quad x = +5$$

b) H in NaH $1(+1) + 1(x) = 0$

$$\text{NaH} \quad x = -1$$

c) Cr in $\text{Cr}_2\text{O}_7^{2-}$

$$2(x) + 7(-2) = -2$$
$$\text{Cr}_2\text{O}_7^{2-} \quad x = +6$$

d) Sn in SnBr_4

$$1x + 4(-1) = 0$$
$$\text{SnBr}_4 \quad x = +4$$

e) O in BaO_2

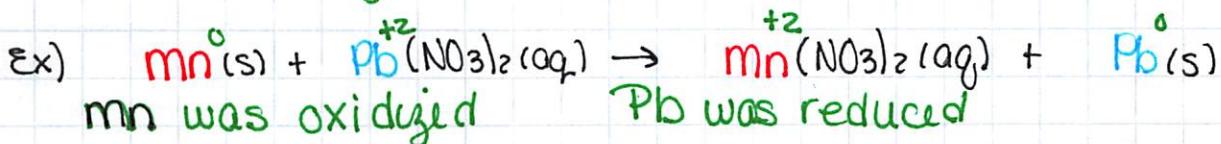
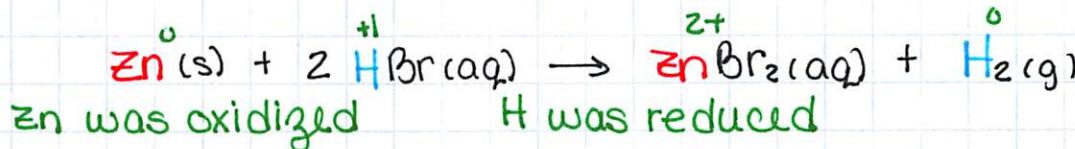
$$1(+2) + 2(x) = 0$$
$$\text{BaO}_2 \quad x = -1$$

4. Oxidation of metals by Acids and Salts

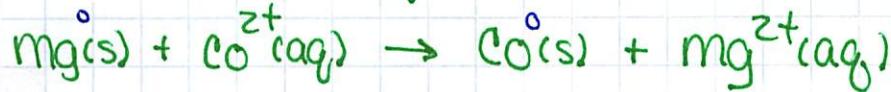
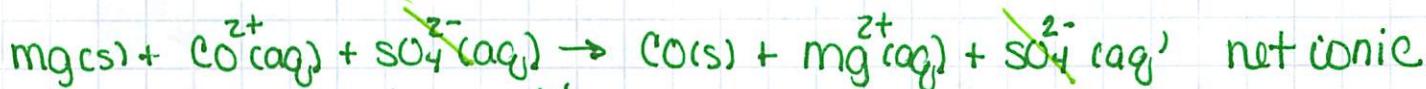
A. Displacement reactions - ion in solution is displaced/replaced through oxidation

* 1) General pattern: $A + BX \rightarrow AX + B$

Ex)



Ex) write the balanced & net ionic equations for the reaction between magnesium and cobalt(II) sulfate. What is oxidized & what is reduced?



Mg is oxidized Co²⁺ is reduced

5. The Activity Series

A. Metals vary in how easily they are oxidized

B. Activity Series - list used to predict the outcome of reaction b/w a metal & a metal salt or an acid. Any metal on the list can be oxidized by ions of the metal below it.

metal

- lithium
- potassium
- barium
- calcium
- sodium
- magnesium
- aluminum
- manganese
- zinc
- chromium
- iron
- cobalt
- nickel
- tin
- lead

Hydrogen

- copper
- silver
- mercury
- platinum
- gold

Oxidation Reaction

- $\text{Li(s)} \rightarrow \text{Li}^+(\text{aq}) + \text{e}^-$
- $\text{K(s)} \rightarrow \text{K}^+(\text{aq}) + \text{e}^-$
- $\text{Ba(s)} \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Ca(s)} \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Na(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{e}^-$
- $\text{Mg(s)} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-$
- $\text{Mn(s)} \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Cr(s)} \rightarrow \text{Cr}^{3+}(\text{aq}) + 3\text{e}^-$
- $\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Co(s)} \rightarrow \text{Co}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Ni(s)} \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Sn(s)} \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Pb(s)} \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
- $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Ag(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{e}^-$
- $\text{Hg(l)} \rightarrow \text{Hg}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Pt(s)} \rightarrow \text{Pt}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Au(s)} \rightarrow \text{Au}^{3+}(\text{aq}) + 3\text{e}^-$

↑
Ease of oxidation increases

Ex) Copper is above silver in the series, so copper will be oxidized by silver ions



Ex) Which of the following metals will be oxidized by $\text{Pb}(\text{NO}_3)_2$: Zn, Cu, Fe?

Zn & Fe are higher on the activity series than Pb, so they will be oxidized by it.

Ex) Will a solution of iron (III) chloride oxidize magnesium metal? If so, write a balanced and a net ionic equation for the reaction.

