

# **Reactions in Aqueous Solution**

# Topics

- General properties of aqueous solutions
- Precipitation reactions
- Acid base reactions
- Oxidation reduction reactions
- Concentration of solutions
- Aqueous reactions and chemical analysis

## **4.1 General Properties of Aqueous Solutions**

A solution is a homogenous mixture of 2 or more substances

The <u>solute</u> is(are) the substance(s) present in the smaller amount(s). The substance dissolved The <u>solvent</u> is the substance present in the larger amount. The substance does the dissolving

<u>Solution</u>	<u>Solvent</u>	<u>Solute(s)</u>
Soft drink (/)	H <sub>2</sub> O	Sugar, CO <sub>2</sub>
Air ( <i>g</i> )	N <sub>2</sub>	$O_2$ , Ar, $CH_4$
Soft Solder (s)	Pb	Sn

# **Electrolytes and Nonelectrolytes**

 <u>Electrolytes</u>- Substances that conduct an electric current in <u>aqueous solution</u>, or in the <u>molten state because the soltions</u> <u>contain ions</u>

$$\operatorname{NaCl}(s) \xrightarrow{H_2O} \operatorname{Na}^+(aq) + \operatorname{Cl}^-(aq)$$

- all ionic compounds are electrolytes because their aqueous soltions contain ions (they are also called "salts")
- barium sulfate- will conduct when molten, but is *insoluble* in water!

Nonelectrolytes - Substances that do not conduct an electric current when dissolved in water

-Most of them are molecular materials, and their solutions *do not contain ions* 

$$C_{12}H_{22}O_{11}(s) \xrightarrow{H_2O} C_{12}H_{22}O_{11}(aq)$$

Not all electrolytes conduct to the same degree
 – there are <u>strong</u> electrolytes, and <u>weak</u>

electrolytes

 Dissociation - ionic compounds separate into constituent ions when dissolved in solution

$$\operatorname{NaCl}(s) \xrightarrow{H_2O} \operatorname{Na}^+(aq) + \operatorname{Cl}^-(aq)$$

Ionization - formation of ions by molecular compounds when dissolved

$$\operatorname{HCl}(g) \xrightarrow{\operatorname{H}_2\operatorname{O}} \operatorname{H}^+(aq) + \operatorname{Cl}^-(aq)$$

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

# Strong and weak electrolytes

- Not all electrolytes conduct to the same degree
- Conductivity depends on: <u>degree of</u> <u>dissociation or ionization</u>
- Strong Electrolyte: 100% dissociation
  - All water soluble ionic compounds, strong acids and strong bases
- Weak electrolytes
  - Partially ionized in solution
  - Exist mostly as the molecular form in solution
  - Weak acids and weak bases

#### **TABLE 4.1**The Strong Acids

Acid	Ionization Equation
Hydrochloric acid	$\operatorname{HCl}(aq) \longrightarrow \operatorname{H}^+(aq) + \operatorname{Cl}^-(aq)$
Hydrobromic acid	$\operatorname{HBr}(aq) \longrightarrow \operatorname{H}^{+}(aq) + \operatorname{Br}^{-}(aq)$
Hydroiodic acid	$\mathrm{HI}(aq) \longrightarrow \mathrm{H}^{+}(aq) + \mathrm{I}^{-}(aq)$
Nitric acid	$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$
Chloric acid	$\text{HClO}_3(aq) \longrightarrow \text{H}^+(aq) + \text{ClO}_3^-(aq)$
Perchloric acid	$\operatorname{HClO}_4(aq) \longrightarrow \operatorname{H}^+(aq) + \operatorname{ClO}_4^-(aq)$
Sulfuric acid*	$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$
	$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$

\*Note that although each sulfuric acid molecule has two ionizable hydrogen atoms, it only undergoes the first ionization completely, effectively producing one H<sup>+</sup> ion and one HSO<sub>4</sub><sup>-</sup> ion per H<sub>2</sub>SO<sub>4</sub> molecule. The second ionization happens only to a very small extent. Examples of weak electrolytes

- Weak acids HC<sub>2</sub>H<sub>3</sub>O<sub>2(aq)</sub>  $\longrightarrow$  C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup> (aq) + H<sup>+</sup> (aq)

- Weak bases NH<sub>3 (aq)</sub> + H<sub>2</sub>O<sub>(l)</sub>  $\longrightarrow$  NH<sub>4</sub><sup>+</sup> (aq) + OH<sup>-</sup> (aq)

