Chapter 3: Solution Chemistry

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Section 3.1: Solubility Rules (Ionic Compounds in Water)

- **Solubility:** the ability of a compound to dissolve in a solvent, here, in water.
- Different compounds have different solubility in water.
- We will only deal with ionic compounds since a number of simple rules exist to decide whether specific ions impart solubility or not.
- Molecular compounds can also exhibit a wide range of solubility in water
  - Sugar is very soluble in water
  - Oil and gasoline are not

Section 3.1.2: Solubility Rules for Chlorides, Bromides, Iodides

- All chloride, bromide and iodide ionic compounds are soluble in water except those containing silver(I), mercury(I), lead(II) and copper(I).

Section 3.1.4: Solubility Rules for Acetate, Chlorate, Perchlorate, Nitrate & Hydroxide Compounds

- All acetate, chlorate, perchlorate and nitrate ionic compounds are soluble in water.
- All group 1 hydroxide compounds are soluble in water.
- Magnesium, calcium, strontium and barium hydroxides are only slightly soluble.
- All other hydroxides are insoluble in water.

Section 3.1.6: Solubility Rules for Sulfides

- Group 1 sulfide ionic compounds are water soluble.
- All other sulfide compounds are not.
- Sulfur lakes in volcano mouths and the healing properties of the Roman Baths (UK) are a result of dissolved sulfur in the water source.

Section 3.1.8: Solubility Rules for Carbonates, Chromates & Sulfates

- Group 1 carbonate and chromate ionic compounds are water soluble.
- All other carbonate and chromate compounds are not.
- Most sulfate ionic compounds are soluble.
  - Except ionic compounds made with Mg, Ca, Sr, Ba, Ra, Hg(I) and Pb(II).

Section 3.1.10: Solubility Rules & Dissociation of Ammonium Compounds

- All ammonium compounds are water soluble.
- Ammonium perchlorate, solid and aqueous on right.

Section 3.2.1: Writing Ionic Equations

- **Reaction of $NaCl_{(aq)}$ with $AgNO_{3\,(aq)}$**
- $NaCl_{(s)}$ is soluble in water, breaking down into $Na^{+}_{(aq)}$ and $Cl^{-}_{(aq)}$ ions.
- $AgNO_{3\,(s)}$ is soluble in water, breaking down into $Ag^{+}_{(aq)}$ and $NO_3^{-}{}_{(aq)}$ ions.

Let's mix these two aqueous solutions. Does a reaction occur and if so, what reaction is it?

- Obviously, $Cl^{-}_{(aq)}$ will not react with $Na^{+}_{(aq)}$. Does $Cl^{-}_{(aq)}$ form a compound with $Ag^{+}_{(aq)}$?
- The solubility rules state that silver chloride is not soluble in water.
- silver and chloride ions form an ionic compound. A **precipitate** of solid silver chloride (white creamy solid) has formed by reaction of sodium chloride with silver nitrate.

Section 3.2.1: Writing Ionic Equations (cont.)

- Will another precipitation reaction takes place between the sodium and the nitrate ions?
  - Solubility rules for nitrate ions tell us that all nitrate compounds are soluble in water.
  - sodium and nitrate ions remain as free ions in solution and do not form a precipitate.

- **Spectator ions:** the sodium and nitrate ions do not participate in the reaction.

- **Complete ionic equation:** $\mathbf{Na^+_{(aq)} + Cl^-_{(aq)} + Ag^+_{(aq)} + NO_3^-{}_{(aq)} \rightarrow AgCl_{(s)} + Na^+_{(aq)} + NO_3^-{}_{(aq)}}$

- **Net ionic equation:** Since the $Na^+_{(aq)}$ and $NO_3^-{}_{(aq)}$ ions are spectator ions (i.e. they do not participate in the reaction), they can be cancelled on both sides of the equation.
  $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$

Section 3.3.1: Electrolytes and Nonelectrolytes

- **Electrolyte:** a substance which, when dissolved in water, makes an electrically conducting solution; dissociate into ions when dissolved in water.
  - Ionic compounds which are water soluble
  - Acids and bases.

