

# CHEMICAL RXS, STOICHIOMETRY \_\_\_ Z Ch 2.9, 4, H Ch 1-2, 7-1-7-2, 16-4-16-6



"The world of chemical events is like a stage on which scene after scene is enacted in a continuous succession. The players on this stage are the elements. To each of them is assigned a characteristic role, either that of supernumerary or that of an actor playing a part."

**Clemens Alexander Winkler, 1897**

"Almost all the chemical processes which occur in nature ... take place between sub-stances in solution."

**Friedrich Wilhelm Ostwald, 1890**

(Nobel Prize for Chemistry in 1909 "in recognition of his work on catalysis and ... investigations into the fundamental principles governing chemical equilibria and rates of reaction".)



## Z 4.4 Types of Chemical Reactions

**dissolution** reactions (solvent, solute)

chemical reaction where two (or more) substances form a homogeneous mixture; dispersion is on the level of individual molecules or ions; size of dispersed particles generally  $< 10^{-9}$  m (nanometer)

**precipitation** reactions

chemical reaction where one substance exceeds its solubility in another so that it separates out of solution as a solid

**acid-base** reactions

"classic" Arrhenius reaction in water of a strong acid and a strong base reacting to form a salt and water

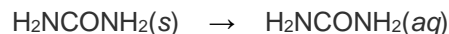
**oxidation-reduction** reactions

chemical reaction where electrons are transferred

### Z 4.1-4.2 Dissolution Reactions

**solubility** – largest amount of substance that can dissolve in a given amount of solvent at a given  $T$

molecular compounds in water (e.g., solid urea dissolving)



ionic compounds in water (**dissociation, ionization**)



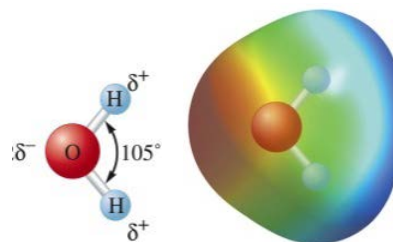
**water is polar**, often dissolves ions: "like dissolves like"

**electrolytes** (conduct electricity better than pure water)

strong:  $\text{Na}_2\text{CO}_3(\text{aq})$ ,  $\text{HCl}(\text{aq})$

weak (produce less ions  $\Rightarrow$  lower conductivity): ammonia, acetic acid

nonelectrolyte: ethanol, sugar



water is polar – unequal charge distribution

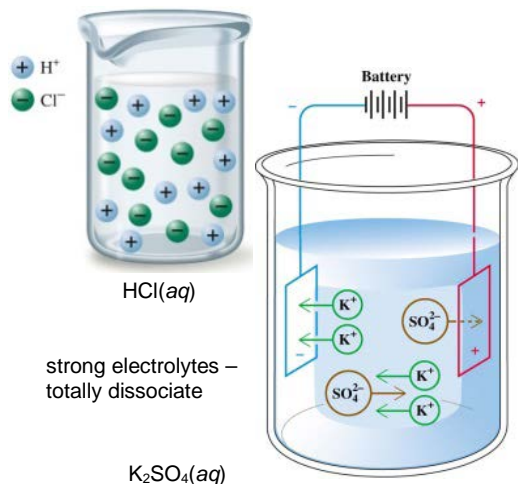
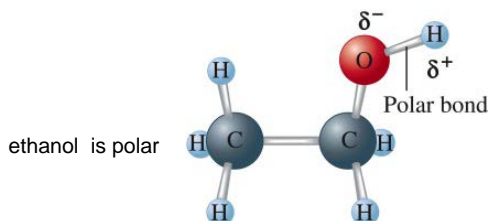