(Note: double arrows indicate a reaction that occurs in both directions - a state of *dynamic equilibrium* exists)

#### **Method to Distinguish Types of Electrolytes**







#### strong electrolyte

#### nonelectrolyte

#### weak electrolyte



#### Acetic acid ammonia

Weak electrolyte



Sodium chloride Hydrochloric acid

**Strong electrolyte** 



**Classify the following as** nonelectrolyte, weak electrolyte or strong electrolyte - NaOH strong electrolyte  $-CH_3OH$ nonelectrolyte  $-H_2CO_3$ weak electrolyte

# **4.2 Precipitation Reactions**

- When aqueous solutions of ionic compounds are mixed together a solid forms (occurs when product is insoluble)
- A solid that forms from mixed solutions is called <u>precipitate</u>
- If the substance is not part of the solution, it is a precipitate
- Solubility is the maximum amount of a solid that can dissolve in a given amount of solvent at a specified temperature
- Prediction based on solubility rules





# Water, the common solvent

# **The Water Molecule, Polarity**

H

Thus water has a partialgative end (Ositigen) and a pahagositive end (Hydrogen) and it is called "polar" because of ິ{+ the unequal charge distribution

δ<sup>-</sup> means a partial negative charge

# Dissolving ionic salts in water and Hydration

- Ions have charges and attract the opposite charges on the water molecules.
- The process of breaking the ions of salts apart is called hydration

 $NH_4NO_3(s) \xrightarrow{H_2O(1)} NH_4^+(aq) + NO_3^-(aq)$ 

**Designates hydration of ions** 

Hydration: process by which water molecules remove and surround individual ions from the solid.

# How lonic solids dissolve in water

These ions have been pulled away from the main crystal structure by water's polarity.

These ions have been surrounded by water, and are now dissolved

**Hydration** 

## Precipitation Reactions (Double replacement or metathesis reaction)

precipitate

 $Pb(NO_3)_2(aq) + 2Nal(aq) \longrightarrow Pbl_2(s) + 2NaNO_3(aq)$ 

 $Pb^{2+} + 2NO_3^- + 2Na^+ + 2I^- \longrightarrow PbI_2(s) + 2Na^+ + 2NO_3^-$ Anions and cations switch partners

 $Pb^{2+} + 2l^{-} \longrightarrow Pbl_{2}(s)$ 

Pbl<sub>2</sub>

Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> are <u>Spectator</u> ions

TABLE 4.2	Solubility Guidelines: Soluble Compounds			
Water-Soluble Compounds		Insoluble Exceptions		
Compounds cont Na <sup>+</sup> , K <sup>+</sup> , Rb <sup>+</sup> , C	taining an alkali metal cation ( $\text{Li}^+$ , $\text{Cs}^+$ ) or the ammonium ion ( $\text{NH}_4^+$ )			
Compounds cont acetate ion ( $C_2H_2$	taining the nitrate ion $(NO_3^-)$ , $_3O_2^-)$ , or chlorate ion $(ClO_3^-)$			
Compounds cont bromide ion (Br	taining the chloride ion $(CI^-)$ , ), or iodide ion $(I^-)$	Compounds containing $Ag^+$ , $Hg_2^{2+}$ , or $Pb^{2+}$		
Compounds cont	taining the sulfate ion $(SO_4^{2-})$	Compounds containing $Ag^+$ , $Hg_2^{2+}$ , $Pb^{2+}$ , $Ca^{2+}$ , $Sr^{2+}$ , or $Ba^{2+}$		

#### TABLE 4.3

#### Solubility Guidelines: Insoluble Compounds

#### Water-Insoluble Compounds

Compounds containing the carbonate ion  $(CO_3^{2^-})$ , phosphate ion  $(PO_4^{3^-})$ , chromate ion  $(CrO_4^{2^-})$ , or sulfide ion  $(S^{2^-})$ 

Compounds containing the hydroxide ion (OH<sup>-</sup>)

#### Soluble Exceptions

Compounds containing Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, or NH<sub>4</sub><sup>+</sup>

Compounds containing Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, or Ba<sup>2+</sup>