- **Nonelectrolyte:** a substance which, when dissolved in water, makes an electrically non-conducting solution; do not dissociate into ions when dissolved in water.
  - Molecular compounds other than acids and bases.

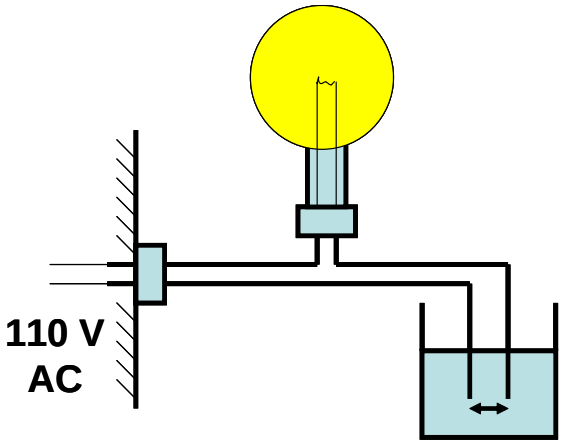
Section 3.3.1: Electrolytes and Nonelectrolytes (cont.)

- **Experiment:** A compound is dissolved in water and the solution placed in a beaker. The two leads of the electrical circuit are dipped in the beaker. If dissolution of the compound is accompanied by dissociation of the compound into ions, the ions will be attracted to the oppositely charged leads.

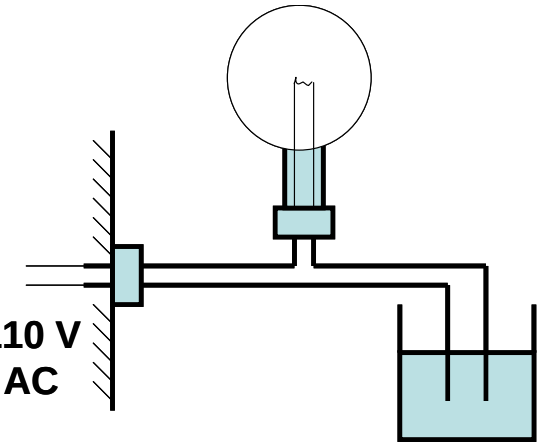
- Motion of the ions between the leads (where the arrow is) closes the electrical circuit and current flows through the light bulb.

- If the solution contains no ions (or a really low concentration of ions as in distilled water), then the circuit is not closed and electrical current does not flow through the light bulb.

Section 3.3.1: Electrolytes and Nonelectrolytes (cont.)



Solution contains an Electrolyte
The bulb is lit !!!



Solution contains a
Non-electrolyte
The bulb is NOT lit!!!