FIG I – Dissolution of  $K_2SO_4$  in Water

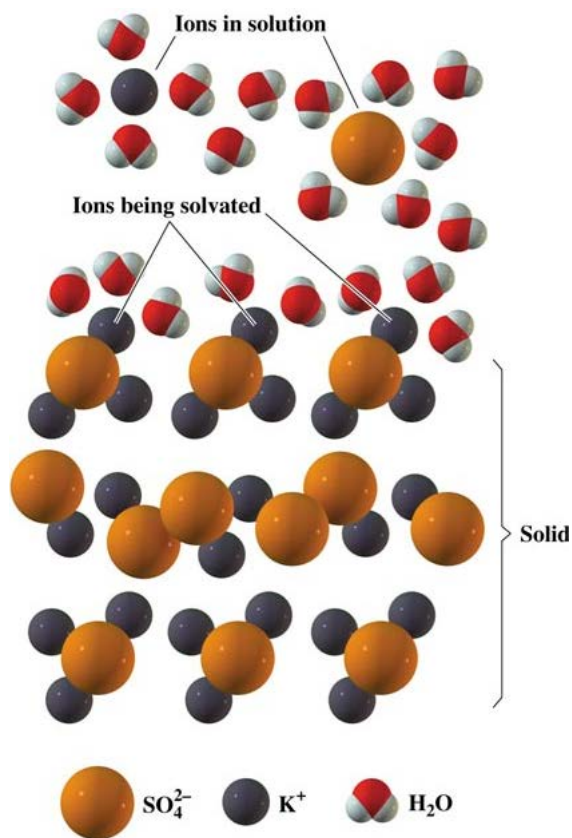
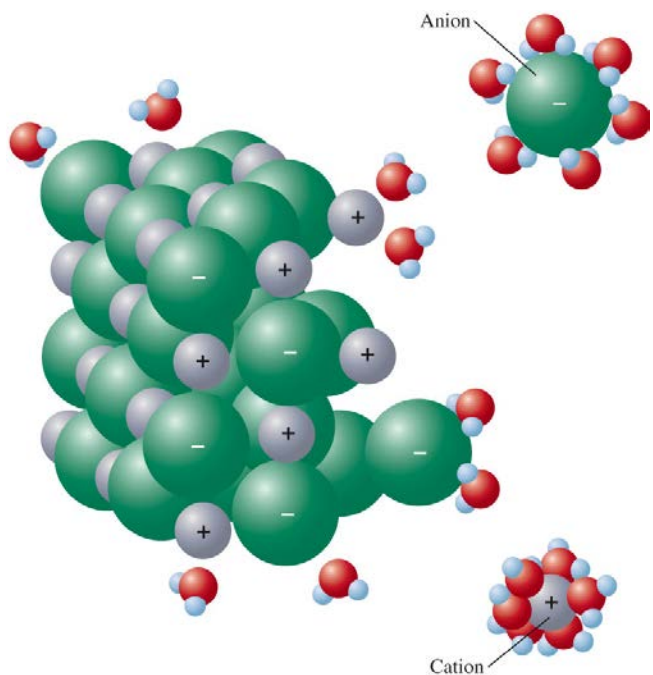


FIG II – Dissolution of  $NaCl$  in Water



### H 1-2; Z 4.3 Composition of Solutions

solute      solvent      solution

mass percent      mole fraction,  $X$

molarity,  $M$       molality,  $m$



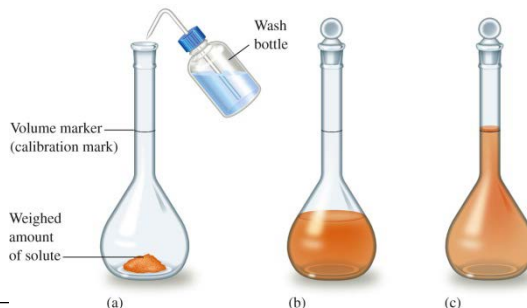
- a) volumetric (transfer) pipet – last drop does not drain out
- b) measuring (Mohr) pipet

**molarity** – number of moles of solute per liter of solution (measuring atoms in solution)

**EX 1.** What is the molarity of the solution which contains 5.00 g of HCl in 200 mL of solution? ( $M_{HCl} = 36.4609 \text{ g mol}^{-1}$ )

**EX 2.** What is the molarity of pure water? ( $M_{\text{H}_2\text{O}} = 18.0152 \text{ g mol}^{-1}$ ,  $d = 1.00 \text{ g cm}^{-3}$ )

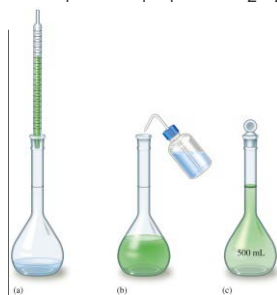
**EX 3.** What mass of silver nitrate is needed to make 100. mL of a 0.100 M  $\text{AgNO}_3$  solution? ( $M_{\text{AgNO}_3} = 169.874 \text{ g mol}^{-1}$ )



### Diluting/Mixing Solutions

number of moles do not change

$$n_1 = M_1 V_1 = M_2 V_2 = n_2$$



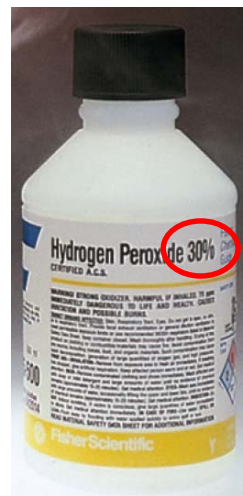
**EX 4.** What is the molarity of the solution prepared by adding 29.0 mL of 17.4 M acetic acid to a 500-mL volumetric and filling to the mark with distilled water?