#### Solubility rules for common ionic compounds in water at 25° c

Soluble Compounds	Exceptions
Compounds containing alkali metal ions and NH <sub>4</sub> +	
NO <sub>3</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , CIO <sub>3</sub> <sup>-</sup>	
Cl <sup>-</sup> , Br <sup>-</sup> , l <sup>-</sup>	Halides of Ag <sup>+</sup> , Hg <sub>2</sub> <sup>2+</sup> , Pb <sup>2+</sup>
SO <sub>4</sub> <sup>2-</sup>	Sulfates of Ag <sup>+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Hg <sup>2+</sup> , Pb <sup>2+</sup>
Slightly soluble Compounds	Exceptions
CO <sub>3</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> , CrO <sub>4</sub> <sup>2-</sup> , S <sup>2-</sup>	Compounds containing alkali metal ions and NH <sub>4</sub> <sup>+</sup>
OH-	Compounds containing alkali metal ions and Ba <sup>2+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> are marginally soluble

Molecular equation: shows all compounds represented by their chemical formulas

 $Na_2SO_4(aq) + Ba(OH)_2(aq) \longrightarrow 2NaOH(aq) + BaSO_4(s)$ 

 Ionic equation: shows all strong electrolytes as ions and all other substances (nonelectrolytes, weak electrolytes, gases) by their chemical formulas

$$Na_2SO_4(aq) \longrightarrow 2Na^+(aq) + SO_4^{2-}(aq)$$
$$Ba(OH)_2(aq) \longrightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

#### **Molecular equation:**

 $Na_2SO_4(aq) + Ba(OH)_2(aq) \longrightarrow 2NaOH(aq) + BaSO_4(s)$ 

#### **Ionic equation:**

 $2\mathrm{Na}^{+}(aq) + \mathrm{SO}_{4}^{2-}(aq) + \mathrm{Ba}^{2+}(aq) + 2\mathrm{OH}^{-}(aq) \longrightarrow 2\mathrm{Na}^{+}(aq) + 2\mathrm{OH}^{-}(aq) + \mathrm{Ba}\mathrm{SO}_{4}(s)$ 

## Net lonic equation: shows only the reacting species in the chemical equation Eliminates spectator ions –

 $2\mathrm{Na}^{+}(aq) + \mathrm{SO}_{4}^{2-}(aq) + \mathrm{Ba}^{2+}(aq) + 2\mathrm{OH}^{-}(aq) \longrightarrow 2\mathrm{Na}^{+}(aq) + 2\mathrm{OH}^{-}(aq) + \mathrm{Ba}\mathrm{SO}_{4}(s)$ 

#### Net ionic equation:

$$\operatorname{Ba}^{2^+}(aq) + \operatorname{SO}_4^{2^-}(aq) \longrightarrow \operatorname{BaSO}_4(s)$$

## Steps in writing a net ionic equation

Aqueous solutions of silver nitrate and sodium sulfate are mixed. Write the net ionic reaction. Step 1:

 $2AgNO_{3}(aq)+Na_{2}SO_{4}(aq) \rightarrow 2NaNO_{3}(?)+Ag_{2}SO_{4}(?)$ 

Step 2: Use solubility table; all nitrates are soluble but silver sulfate is insoluble

 $2Ag^{+}(aq) + 2NO_{3}^{-}(aq) + 2Na^{+}(aq) + SO_{4}^{2-}(aq)$ 

 $\rightarrow$  2Na<sup>+</sup>(aq) + 2NO<sub>3</sub><sup>-</sup>(aq) + Ag<sub>2</sub>SO<sub>4</sub>(s)

#### **Step 3: Cancel spectators**

 $2Ag^{+}(aq) + 2NO_{3}^{-}(aq) + 2Na^{+}(aq) + SO_{4}^{2-}(aq)$  $\rightarrow 2Na^{+}(aq) + 2NO_{3}^{-}(aq) + Ag_{2}SO_{4}(s)$ 

**Step 4: Write the net ionic reaction** 

 $2Ag^{+}(aq) + SO_{4}^{2-}(aq) \rightarrow Ag_{2}SO_{4}(s)$ 

#### **4.3 Acid-Base Reactions**

- Termed neutralization reactions.
- Involve an acid and a base.
- Double replacement (or metathesis) reaction
- A molecular compound (water) is a common product along with a salt (ionic compound).