Section 3.3.2: Strong and Weak Electrolytes

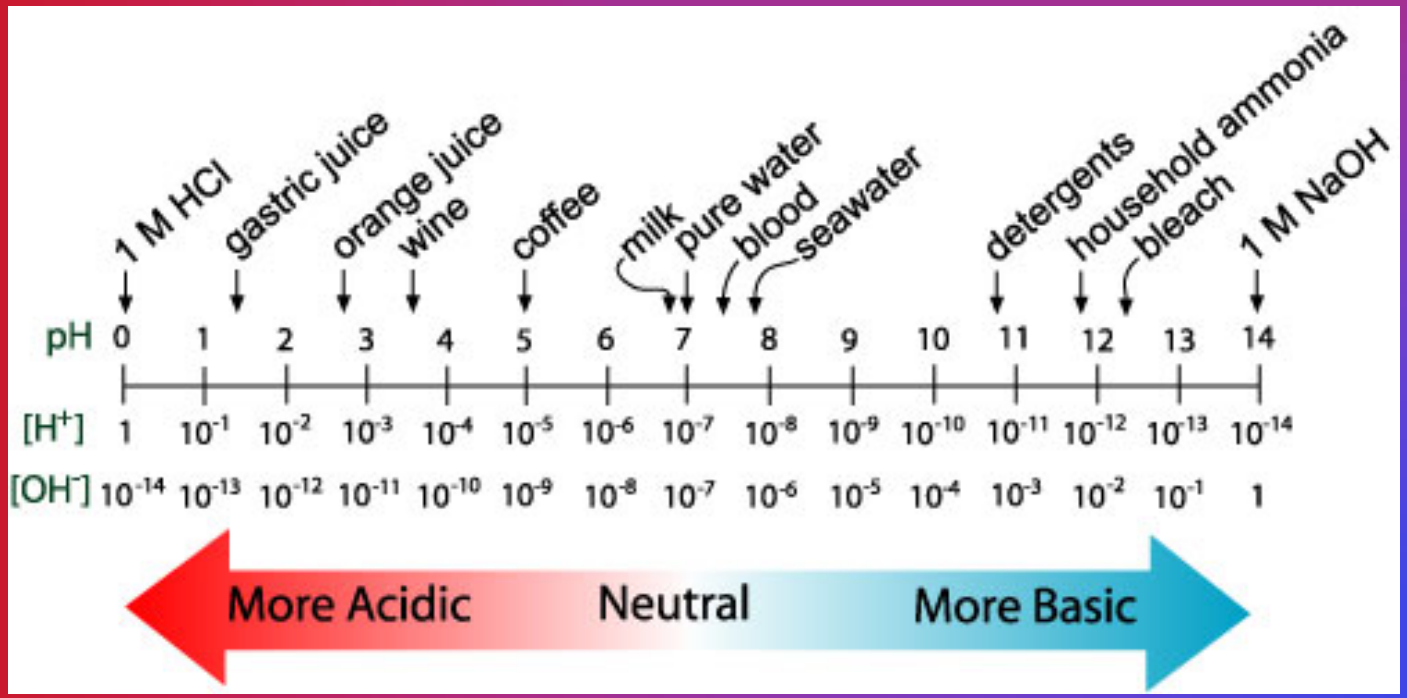
- Electrolytes dissolved in water produce ions to various extents.
- **Strong electrolytes:** some electrolytes, when dissolved in water, **dissociate completely** into cations and anions.
- Examples:
  - **Soluble ionic compounds:** when $NaCl_{(s)}$ is dissolved in water all NaCl dissociates into $Na^{+}_{(aq)}$ and $Cl^{-}_{(aq)}$. NaCl is a strong electrolyte.
  - **Strong acids:** when dissolving HCl gas (hydrogen chloride) in water, we form hydrochloric acid. Hydrochloric acid is written as $HCl_{(aq)}$ and exists as $H^{+}_{(aq)}$ and $Cl^{-}_{(aq)}$ ions.
  - **Strong bases**

Section 3.3.2: Strong and Weak Electrolytes (cont.)

- **Weak electrolytes: s**ome electrolytes, when dissolved in water, **dissociate partially** into cations and anions. Partial dissociation means that some of the original compound exists in solution in the **undissociated** (molecular) form.
- Exampes:
  - **Weak acids:** acetic acid, $HC_2H_3O_{2(l)}$, the main component of vinegar dissolves in water and dissociates partially into $H^+_{(aq)}$ and $C_2H_3O_2^-{}_{(aq)}$ ions. Most molecules remain undissociated.
  - **Weak bases**

Section 3.4.1: Properties of Acids and Bases

- Acids: taste sour, turn litmus red, are corrosive to metals, turn red cabbage juice red, and turn Phenolphthalein white.
- Bases: feel slippery, change litmus blue, turn Phenolphthalein magenta/pinkish, and turn red cabbage juice blue/green



Section 3.4.2: Arrhenius Acids and Bases

- Svante Arrhenius proposed the first definition for acids and bases.
- **Acid**: a substance which, when dissolved in water, produces hydrogen ions (protons), $H^+_{(aq)}$.
  - Consider HCl gas. The dissolution reaction is written as:

    $HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$
- **Base**: a substance which, when dissolved in water, produces hydroxide ions, $OH^-_{(aq)}$.
  - Consider NaOH solid. The dissolution reaction is written as:

    $NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

Section 3.4.3: Brønsted - Lowry Acids and Bases

- **Acids** according to **Brønsted-Lowry** are substances that donate protons (H^+) to another species.
- Consider $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$
  - $H_3O^+_{(aq)}$ is called the hydronium ion.
  - This reaction is also written as: $HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ as $H^+_{(aq)}$ is equivalent to $H_3O^+_{(aq)}$.