Ans. Yes it will
oxidize Mg



4.5 Concentrations of Solutions

1. concentration - the amount of solute dissolved in a given quantity of solvent/solution.
2. molarity (M) - #moles of solute per liter of solution.

$$M = \frac{n}{V}$$

Ex) calculate the molarity of a solution made by dissolving 23.4g of sodium sulfate in enough water to form 125mL of solution.

$$n_{Na_2SO_4} = 23.4\text{ g Na}_2SO_4 \left(\frac{1\text{ mol}}{142.1\text{ g}} \right) = .165\text{ mol Na}_2SO_4$$

$$\text{L}_{\text{soln}} = 125\text{ mL} = .125\text{ L}$$

$$M = \frac{n}{V} = \frac{.165\text{ mol}}{.125\text{ L}} = 1.32\text{ mol/L or } 1.32\text{ M}$$

3. Expressing the concentration of an Electrolyte - the relative concentrations of the ions in solution depend on the chemical formula of the compound.

Ex) what are the molar concentrations of each ion in a 0.025M calcium nitrate solution?



$$.025\text{ M } Ca(NO_3)_2 \left(\frac{1\text{ mol } Ca^{2+}}{1\text{ mol } Ca(NO_3)_2} \right) = .025\text{ M } Ca^{2+}$$

$$.025\text{ M } Ca(NO_3)_2 \left(\frac{2\text{ mol } NO_3^-}{1\text{ mol } Ca(NO_3)_2} \right) = .050\text{ M } NO_3^-$$

4. Dilution - lower the concentration of a solution by adding more solvent.

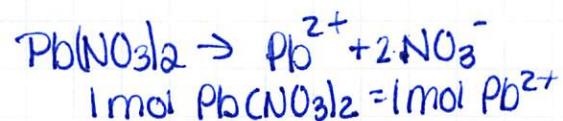
$$n_{\text{before}} = n_{\text{after}} \quad n = M \cdot V$$

$$(M \cdot V)_{\text{before}} = (M \cdot V)_{\text{after}}$$

Ex) what volume of 2.50M lead (II) nitrate solution contains .0500 mol of Pb²⁺

$$V = \frac{n}{M} = \frac{.0500\text{ mol}}{2.50\text{ M}}$$

$$V = .02\text{ L} = 20.0\text{ mL}$$



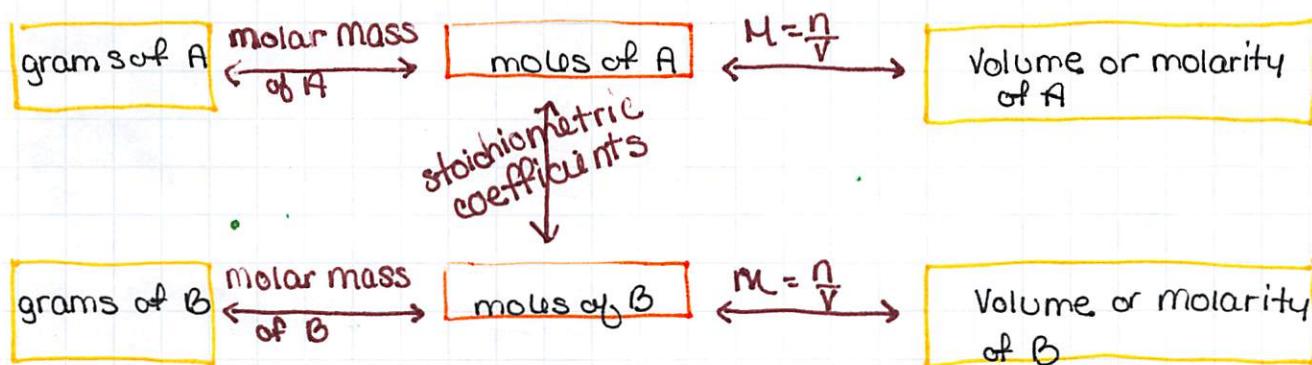
Ex) How many milliliters of 5.0M K₂Cr₂O₇ must be diluted to prepare 250mL of .10M solution?

$$M_b V_b = M_a V_a$$

$$(5.0\text{ M}) V_b = (.10\text{ M})(.25\text{ L})$$

$$V_b = .0050\text{ L or }5.0\text{ mL}$$

4.6 Solution Stoichiometry & Chemical Analysis



Ex) How many grams of NaOH are needed to neutralize 20.0mL of .150M H₂SO₄ solution?



1st = Figure the # mol's of H₂SO₄

$$M = \frac{n}{V} \quad n = M \cdot V$$

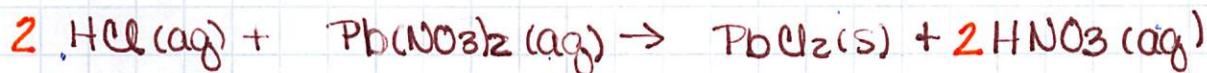
$$n = (.150\text{ M}) \times (.0200\text{ L})$$

$$n = 3.00 \times 10^{-3}\text{ mol H}_2\text{SO}_4$$

2nd = use stoichiometry to convert to grams of NaOH

$$3.00 \times 10^{-3}\text{ mol H}_2\text{SO}_4 \left(\frac{2\text{ mol NaOH}}{1\text{ mol H}_2\text{SO}_4} \right) \left(\frac{40.0\text{ g NaOH}}{1\text{ mol NaOH}} \right) = .240\text{ g NaOH}$$

Ex) How many liters of .500M HCl(aq) are needed to react completely with .100mol of Pb(NO₃)₂(aq), forming a precipitate of PbCl₂(s)?