#### **TABLE 4.4**Strong Acids and Strong Bases

Strong Acids	Strong Bases	Strong Acids	Strong Bases
HCl	LiOH	HClO <sub>3</sub>	CsOH
HBr	NaOH	$HClO_4$	Ca(OH) <sub>2</sub>
HI	КОН	$H_2SO_4$	Sr(OH) <sub>2</sub>
HNO <sub>3</sub>	RbOH		Ba(OH) <sub>2</sub>

# All the other acids and bases are weak electrolytes (important for net ionic equations).

#### **Definitions of acids and bases**

- Arrhenius acid produces H<sup>+</sup> in solution
- Arrhenius base produces OH<sup>-</sup> in solution
- More inclusive definitions:
  - Brønsted acid proton donor
  - Brønsted base proton acceptor

# Examples of a weak base and weak acid Ammonia with water:



#### Hydrofluoric acid with water:





Monoprotic: one ionizable hydrogen

 $HCI + H_2O \rightarrow H_3O^+ + CI^-$ 

- Diprotic: two ionizable hydrogens

 $H_{2}SO_{4} + H_{2}O \rightarrow H_{3}O^{+} + HSO_{4}^{-}$  $HSO_{4}^{-} + H_{2}O \rightarrow H_{3}O^{+} + SO_{4}^{2-}$ 

#### Triprotic: three ionizable hydrogens

 $H_{3}PO_{4} + H_{2}O \rightarrow H_{3}O^{+} + H_{2}PO_{4}^{-}$  $H_{2}PO_{4}^{-} + H_{2}O \rightarrow H_{3}O^{+} + HPO_{4}^{2-}$  $HPO_{4}^{2-} + H_{2}O \rightarrow H_{3}O^{+} + PO_{4}^{3-}$ 

 Polyprotic: generic term meaning more than one ionizable hydrogen



#### – Monobasic: One OH<sup>–</sup> group

#### $KOH \rightarrow K^+ + OH^-$

#### – Dibasic: Two OH<sup>–</sup> groups

# $Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

**Acid-Base Neutralization** Neutralization: Reaction between an acid and a base Acid + Base  $\rightarrow$  Salt + Water Molecular equation: (Strong acid-strong base)  $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(I)$ **Ionic equation:**  $H^+(aq) + CF^-(aq) + Na^+(aq) + OH^-(aq)$  $\rightarrow$  Na<sup>+</sup>(aq) +  $\mathcal{G}^{-}(aq) + H_2O(I)$ Net ionic equation:  $H^+(aq) + OH^-(aq) \rightarrow H_2O(I)$ 

#### Describing weak acid- strong base reactions

Weak acid  $HC_2H_3O_2(aq) + NaOH(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(I)$  $HC_{2}H_{3}O_{2}(aq) + Na^{+}(aq) + OH^{-}(aq) \longrightarrow C_{2}H_{3}O_{2}^{-}(aq) + Na^{+}(aq) + H_{2}O(l)$  $HC_2H_3O_2(aq) + OH^2(aq) \longrightarrow C_2H_3O_2(aq) + H_2O(l)$ 

# **4.4 Oxidation-Reduction Reactions**

- Often called "redox" reactions
- Electrons are transferred between the reactants
  - One substance is oxidized, loses electrons (electron donor)
    - Reducing agent
  - Another substance is reduced, gains electrons (electron acceptor)
    Oxidizing agent
- Oxidation numbers change during the reaction
- Example  $Zn(s) + CuSO_{4}(aq) \rightarrow ZnSO_{4}(aq) + Cu(s)$  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ - Zinc is losing 2 electrons and oxidized. Reducing agent  $\square$  Zn(s)  $\rightarrow$  Zn<sup>2+</sup>(aq) + 2e<sup>-</sup> - Copper ions are gaining the 2 electrons. Oxidizing agent  $- Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ 

#### Reaction of Cu and Zn<sup>2+</sup> ions



# **Example of redox reactions**

$$2\overset{\scriptscriptstyle 0}{Na}(s)+\overset{\scriptscriptstyle 0}{Cl}_2(g)\rightarrow 2\overset{\scriptscriptstyle +1}{Na}\overset{\scriptscriptstyle -1}{Cl}(s)$$

#### Each sodium atom loses one electron:

$$\stackrel{0}{Na} \xrightarrow{+1} Na + e^{-}$$

Each chlorine atom gains one electron:

$$\begin{array}{ccc} 0 & & -1 \\ Cl &+ & e^- & \longrightarrow & Cl \end{array}$$

# **Definitions**

# Loss of Electrons = Oxidation

$$\overset{0}{Na} \rightarrow \overset{+1}{Na} + e^{-}$$

# Sodium is oxidized

#### Increase of the oxidation state

# **Gain of Electrons = Reduction**

# $\begin{array}{ccc} 0 & -1 \\ Cl + e^{-} \rightarrow Cl \end{array} \end{array}$ Chlorine is reduced

Decrease of the oxidation state

#### **Not All Reactions are Redox Reactions**

- Reactions in which there has been no change in oxidation number are not redox reactions.