Section 3.4.3: Brønsted - Lowry Acids and Bases (cont.)

- **Bases** according to **Brønsted-Lowry** are substances that accept a proton (H^+) from another species.

- Consider the dissolution of ammonia in water:
  $NH_{3(g)} + H_2O_{(l)} \rightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

  - $NH_4^+{}_{(aq)}$ is the ammonium ion, which accepted a proton.

Section 3.4.4: Strong Acids and Weak Acids

- Strong acids completely ionize when dissolved in water.
- The following list of strong acids is a list you need to memorize.
- All acids in this list are strong acids. All other acids are weak acids.

Strong Acids:	
$HCl_{(aq)}$	hydrochloric acid
$HBr_{(aq)}$	hydrobromic acid
$HI_{(aq)}$	hydroiodic acid
$HNO_{3\,(aq)}$	nitric acid
$HClO_{4\,(aq)}$	perchloric acid
$HClO_{3\,(aq)}$	chloric acid
$H_2SO_{4\,(aq)}$	sulfuric acid

MEMORIZE THE ABOVE LIST

Weak Acids	
$HClO_{2\,(aq)}$	chlorous acid
$HClO_{(aq)}$	hypochlorous acid
$HBrO_{4\,(aq)}$	perbromic acid
$HBrO_{3\,(aq)}$	bromic acid
$HBrO_{2\,(aq)}$	bromous acid
$HBrO_{(aq)}$	hypobromous acid
$HF_{(aq)}$	hydrofluoric acid
$HC_2H_3O_{2\,(aq)}$	acetic acid
$HNO_{2\,(aq)}$	nitrous acid
$H_2SO_{3\,(aq)}$	sulfurous acid
$H_3PO_{4\,(aq)}$	phosphoric acid
$H_3PO_{3\,(aq)}$	phosphorous acid
etc…	

Section 3.4.4: Strong Acids and Weak Acids (cont.)

- The complete dissociation of a **strong acid** is represented by the following chemical equation:

  $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$
- The **single arrow** indicates that the ionization of HCl goes to completion.
  - All HCl dissociates to $H^+_{(aq)}$ and $Cl^-_{(aq)}$ ions.
  - Strong acids are strong electrolytes.

- The partial dissociation of a **weak acid** is represented by the following chemical equation:

  $HF_{(aq)} \leftrightarrows H^+_{(aq)} + F^-_{(aq)}$
- The **double arrow** indicates that the ionization of HF does not go to completion.
  - Some HF dissociates to $H^+_{(aq)}$ and $F^-_{(aq)}$ ions and some HF remains in molecular form. We say that the dissociation (or ionization) of HF reaches an equilibrium where HF molecules, $H^+_{(aq)}$ and $F^-_{(aq)}$ ions coexist in solution.
  - Weak acids are weak electrolytes.

Section 3.4.5: Strong Bases and Weak Bases

- Strong bases completely ionize when dissolved in water.
- All bases in this list are strong bases. All other bases are weak bases, and we have listed a few common ones.

Strong Bases:		Weak Bases	
$LiOH_{(aq)}$	lithium hydroxide	$Mg(OH)_{2\,(aq)}$	magnesium hydroxide
$NaOH_{(aq)}$	sodium hydroxide	$NH_{3\,(aq)}$	ammonia
$KOH_{(aq)}$	potassium hydroxide	$F^-_{(aq)}$	fluoride ion
$CsOH_{(aq)}$	cesium hydroxide	$C_2H_3O_2^-{}_{(aq)}$	acetate ion
$Ca(OH)_{2\,(aq)}$	calcium hydroxide	$ClO_2^-{}_{(aq)}$	chlorite ion
$Sr(OH)_{2\,(aq)}$	strontium hydroxide		
$Ba(OH)_{2\,(aq)}$	barium hydroxide		

MEMORIZE THE ABOVE LIST

Section 3.4.5: Strong Bases and Weak Bases (cont.)