**EX 5.** How would you prepare 1.5 L of 0.10 M  $\text{H}_2\text{SO}_4$  from a 16 M supply?

**EX 6.** What is the molarity of the sodium chloride solution obtained from mixing 53 mL of 0.52 M  $\text{NaCl}$  with 62 mL of 0.47 M  $\text{NaCl}$ ?

## Density in Molarity Calculations

**EX 7.** A solution which is 5.50% (by mass) sulfuric acid ( $M = 98.0778$ ) has a density of  $1.0352 \text{ g cm}^{-3}$ . What is the molarity of the solution?



**Z 4.5-4.6, 4.8 Precipitation Reactions** (omit 4.7 for now, will do these types of problems when we have the equilibrium constant for solubility,  $K_{sp}$ )

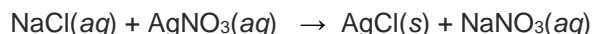
(or **WHY YOU NEED TO KNOW YOUR IONS**)

STRATEGY (do not memorize solubility tables)

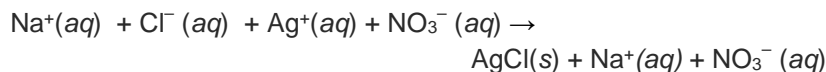
- write down formulas of reactants
- identify nature of reactants in solution (if ionic, what ions are in solution)
- consult solubility table for any combination of cations/anions that will precipitate
- write balanced equation
- write **total ionic equation**
- write **net ionic equation** - omits **spectator ions**

for example: if aqueous solutions of sodium chloride and silver nitrate were mixed, the solubility table identifies silver chloride as an insoluble species so

balanced equation:



total ionic equation:



net ionic equation (**contains the CHEMISTRY**):

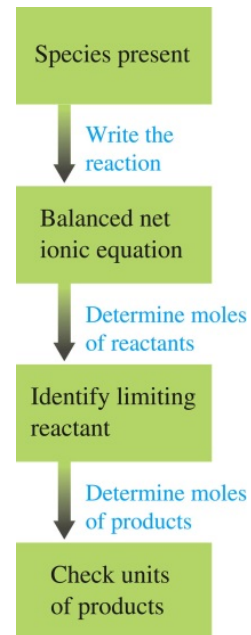
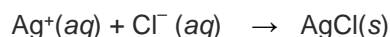


TABLE 4-1

| Solubilities of Ionic Compounds in Water    |  |  |  |
|---|--|--|--|
| Anion                                       | Soluble <sup>a</sup>                                     | Slightly Soluble   | Insoluble  |
| NO <sub>3</sub> <sup>-</sup> (nitrate)      | All  | —  | —  |
| ClO <sub>3</sub> <sup>-</sup> (chlorate)    | All  | —  | —  |
| ClO <sub>4</sub> <sup>-</sup> (perchlorate) | Most   | KClO <sub>4</sub>  | —  |
| CH <sub>3</sub> COO <sup>-</sup> (acetate)  | Most   | —  | Be(CH <sub>3</sub> COO) <sub>2</sub>   |
| F <sup>-</sup> (fluoride)                   | Group I, AgF, BeF <sub>2</sub>                           | SrF <sub>2</sub> , BaF <sub>2</sub> , PbF <sub>2</sub>                                   | MgF <sub>2</sub> , CaF <sub>2</sub>  |
| Cl <sup>-</sup> (chloride)                  | Most   | PbCl <sub>2</sub>  | AgCl, Hg <sub>2</sub> Cl <sub>2</sub>  |
| Br <sup>-</sup> (bromide)                   | Most   | PbBr <sub>2</sub> , HgBr <sub>2</sub>  | AgBr, Hg <sub>2</sub> Br <sub>2</sub>  |
| I <sup>-</sup> (iodide)                     | Most   | —  | AgI, Hg <sub>2</sub> I <sub>2</sub> ,<br>PbI <sub>2</sub> , HgI <sub>2</sub> |
| SO <sub>4</sub> <sup>2-</sup> (sulfate)     | Most   | CaSO <sub>4</sub> , Ag <sub>2</sub> SO <sub>4</sub> ,<br>Hg <sub>2</sub> SO <sub>4</sub> | SrSO <sub>4</sub> , BaSO <sub>4</sub> ,<br>PbSO <sub>4</sub>                 |
| S <sup>2-</sup> (sulfide)                   | Groups I and II<br>(NH <sub>4</sub> ) <sub>2</sub> S     | —  | Most   |
| CO <sub>3</sub> <sup>2-</sup> (carbonate)   | Group I, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> | —  | Most   |
| SO <sub>3</sub> <sup>2-</sup> (sulfite)     | Group I, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub> | —  | Most   |
| PO <sub>4</sub> <sup>3-</sup> (phosphate)   | Group I, (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> | Li <sub>3</sub> PO <sub>4</sub>  | Most   |
| OH <sup>-</sup> (hydroxide)                 | Group I, Ba(OH) <sub>2</sub>                             | Sr(OH) <sub>2</sub> , Ca(OH) <sub>2</sub>  | Most   |