### Examples:

 $\begin{array}{c} {}^{+1}_{Ag} {}^{+5}_{N} {}^{-2}_{3}(aq) + {}^{+1}_{Na} {}^{-1}_{Cl}(aq) \rightarrow {}^{+1}_{Ag} {}^{-1}_{Cl}(s) + {}^{+1}_{Na} {}^{+5}_{N} {}^{-2}_{3}(aq) \end{array}$ 

 $2 \overset{+1}{Na} \overset{-2}{O} \overset{+1}{H} (aq) + \overset{+1}{H} \overset{+6}{_2} \overset{-2}{_3} O_4(aq) \rightarrow + \overset{+1}{Na} \overset{+6}{_2} \overset{-2}{_3} O_4(aq) + \overset{+1}{H} \overset{-2}{_2} O(l)$ 

# **Assigning Oxidation States**

 An "oxidation state" (oxidation number) is a positive or negative number assigned to an atom to indicate its degree of oxidation or reduction. **Rules for Assigning Oxidation States** 

1) The oxidation State of any uncombined element is zero.

2) The oxidation State of a monatomic ion equals its charge.

 $\begin{array}{ccccccccc} 0 & 0 & & +1 & -1 \\ 2Na & + & Cl_2 & \longrightarrow & 2Na & Cl \end{array}$ 

**Rules for Assigning Oxidation States** 

3) The oxidation state of oxygen in compounds is -2, except in peroxides, such as  $H_2O_2$  where it is -1.

4) The oxidation state of hydrogen in compounds is +1, except in metal hydrides, like NaH, where it is -1.



#### **Rules for Assigning Oxidation states**

5) The sum of the oxidation states of the atoms in the compound must equal <u>0</u>.

 $\begin{array}{c} +1 & -2 \\ H & 2 & O \end{array} +2 & -2 & +1 \\ Ca(OH)_{2} \\ \\ 2(+1) + (-2) = 0 \\ H & O \end{array} + (+2) + 2(-2) + 2(+1) = 0 \\ Ca & O & H \\ \end{array}$ 

#### **Rules for Assigning Oxidation States**

6) The sum of the oxidation States in the formula of a polyatomic ion is equal to its ionic charge.

 $\begin{array}{c} ? & -2 \\ N & O_{3}^{-} \end{array} \qquad \begin{array}{c} ? & -2 \\ S & O_{4}^{-} \end{array} \\ \times + 3(-2) = -1 \\ N & O \end{array} \qquad \begin{array}{c} \times + 4(-2) = -2 \\ S & O \end{array} \\ \therefore X = +5 \end{array} \qquad \begin{array}{c} \therefore X = +6 \end{array}$ 



#### **Guidelines for Assigning Oxidation Numbers**

TABLE 4.5	Elements with Reliable Oxidation Numbers in Compounds or Polyatomic Ions	
Element	<b>Oxidation Number</b>	Exceptions
Fluorine	-1	
Group 1A or 2A metal	+1 or $+2$ , respectively	
Hydrogen	+1	Any combination with a Group 1A or 2A metal to form a metal hydride. Examples: LiH and CaH <sub>2</sub> —the oxidation number of H is $-1$ in both examples.
Oxygen	-2	hething higher on the list that necessitates its naving a different oxidation number (see rule 2 for assigning oxidation numbers). Examples: $H_2O_2$ and $KO_2$ —the oxidation number of O for $H_2O_2$ is 1 and for $KO_2$ is $-\frac{1}{2}$ .
Group 7A (other than fluorin	-1 ne)	Any combination with something higher on the list that necessitates its having a different oxidation number (see rule 2 for assigning oxidation numbers). Examples: CIF, $BrO_4^-$ , and $IO_3^-$ —the oxidation numbers of Cl, Br, and I are +1, +7, and +5, respectively.

# Oxidation of metals in aqueous solutions Displacement reactions

 A common reaction: active metal replaces (displaces) a metal ion from a solution

 $Mg(s) + CuCl_2(aq) \rightarrow Cu(s) + MgCl_2(aq)$ 

#### Does this reaction work? $Cu(s) + MgCl_2 \rightarrow Mg(s) + CuCl_2$ ?? NOOOOOO

 The activity series of metals is useful in order to predict the outcome of the reaction.