- Note that strong bases are groups I and II hydroxides except beryllium and magnesium hydroxides.
- The complete dissociation of a **strong base** is represented by the following chemical equation (in the case of NaOH):

  $NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$
- The **single arrow** (→) indicates that the dissociation of NaOH goes to completion.
  - All NaOH dissociate to $Na^{+}_{(aq)}$ and $OH^{-}_{(aq)}$ ions.
  - Strong bases are strong electrolytes.

Section 3.4.5: Strong Bases and Weak Bases (cont.)

- The partial dissociation of a **weak base** is represented by the following chemical equation (in the case of NH_3):

  $NH_{3\,(aq)} + H_2O_{\,(aq)} \leftrightarrows NH_4^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$

- The **double arrow** (⇆) indicates that the ionization of $NH_{3\,(aq)}$ does not go to completion.
  - Some $NH_{3\,(aq)}$ ionizes to $NH_4^{+}{}_{(aq)}$ and some NH_3 remains in molecular form. We say that the ionization of NH_3 reaches an equilibrium where NH_3 molecules, $NH_4^{+}{}_{(aq)}$ and $OH^{-}{}_{(aq)}$ ions coexist in solution.
  - Weak bases are weak electrolytes.

Section 3.5-3.6: Introduction to Molarity

- **Molarity** refers to the concentration of species in solution.
  - The species is called **solute**.
  - The solute dissolves in a liquid called the **solvent**.
  - A **solution** is composed of solute and solvent.

Qualitatively, a dilute solution has a low concentration of solute and a concentrated solution has a high concentration of solute.

Section 3.5-3.6: Introduction to Molarity (cont.)

- The terms dilute and concentrated are used in a comparative sense.

$$\text{Molarity} = \frac{\text{moles of solute (mol)}}{\text{volume of solution (L)}} \qquad \text{moles (n)} = \frac{\text{mass (g)}}{\text{molar mass (g/mol)}}$$

$$\text{Molarity (M)} = \frac{\text{mass (g)}}{\text{molar mass (g/mol)} \times \text{liters of solution (L)}}$$

- Thus, mass (g) = Molarity (M) x molar mass (g/mol) x liters of solution (L)

- The molarity (M) of a solution can be used to calculate:
  - The amount of solute (moles or mass) in a given volume of solution.
  - The volume of solution containing a given amount (moles) of solute.

Section 3.5-3.6: Introduction to Molarity (cont.)

- **Example: Calculate the mass of $KMnO_4$ needed to prepare 700. mL of a 0.583 M solution of $KMnO_4$.**
  - Molar Mass ($KMnO_4$) = 39.1 + 54.9 + 4 x 16.0 = 158.0 g/mol ($KMnO_4$).

$$\text{Molarity} = \frac{\text{mass of solute (g)}}{\text{molar mass (g/mol)} \times \text{volume of solution (L)}}$$

  - Hence, Mass (g) = Molarity (mol/L) x molar mass (g/mol) x volume (L)
  - Note that the volume must be expressed in liter (L) and 1 L = 1000 mL
  - Mass (g) = 0.583 mol/L x 158.04 g/mol x 0.700 L = 64.5 g
  - Therefore, 64.5 g of $KMnO_4$ dissolved in 700.mL of water produces a 0.583 M $KMnO_4$ solution.

Section 3.7-3.8: Molarity of Ionic Solutions

- Aqueous solutions of salts conduct electricity, showing that salts break into ions in solution.
- The ratio of cations and anions produced is given by the ion's chemical formula.
- Polyatomic ions remain intact as ions in solution.

Section 3.7-3.8: Molarity of Ionic Solutions (cont.)