<sup>a</sup>Soluble compounds have solubilities exceeding 1 g/100 g water. Slightly soluble compounds have solubilities between 0.01 and 1 g/100 g; insoluble compounds have solubilities less than 0.01 g/100 g at room temperature.

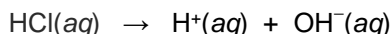
Group I, NH<sub>4</sub><sup>+</sup> always solubleAg<sup>+</sup>  
Hg<sub>2</sub><sup>2+</sup>

**EX 8.** Aqueous solutions of iron(III) bromide and potassium sulfide are mixed. Write a net ionic equation for the reaction.

**EX 9.** Aqueous solutions of sodium hydroxide and magnesium chloride are mixed. Write a net ionic equation for the reaction.

## Z 4.9 Acid-Base Reactions: Properties of Acids and Bases

**Arrhenius acids** - produce  $H^+(aq)$  ions upon dissolution in water

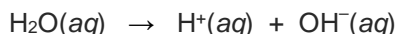


**Arrhenius bases** - produce  $OH^-(aq)$  ions upon dissolution in water



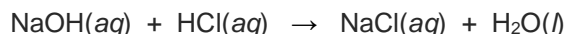
| seven strong acids to know |                                | soluble strong bases to know |                     |
|----------------------------|--------------------------------|------------------------------|---------------------|
| hydrochloric acid          | HCl                            | lithium hydroxide            | LiOH                |
| hydrobromic acid           | HBr                            | sodium hydroxide             | NaOH                |
| hydroiodic acid            | HI                             | potassium hydroxide          | KOH                 |
| perchloric acid            | HClO <sub>4</sub>              | rubidium hydroxide           | RbOH                |
| chloric acid               | HClO <sub>3</sub>              | cesium hydroxide             | CsOH                |
| sulfuric acid              | H <sub>2</sub> SO <sub>4</sub> | barium hydroxide             | Ba(OH) <sub>2</sub> |
| nitric acid                | HNO <sub>3</sub>               |                              |                     |

Arrhenius definition works since pure water ionizes to a very small extent in a process called **autoionization**



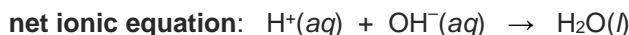
so water is both an Arrhenius acid and an Arrhenius base. A substance having both acidic and basic properties is called **amphoteric**.

**neutralization** - reaction of an Arrhenius acid with an Arrhenius base to form a **salt (ionic compound not containing OH<sup>-</sup>)** and water; driving force is the formation of stable, low energy water



species present:

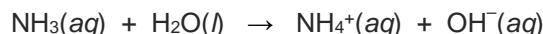
omit spectator ions:



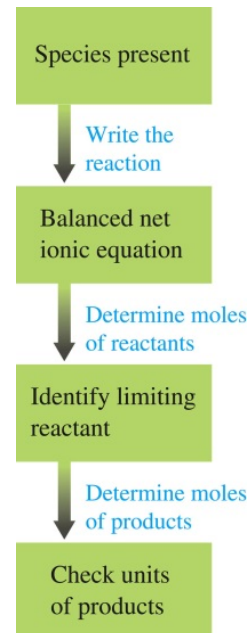
**weak acids** are not strong electrolytes like the strong acids, *e.g.*, organic acids (contain COOH group) like acetic acid,  $CH_3COOH(aq)$ , though they neutralize strong bases – leave H undissociated when writing. We will examine weak acids rather thoroughly in Chapter 7.