1st/ use stoichiometry to convert to HCl.

$$\cdot 100 \text{ mol Pb(NO}_3)_2 \left(\frac{2 \text{ mol HCl}}{1 \text{ mol Pb(NO}_3)_2} \right) = .200 \text{ mol HCl}$$

2nd/ use $M = n/V$ to solve for volume

$$V = \frac{n}{M} = \frac{.200 \text{ mol HCl}}{.500 \text{ M HCl}} = .400 \text{ L HCl}$$

1. Titrations - used to determine the concentration of a particular solute in a solution. Involves combining a sample of the solution with a reagent solution of known concentration (standard solution).

- Can be done using acid-base, precipitation, or redox reactions
- The point at which stoichiometrically equivalent quantities are brought together is called the equivalence point.

i) Acid-Base reactions are titrated along with dyes called acid-base indicators to show the end point of a titration, which is really close to the equivalence point.

Ex) A sample of an iron ore is dissolved in acid and the iron is converted to Fe²⁺. The sample is then titrated with 47.20mL of .02240M MnO₄⁻ solution.

The redox reaction is: MnO₄⁻(aq) + 5Fe²⁺(aq) + 8H⁺(aq) → Mn²⁺(aq) + 5Fe³⁺(aq) + 4H₂O(l)

a) How many moles of MnO₄⁻ were added to the solution?

$$M = n/V \quad n = (.02240 \text{ M})(0.4720 \text{ L}) = 0.01057 \text{ mol MnO}_4^-$$

b) How many moles of Fe²⁺ were in the sample?

$$0.01057 \text{ mol MnO}_4^- \left(\frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} \right) = 0.05284 \text{ mol Fe}^{2+}$$

c) How many grams of iron were in the sample?

$$0.05284 \text{ mol Fe}^{2+} \left(\frac{55.8 \text{ g}}{1 \text{ mol}} \right) = .2950 \text{ g Fe}$$

d) If the sample had a mass of .8890g, what is the %Fe in the sample?

$$\% \text{ Fe} = (.2950 \text{ g} / .8890 \text{ g}) \times 100 = 33.18\%$$

Ex) what is the molality of an NaOH solution if 48.0mL is needed to neutralize 35.0mL of .144M H₂SO₄?



$$n_{\text{H}_2\text{SO}_4} = (.144 \text{M})(.0350 \text{L}) = 5.04 \times 10^{-3} \text{ mol}$$

$$n_{\text{NaOH}} = \frac{5.04 \times 10^{-3} \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}} = 1.01 \times 10^{-3} \text{ mol NaOH}$$

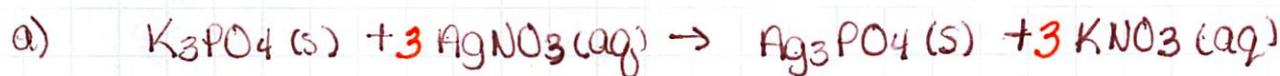
$$M_{\text{NaOH}} = \frac{1.008 \times 10^{-2} \text{ mol NaOH}}{.0480 \text{ L}} = .210 \text{ M}$$

Ex) A sample of 70.5mg of potassium phosphate is added to 15.0mL of 0.050M silver nitrate, resulting in the formation of a precipitate.

a) write the balanced equation for the reaction.

b) what is the limiting reactant?

c) calculate the theoretical yield, in grams, of the precipitate that forms.



b) 70.5mg K₃PO₄ $\left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) \left(\frac{1 \text{ mol K}_3\text{PO}_4}{212.3 \text{ g K}_3\text{PO}_4} \right) \left(\frac{3 \text{ mol KNO}_3}{1 \text{ mol K}_3\text{PO}_4} \right) = 9.96 \times 10^{-4} \text{ mol KNO}_3$

$$(.050 \text{ M AgNO}_3)(.0150 \text{ L}) = 7.5 \times 10^{-4} \text{ mol AgNO}_3 \left(\frac{3 \text{ mol KNO}_3}{3 \text{ mol AgNO}_3} \right) = 7.50 \times 10^{-4} \text{ mol KNO}_3$$

Limiting reactant is AgNO₃.

c) $7.50 \times 10^{-4} \text{ mol AgNO}_3 \left(\frac{1 \text{ mol Ag}_3\text{PO}_4}{3 \text{ mol AgNO}_3} \right) \left(\frac{418.7 \text{ g Ag}_3\text{PO}_4}{1 \text{ mol Ag}_3\text{PO}_4} \right) = .10 \text{ g Ag}_3\text{PO}_4$