- **Example:** Sodium sulfate (Na_2SO_4) dissolved in water breaks down into $Na^+_{(aq)}$ and $SO_4^{-2}{}_{(aq)}$ ions. SO_4^{-2} is a polyatomic ion. From the chemical formula Na_2SO_4, the ratio of ions in solution is: 2 $Na^+_{(aq)}$ to 1 $SO_4^{-2}{}_{(aq)}$

- **Example:** Consider an aqueous solution of 1 M NaCl. In solution, NaCl breaks down into 1 $Na^+_{(aq)}$ and 1 $Cl^-_{(aq)}$ ions. The concentration of $Na^+_{(aq)}$ is 1 M and that of $Cl^-_{(aq)}$ is 1 M

- **Example:** Now, consider a 1 M aqueous solution of Na_3PO_4. In solution, Na_3PO_4 breaks down into 3 $Na^+_{(aq)}$ and 1 $PO_4^{-3}{}_{(aq)}$. Hence, in 1 M Na_3PO_4 solution, the concentration of $Na^+_{(aq)}$ is 3 M and that of $PO_4^{-3}{}_{(aq)}$ is 1 M.

Thus, an ionic solution contains a mixture of ions, each with its own molarity.

Section 3.7-3.8: Molarity of Ionic Solutions (cont.)

- **Example: Calculate the molarity of ionic species present in 250 mL of an aqueous solution containing 1.85 g of ammonium sulfate.**
  - Ammonium sulfate has a chemical formula: $(NH_4)_2SO_4$
  - The molar mass of $(NH_4)_2SO_4$ is: 2 x 14.0 + 8 x 1.0 + 32.1 + 4 x 16.0 = 132.1 g/mol

$$\text{Molarity } ((NH_4)_2SO_4) = \frac{\text{mass of solute (g)}}{\text{molar mass (g/mol) x volume of solution (L)}}$$

$$\text{Molarity } ((NH_4)_2SO_4) = \frac{1.85\ \text{g}}{132.1\ \text{g/mol} \times 0.25\ \text{L}} = 0.056\ \text{mol/L}$$

  - Hence, the concentration of $(NH_4)_2SO_4$ is 0.056 M.
  - In solution, $(NH_4)_2SO_4$ breaks down as 2 $NH_4^+{}_{(aq)}$ and 1 $SO_4^{-2}{}_{(aq)}$

Thus, the concentration of $NH_4^+{}_{(aq)}$ = 2 x 0.056 = 0.11 M and
the concentration of $SO_4^{-2}{}_{(aq)}$ = 0.056 M

Section 3.9-3.10: Diluting Solutions

- When solutions of acids, bases and soluble ionic compounds are manufactured and transported, they are often prepared as highly concentrated **stock solutions.**

- To prepare a solution of lower concentration from a stock solution we will need to dilute the stock solution.

Section 3.9-3.10: Diluting Solutions (cont.)

- **Example: Commercially available concentrated HCl is usually a 12.0 M solution. How does one prepare 100. mL of 1.0 M HCl solution from 12.0 M HCl solution?**
- The obvious answer is to dilute the HCl solution. But, what volume of 12.0 M HCl should be diluted? Recall the definition of molarity.

$$\text{Molarity (M)} = \frac{\text{moles of solute (n)}}{\text{liters of solution (L)}}$$

- Moles of solute (n) = Molarity (M) x liters of solution (L)
- This equation can be written as: moles of solute (n) = M_i x V_i . The subscript "i" stands for "initial".

Thus, M_i = initial molarity
and V_i = initial volume

Section 3.9-3.10: Diluting Solutions (cont.)

- Now, add water to the stock solution. This changes the concentration from M_i to M_f and the volume from V_i to V_f. The subscript "f" stands for "final".

Thus, M_f = final molarity
and V_f = final volume

- Because the number of moles of solute has not changed during dilution, moles of solute (n) = $M_f \times V_f$, and, $M_i \times V_i = M_f \times V_f$

Section 3.9-3.10: Diluting Solutions (cont.)