### EXPANDED DEFINITIONS

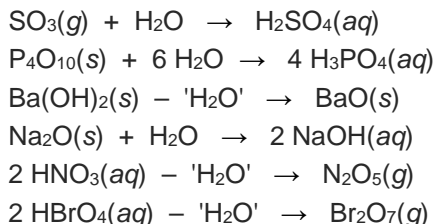
**Arrhenius bases** (modified definition) – increase concentration of  $OH^-$  above that present in pure water by reacting with water; so for the weak base ammonia



**Arrhenius acids** (modified definition) - increase concentration of  $H^+$  above that present in pure water by reacting with water



**acid** and **base anhydrides** - modified definitions allow the binary oxides of the nonmetals (generally covalent) to be recognized as acids and those of the metals (generally ionic) as bases



- to find acid add 'H<sub>2</sub>O' to formula of nonmetal oxide
- to find base add 'H<sub>2</sub>O' to formula of metal oxide
- to find acid anhydride subtract enough 'H<sub>2</sub>O' from formula of acid to remove all hydrogens
- to find base anhydride subtract enough 'H<sub>2</sub>O' from formula of base to remove all hydrogens

Increasing acidity →

|                          | I                     | II  | III                            | IV               | V                              | VI                | VII                            |
|--------------------------|-----------------------|-----|--------------------------------|------------------|--------------------------------|-------------------|--------------------------------|
| Increasing basicity<br>↓ | Li <sub>2</sub> O     | BeO | B <sub>2</sub> O <sub>3</sub>  | CO <sub>2</sub>  | N <sub>2</sub> O <sub>5</sub>  | (O <sub>2</sub> ) | OF <sub>2</sub>                |
|                          | Na <sub>2</sub> O     | MgO | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>4</sub> O <sub>10</sub> | SO <sub>3</sub>   | Cl <sub>2</sub> O <sub>7</sub> |
|                          | K <sub>2</sub> O      | CaO | Ga <sub>2</sub> O <sub>3</sub> | GeO <sub>2</sub> | As <sub>2</sub> O <sub>5</sub> | SeO <sub>3</sub>  | Br <sub>2</sub> O <sub>7</sub> |
|                          | Rb <sub>2</sub> O     | SrO | In <sub>2</sub> O <sub>3</sub> | SnO <sub>2</sub> | Sb <sub>2</sub> O <sub>5</sub> | TeO <sub>5</sub>  | I <sub>2</sub> O <sub>7</sub>  |
|                          | Cs <sub>2</sub> O     | BaO | Tl <sub>2</sub> O <sub>3</sub> | PbO <sub>2</sub> | Bi <sub>2</sub> O <sub>5</sub> | PoO <sub>3</sub>  | At <sub>2</sub> O <sub>7</sub> |
|                          | ← Increasing basicity |     |                                |                  |                                |                   | ↑<br>Increasing acidity        |

### Z 2.9 Nomenclature of Nonmetallic Compounds Containing Hydrogen

| H-Nonmetal   | H-Oxyanion   |
|--|--|
| <p><b>Rule 1:</b><br/>(without the presence of H<sub>2</sub>O)<br/>hydrogen _ide</p> <p><b>Examples:</b><br/>HCl hydrogen chloride<br/>HF hydrogen fluoride<br/>H<sub>2</sub>S hydrogen sulfide<br/>H<sub>2</sub>Se hydrogen selenide</p> <p><b>Rule 2:</b><br/>(H acids, when dissolved in H<sub>2</sub>O)<br/>hydro _ic acid</p> <p><b>Examples:</b><br/>HCl hydrochloric acid<br/>HF hydrofluoric acid<br/>H<sub>2</sub>S hydrosulfuric acid<br/>H<sub>2</sub>Se hydroselenic acid</p> <p><b>Comment:</b><br/>(a) These H-containing compounds are named as if they were ionic. (b) Often the (aq) in the formulas of the acids is omitted when it is obvious from the context that they are acids.</p> | <p><b>Rule 1:</b><br/>(without the presence of H<sub>2</sub>O)<br/>hydrogen hypo_ite<br/>hydrogen _ite<br/>hydrogen _ate<br/>hydrogen per_ate</p> <p><b>Rule 2:</b><br/>(HO acids, when dissolved in H<sub>2</sub>O)<br/>hypo_ous acid<br/>_ous acid<br/>_ic acid<br/>per_ic acid</p> <p><b>Examples:</b><br/>HClO hypochlorous acid<br/>HClO<sub>2</sub> chlorous acid<br/>HClO<sub>3</sub> chloric acid<br/>HClO<sub>4</sub> perchloric acid<br/>HNO<sub>2</sub> nitrous acid<br/>HNO<sub>3</sub> nitric acid<br/>H<sub>2</sub>SO<sub>3</sub> sulfurous acid<br/>H<sub>2</sub>SO<sub>4</sub> sulfuric acid<br/>H<sub>3</sub>PO<sub>4</sub> phosphoric acid</p> |