TABLE 4.6         Activity Series		
	Element	<b>Oxidation Half-Reaction</b>
Increasing ease of oxidation	Lithium	$Li \longrightarrow Li^+ + e^-$
	Potassium	$K \longrightarrow K^+ + e^-$
	Barium	$Ba \longrightarrow Ba^{2+} + 2e^{-}$
	Calcium	$Ca \longrightarrow Ca^{2+} + 2e^{-}$
	Sodium	$Na \longrightarrow Na^+ + e^-$
	Magnesium	$Mg \longrightarrow Mg^{2+} + 2e^{-}$
	Aluminum	$Al \longrightarrow Al^{3+} + 3e^{-}$
	Manganese	$Mn \longrightarrow Mn^{2+} + 2e^{-}$
	Zinc	$Zn \longrightarrow Zn^{2+} + 2e^{-}$
	Chromium	$Cr \longrightarrow Cr^{3+} + 3e^{-}$
	Iron	$Fe \longrightarrow Fe^{2+} + 2e^{-}$
	Cadmium	$Cd \longrightarrow Cd^{2+} + 2e^{-}$
	Cobalt	$Co \longrightarrow Co^{2+} + 2e^{-}$
	Nickel	$Ni \longrightarrow Ni^{2+} + 2e^{-}$
	Tin	$\operatorname{Sn} \longrightarrow \operatorname{Sn}^{2^+} + 2e^-$
	Lead	$Pb \longrightarrow Pb^{2+} + 2e^{-}$
	Hydrogen	$H_2 \longrightarrow 2H^+ + 2e^-$
	Copper	$Cu \longrightarrow Cu^{2+} + 2e^{-}$
	Silver	$Ag \longrightarrow Ag^+ + e^-$
	Mercury	$Hg \longrightarrow Hg^{2+} + 2e^{-}$
	Platinum	$Pt \longrightarrow Pt^{2+} + 2e^{-}$
	Gold	$Au \longrightarrow Au^{3+} + 3e^{-}$

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#### **Balancing redox reactions**

 Electrons (charge) must be balanced as well as number and types of atoms

 Consider this net ionic reaction: Al(s) + Ni<sup>2</sup>+(aq) → Al<sup>3</sup>+(aq) + Ni(s)
 The reaction appears balanced as far as number and type of atoms are concerned, but look closely at the charge on each side.  $AI(s) + Ni^{2+}(aq) \rightarrow AI^{3+}(aq) + Ni(s)$ 

- Divide reaction into two half-reactions
  Al(s) → Al<sup>3+</sup>(aq) + 3e<sup>-</sup>
  Ni<sup>2+</sup>(aq) + 2e<sup>-</sup> → Ni(s)
- Multiply by a common factor to equalize electrons (the number of electrons lost must equal number of electrons gained)
   2 [Al(s) → Al<sup>3+</sup>(aq) + 3e<sup>-</sup>]
   3 [Ni<sup>2+</sup>(aq) + 2e<sup>-</sup> → Ni(s)]

- Cancel electrons and write balanced net ionic reaction 2Al(s) → 2Al<sup>3+</sup>(aq) + 6e<sup>-</sup> 3Ni<sup>2+</sup>(aq) + 6e<sup>-</sup> → 3Ni(s)

 $2AI(s) + 3Ni^{2+}(aq) \rightarrow 2AI^{3+}(aq) + 3Ni(s)$ 

Predict whether each of the following will occur. For the reactions that do occur, write a balanced net ionic reaction for each.

- Copper metal is placed into a solution of silver nitrate

A gold ring is accidentally dropped into a solution of hydrochloric acid
 No reaction occurs, gold is below
 hydrogen on the activity series.

**Other Types of Redox Reactions** 

**1. Combination Reactions** 

- Many combination reactions may also be classified as redox reactions
- Consider:
- Hydrogen gas reacts with oxygen gas  $2H_2(g) + O_2(g) \rightarrow 2H_2O(I)$

Identify the substance oxidized and the substance reduced.

2. Decomposition reactions

 Many decomposition reactions may also be classified as redox reactions

-Consider:

Potassium chlorate is strongly heated

 $2\text{KCIO}_3(s) \rightarrow 2\text{KCI}(s) + 3O_2(g)$ 

Identify substances oxidized and reduced.