- M_i = 12.0 M
- V_i = To be calculated
- M_f = 1.0 M
- V_f = 100. mL
- 12.0 M x V_i = 1.0 M x 100. mL
- 8.3 mL of HCl should be put into a 100mL volumetric flask and filled with water to create a 1.0M solution.

$$V_i = \frac{1.0\ \text{M} \times 100.\ \text{mL}}{12.0\ \text{M}} = 8.3\ \text{mL}$$

Section 3.11: Volumetric Analysis

- An acid – base reaction is often called a neutralization reaction. When just enough base is added to the acid, the acid is neutralized.
- Acids and bases are classified as strong and weak. The nature of neutralization depends upon the strengths of acids and bases.
- The acid – base reactions are classified into three categories:

Category 1: Strong acid – Strong base
Category 2: Weak acid – Strong base
Category 3: Strong acid – Weak base

Section 3.11: Volumetric Analysis (cont.)

- In all three categories, there are a few common steps that should be applied to perform a volumetric analysis.

- **Step 1:**List the ions present in a combined solution.

  For example: In the reaction of HCl and NaOH, the ions present in a combined solution will be H^+, Cl^-, Na^+, OH^-

- **Step 2:** Figure out what reactions would occur with these ions and determine the net ionic equation. In the example, there are two possibilities.
  - H^+ combines with OH^- to form H_2O
  - Na^+ combines with Cl^- to form NaCl

Section 3.11: Volumetric Analysis (cont.)

- **The net ionic equation is: $H^+ + OH^- \rightarrow H_2O$**
  - This is the net ionic equation, in general, for a reaction between a strong acid and a strong base.

- **Step 3:** Perform volumetric calculation using the relationship:

  $M_i \times V_i = M_f \times V_f$
  - This equation can be written as $M_{H+} \times V_{H+} = M_{OH-} \times V_{OH-}$
  - Since the neutralization reaction is carried out under stoichiometric conditions only when the number of moles of OH^- is equal to the number of moles of H^+.
  - Remember moles = molarity x volume

Section 3.12-3.13: Gravimetric Analysis

- **Gravimetric analysis:** a chemical analysis method based on the measurement of masses.
- Can be used in combination with precipitation reactions to determine the amount of a species present in solution.
- First isolate the precipitate by filtration and drying and subsequently weigh it.
- Using this mass and stoichiometry relationships, we can determine the amount (mass or moles) of species present in solution.

Section 3.12-3.13: Gravimetric Analysis (cont.)

- **Example: A liter sample of polluted water is analyzed for lead, believed to be in the lead(II) ionic form. This is done by adding excess sodium sulfate to the polluted water sample. The mass of $PbSO_4$ produced is 300.0 mg. Calculate the mass of Pb in one liter solution.**

- All the lead in water reacts with the sulfate ions to form a $PbSO_4$ precipitate.

- The balanced chemical reaction is written as:
  $Na_2SO_4 + Pb(NO_3)_2 \rightarrow PbSO_4 + 2\ NaNO_3$

Section 3.12-3.13: Gravimetric Analysis (cont.)

- The net ionic reaction is written as: $SO_4^{-2} + Pb^{+2} \rightarrow PbSO_4$
  - Molar mass ($PbSO_4$) = 303.3 g/mol
  - Molar mass (Pb) = 207.2 g/mol
- Using the method of conversion factors, we transform the mass of $PbSO_4$ into the mass of Pb.

$$\text{Mass (Pb)} = 300.0\ \text{mg}\ PbSO_4 \times \frac{1\ \text{g}\ (PbSO_4)}{1000\ \text{mg}\ (PbSO_4)} \times \frac{1\ \text{mol}\ (PbSO_4)}{303.3\ \text{g}\ (PbSO_4)} \times \frac{1\ \text{mol (Pb)}}{1\ \text{mol}\ (PbSO_4)} \times \frac{207.2\ \text{g (Pb)}}{1\ \text{mol (Pb)}}$$

- Mass (Pb) = 0.2049 g Pb = 204.9 mg Pb