**Reactions of Acids and Bases: ACID + BASE → SALT + WATER**

chemistry contained in net ionic equation (or **WHY YOU NEED TO KNOW YOUR IONS**)

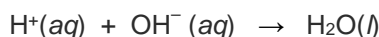
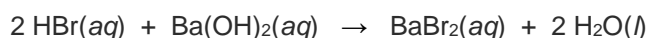
**ACIDS** react with

**BASES** react with

1. **bases**

1. **acids**

----- to yield **salt and water** -----

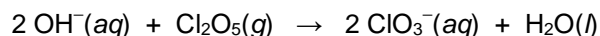
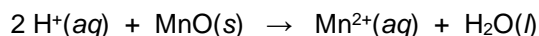
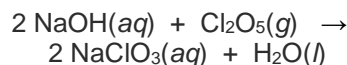
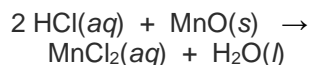


2. **metal oxides**

(not main group)

2. **nonmetal oxides**

----- to yield **salt and water** -----



3. **carbonates**

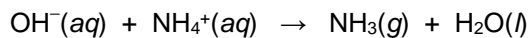
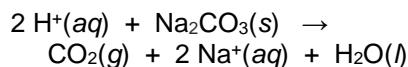
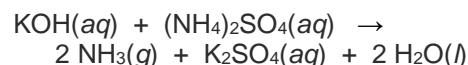
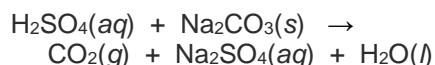
**hydrogen carbonates**

+ **CO<sub>2</sub>(g)**

3. **ammonium salts**

+ **NH<sub>3</sub>(g)**

----- to yield **salt and water** -----

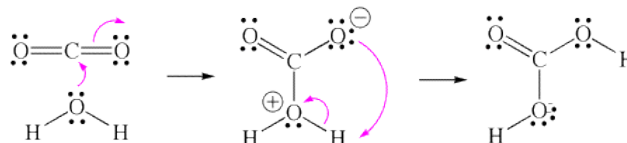
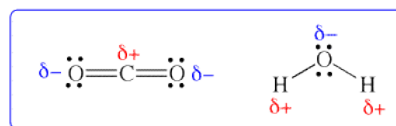
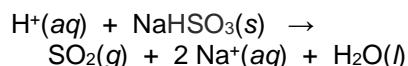
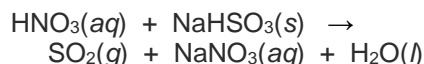


4. **sulfites**

**hydrogen sulfites**

----- to yield **salt and water** -----

+ **SO<sub>2</sub>(g)**



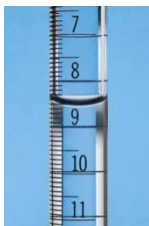
carbonic acid ( $\text{H}_2\text{CO}_3$ ) and sulfurous acid ( $\text{H}_2\text{SO}_3$ ) are unstable and decompose to  $\text{CO}_2$  and  $\text{SO}_2$ , respectively (reverse of above reaction)



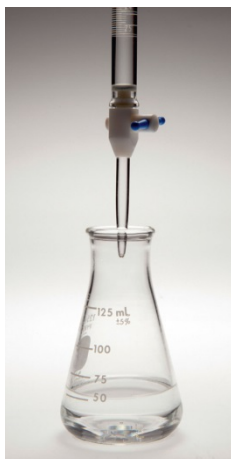
## H 7-1-7-2; Z 4.9 Acid-Base Titrations

- balanced equation
- concentrations
- end-point = equivalence point

### acid/base titrations



reading a meniscus



(a)



(b)

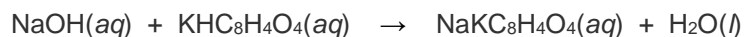


(c)

### The Phenolphthalein End-Point

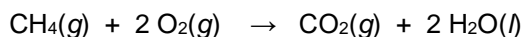
**EX 10.** A 25.0 mL sample of acetic acid ( $\text{CH}_3\text{COOH}$ ) requires 28.33 mL of 0.953 M NaOH to reach the phenolphthalein end-point. What is the concentration of acetic acid?