3. Disproportionation reactions

 One element undergoes both oxidation and reduction
 Consider:



#### 4. Combustion reactions

 Common example, hydrocarbon fuel reacts with oxygen to produce carbon dioxide and water
 –Consider:



#### **Oxidation Numbers on the Periodic Table**



#### **4.5 Concentration of Solutions**

- Concentration is the amount of solute dissolved in a given amount of solution.
- Qualitative expressions of concentration
  - –Concentrated higher ratio of solute to solvent
  - –Dilute smaller ratio of solute to solvent

#### **Comparison of a Concentrated and Dilute Solution**



Concentrated solution: More solute particles per unit volume



Dilute solution: Fewer solute particles per unit volume

#### Molarity

Quantitative concentration term

Molarity is the ratio of moles solute per liter of solution

 $molarity = \frac{moles \ solute}{liters \ solution}$ 

Symbols: *M* or []Different forms of molarity equation

$$M = \frac{mol}{L}$$

$$L = \frac{mol}{M}$$



# **Molarity Calculation**

# If 4.0 g NaOH are used to make 500. mL of NaOH solution, what is the molarity (M) of the solution?

# **Calculating Molarity**

### 4.0 g NaOH x <u>1 mole NaOH</u> = 0.10 mole NaOH 40.0 g NaOH



0.10 mole NaOH = 0.20 mole NaOH 0.500 L 1 L = 0.20 M NaOH



An acid solution is a 0.10 M HCl. How many moles of HCl are in 1500 mL of this acid solution?

 $1500 \text{ mL x} \ \underline{1 \text{ L}} = 1.5 \text{ L}$ 1000 mL

> 1.5 L x <u>0.10 mole HCI</u> = 0.15 mole HCI 1 L

#### Example

# How many grams of KCl are present in 2.5 L of 0.50 M KCl?

# 2.5 L x 0.50 mole x 74.6 g KCI = 93 g KCI 1 L 1 mole KCI



# How many milliliters of a 0.10 M HCI solution that contains 0.15 mole HCI?

# 0.15 mole HCI x <u>1 L solution</u> x <u>1000 mL</u> 0.10 mole HCI <u>1 L</u> = 1500 mL HCI

#### Example

How many grams of NaOH are required to prepare 400. mL of 3.0 *M* NaOH solution?

#### 400. mL x 1 L = 0.400 L1000 mL

# 0.400 L x <u>3.0 mole NaOH</u> x <u>40.0 g NaOH</u> 1 L 1 mole NaOH

#### = 48 g NaOH

#### **Preparing a Solution of Known Molarity**



#### Example

A sample of 0.14 M NaCl. What volume of sample contains 1.0 mg NaCl?

1.0mg NaCl 
$$\times \frac{19}{1000 \text{ mg}} \xrightarrow{1 \text{ mor NaCl}}{58.5 \text{ g NaCl}} \frac{1L}{0.14 \text{ mol NaCl}} = 1.2 \times 10^{-4} \text{ L}$$
  
# mol = M X V (L)  $\Rightarrow$   $V(L) = \frac{\# \text{ mol}}{M}$   
 $V(L) = \frac{0.1 \times 10^{-3} \text{ g} / 58.5 \text{ g / mol}}{0.14 \text{ mol} / L} = 1.2 \times 10^{-4} \text{ L}$ 

# Dilution

- Adding more solvent to a known solution.
- The moles of solute stay the same.
- #moles = M x volume (L)
- # moles before dilution (1) = # moles after dilution

# $\mathbf{M}_1 \mathbf{V}_1 = \mathbf{M}_2 \mathbf{V}_2$

Stock solution is a solution of known concentration used to make more dilute solutions

#### Preparing a less concentrated solution from a more concentrated solution by dilution



 $\begin{array}{ll} \text{Moles of solute} \\ \text{before dilution (i)} \end{array} = & \begin{array}{l} \text{Moles of solute} \\ \text{after dilution (f)} \end{array} \\ \hline M_i V_i \end{array} = & \begin{array}{l} M_f V_f \end{array} \end{array}$
### Example

How would you prepare 60.0 mL of 0.200 *M* HNO<sub>3</sub> from a stock solution of 4.00 *M* HNO<sub>3</sub>?

What volume of 4.00 M *M* HNO<sub>3</sub> must be used to prepare 60.0 mL of 0.2M *M* HNO<sub>3</sub>

 $M_1 = 4.00$   $M_2 = 0.200$   $V_2 = 60.0$  m L  $V_1 = ?mL$  $M_1V_1 = M_2V_2$ 



#### **Dilution process**



### **Solution Stoichiometry**

- Soluble ionic compounds dissociate completely in solution.
- Using mole ratios we can calculate the concentration of all species in solution.