**EX 11.** 0.6135 g of potassium acid phthalate (KHP,  $M = 204.22$  g/mol) that has been dissolved in water requires 37.65 mL of an NaOH solution to reach the phenolphthalein end-point. What is the molarity of the base?

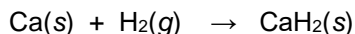


## Z 4.10 Oxidation-Reduction Reactions

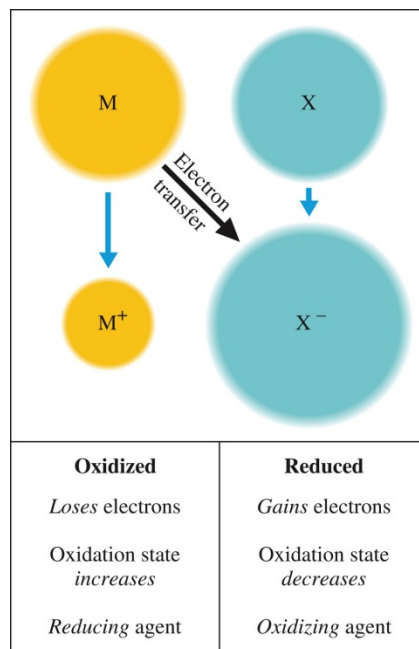
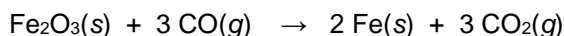
“classic” oxidation (combining with oxygen)



“classic” reduction (combining with hydrogen)



many other reactions also involve redox



### Identifying Redox Reactions

species that is oxidized (**reducing agent**)

species that is reduced (**oxidizing agent**)

**oxidation numbers** (in order of priority)

- Sum of the oxidation numbers (**ON**) of the atoms is zero for a neutral molecule and is the charge for an ion.
- Group I ON = 1, Group II ON = 2, Group III usually have ON = 3.
- Fluorine ON = -1 **always**. Other halogens usually have ON = -1 except in compounds with oxygen or other halogens when the oxidation number follows electronegativity and can be positive.
- Hydrogen has ON = 1 except in metal hydrides when the oxidation number is -1.
- Oxygen has ON = -2 except in compounds with fluorine when the oxidation number can be positive and in compounds containing the O-O bond. For peroxides ( $\text{O}_2^{2-}$ ) ON = -1

**EX 12.** Assign oxidation numbers (ON) to all of the elements in the following chemical compounds.

NaCl

$\text{ClO}^-$

$\text{Fe}_2(\text{SO}_4)_3$

$\text{KMnO}_4$

$\text{H}_2\text{O}_2$

$\text{SO}_2$

$\text{I}_2$

$\text{CaH}_2$

$\text{CH}_4$

$\text{K}_2\text{O}$

**EX 13.** Assign oxidation numbers (ON) to the chlorine atom in the following acidic oxides.

oxide

acid

$\text{Cl}_2\text{O}$

$\text{HClO}$

$\text{Cl}_2\text{O}_3$

$\text{HClO}_2$

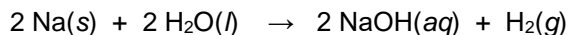
$\text{Cl}_2\text{O}_5$

$\text{HClO}_3$

$\text{Cl}_2\text{O}_7$

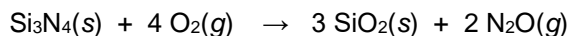
$\text{HClO}_4$

**EX 14.** The alkali metals react with water, evolving hydrogen gas.

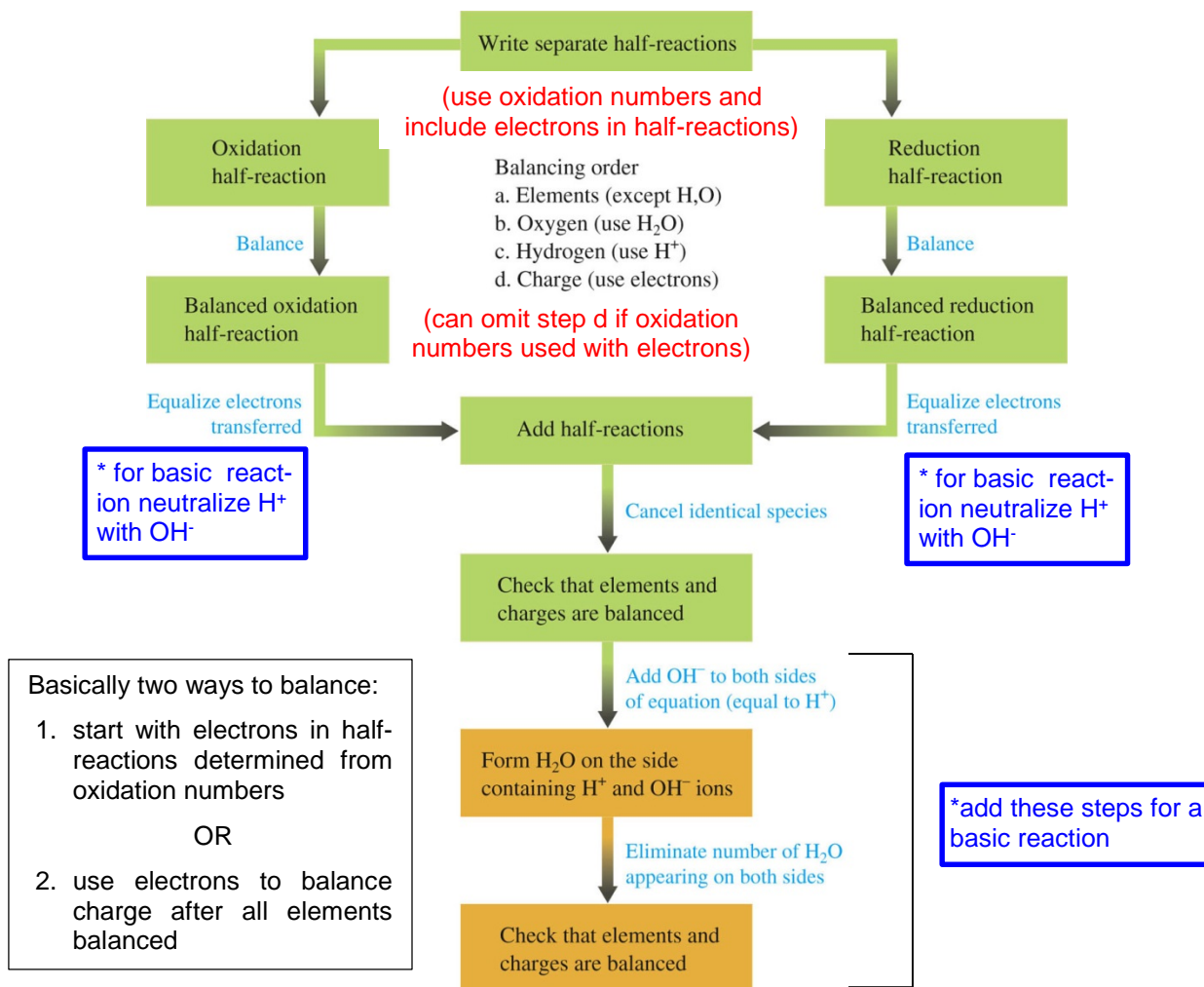


What is being oxidized, what is being reduced, and how many moles of electrons are transferred?

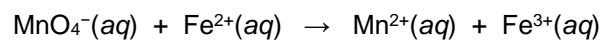
**EX 15.** For the following redox reaction what is the oxidizing agent, what is the reducing agent, and how many moles of electrons are transferred?



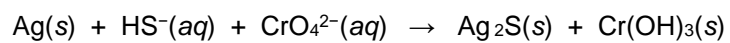
### Z 4.11 Steps in Balancing Redox Equations by Half-Reaction Method



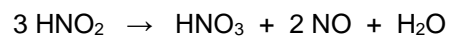
**EX 16.** Balance in acidic solution



**EX 17.** Balance in basic solution



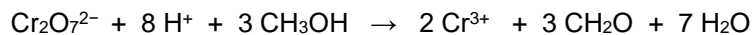
**disproportionation** (H box p. 124, Z p. 768)



**H 16-4–16-6; Z 4.12 Oxidation-Reduction Titrations**

common reagents for analytical redox titrations: permanganate,  $\text{MnO}_4^-$ ; dichromate,  $\text{Cr}_2\text{O}_7^{2-}$ ; and ceric,  $\text{Ce}^{4+}$

**EX 18.** How many moles of  $\text{CH}_2\text{O}$  form when 37 mL of 0.52 M  $\text{Cr}_2\text{O}_7^{2-}$  reacts with excess  $\text{CH}_3\text{OH}$  according to



**EX 19.** The iron in a 1.026 g sample of ore is quantitatively all converted to Fe(II) and then titrated with 0.0195 M  $\text{KMnO}_4$ . If 24.35 mL is required to reach the endpoint what is the mass percent iron in the ore? ( $M = 55.845 \text{ g/mol}$ )