1 mol NaCl dissociates into 1 mol Na<sup>+</sup> and 1 mol Cl<sup>-</sup> 1 mol Na<sub>2</sub>SO<sub>4</sub> dissociates into 2 mol Na<sup>+</sup> and 1 mol SO<sub>4</sub><sup>2-</sup> 1 mol AlCl<sub>3</sub> dissociates int 1 mol Al<sup>3+</sup> and 3 mol Cl<sup>-</sup> Find the concentration of all species in a 0.25 *M* solution of MgCl<sub>2</sub>

 $MgCl_2 \rightarrow Mg^{2+} + 2Cl^{-1}$ 

Given:  $MgCl_2 = 0.25 M$ 

 $[Mg^{2+}] = 0.25 M (1:1 ratio)$  $[CI^{-}] = 0.50 M (1:2 ratio)$ 

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Using the square bracket notation, express the molar concentration for all species in the following solutions 0.42 *M* Ba(OH)<sub>2</sub>  $[Ba^{2+}] = 0.42 M (1:1 ratio)$  $[OH^{-}] = 0.84 M (2:1 ratio)$ **1.2** *M* NH₄CI  $[NH_4^+] = 1.2 M (1:1 ratio)$ [CI<sup>-</sup>] = 1.2 *M* (1:1 ratio)

### 4.6 Aqueous Reactions and Chemical Analysis

Types of quantitative analysis

 Gravimetric analysis (mass analysis)
 Example: precipitation reaction
 Volumetric analysis (volume analysis)
 Example: titration

### **Gravimetric Analysis**

- One form: isolation of a precipitate
- Typical steps:
  - Determine mass of unknown solid
  - Dissolve unknown in water
  - Combine with excess amount of known substance to form a precipitate (excess drives reaction to completion)
  - Filter, dry and weigh the precipitate
  - Use formula and mass of ppt to find % of ion in unknown solid

A 0.825 g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with excess silver nitrate. If 1.725 g of AgCl precipitate forms, what is the percent by mass of CI in the original sample?

### **Steps in solution:**

- Find the % of Cl in AgCl
- Multiply the % of CI by the mass of the precipitate to obtain the CI in the sample
- Divide the mass of Cl in sample by total mass of sample (multiply by 100 for %)

# % Cl = $\frac{35.45 \text{ gCl}}{143.35 \text{ g AgCl}} \times 100 = 24.7\%$

#### $0.247 \times 1.725$ g AgCl ppt = 0.427 g Cl in sample

# % Cl in unknown = $\frac{0.427 \text{ g Cl}}{0.825 \text{ g sample}} \times 100 = 51.7\% \text{ Cl}$

### **Volumetric analysis**

 Commonly accomplished by *titration* Addition of a solution of known concentration (standard solution) to another solution of unknown concentration.

### **Apparatus for a Titration**





### **Volumetric analysis**

- Standardization is the determination of the exact concentration of a solution.
- *Equivalence point* represents completion of the reaction.
- *Endpoint* is where the titration is stopped.
- An *indicator* is used to signal the endpoint.

A student measured exactly 15.0 mL of an unknown monoprotic acidic solution and placed in an Erlenmeyer flask. An indicator was added to the flask. At the end of the titration the student had used 35.0 mL of 0.12 M NaOH to neutralize the acid. Calculate the molarity of the acid.

 $0.035 \text{ L NaOH} \times \frac{0.12 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol acid}}{1 \text{ mol base}} = 0.0042 \text{ mol acid}$  $M = \frac{0.0042 \text{ mol}}{0.015 \text{ L}} = 0.28 \text{ M acid}$ 

## Calculate the molarity of 25.0 mL of a monoprotic acid if it took 45.50 mL of 0.25 *M* KOH to neutralize the acid.



$$\frac{0.01338 \text{ mol acid}}{0.0250 \text{ L}} = 0.455 M$$

### **Titration**

A 50.00 mL sample of aqueous Ca(OH)<sub>2</sub> requires 34.66 mL of 0.0980 M Nitric acid for neutralization. What is [Ca(OH)<sub>2</sub>]?

•  $Ca(OH)_2 + 2 HNO_3 \rightarrow Ca(NO_3)_2 + H_2O_3$ 

 $Ca(OH)_{\gamma}$ 

- # of moles of HNO<sub>3</sub> = # of moles of Ca(OH)<sub>2</sub> X  $2HNO_3$
- 0.098 X 34.66 = M<sub>Ca(OH)2</sub> X 50.00
- M<sub>Ca(OH)2</sub> = (0.098 X 34.66/ 50.00)

## **Key Points**

- Electrolytes (strong, weak, and non)
  Precipitation reactions

  Solubility rules

  Molecular, ionic, and net ionic reactions
- Acid-base neutralization reactions
- Oxidation-reduction reactions