Chapter 4. Aqueous Reactions and Solution Stoichiometry

Common Student Misconceptions
- Molarity is moles of solute per *liter of solution*, not per liter of solvent.
- Students sometimes use moles instead of molarity in $M_{initial}V_{initial} = M_{final}V_{final}$.
- Students sometimes think that water is a good conductor.
- Students sometimes have a problem with the arbitrary difference between strong and weak electrolytes.
- The symbols — (equilibrium) and ℑ (resonance) are often confused.
- Students often do not see that the net ionic equation for the reaction between strong acids and strong bases is always $H^+(aq) + OH^-(aq) \square H_2O(l)$.
- Weaknesses in recollection of ionic nomenclature and the structure of common ions often makes it difficult for students to write molecular, complete ionic, and net ionic equations for metathesis reactions.
- Students try to split polyatomic ions into smaller ions when they write net ionic equations.
- Students do not appreciate the difference between equivalence point and end point.

Lecture Outline

4.1 General Properties of Aqueous Solutions
- A *solution* is a homogeneous mixture of two or more substances.
- A solution is made when one substance (the **solute**) is dissolved in another (the **solvent**).
- The solute is the substance that is present in the smallest amount.
- Solutions in which water is the solvent are called **aqueous solutions**.

Electrolytic Properties
- All aqueous solutions can be classified in terms of whether or not they conduct electricity.
- If a substance forms ions in solution, then the substance is an **electrolyte** and the solution conducts electricity. An example is NaCl.
- If a substance does not form ions in solution, then the substance is a **nonelectrolyte** and the solution does not conduct electricity. An example is sucrose.

Ionic Compounds in Water
- When an ionic compound dissolves in water, the ions are said to *dissociate*.
  - This means that in solution, the solid no longer exists as a well-ordered arrangement of ions in contact with one another.
  - Instead, each ion is surrounded by a shell of water molecules.
  - This tends to stabilize the ions in solution and prevent cations and anions from recombining.
  - The positive ions have the oxygen atoms of water pointing towards the ion; negative ions have the hydrogen atoms of water pointing towards the ion.
 - The transport of ions through the solution causes electric current to flow through the solution.

Molecular Compounds in Water
- When a molecular compound (e.g. CH_3OH) dissolves in water, there are no ions formed.
- Therefore, there is nothing in the solution to transport electric charge and the solution does not conduct electricity.
- There are some important exceptions.
  - For example, $NH_3(g)$ reacts with water to form $NH_4^+(aq)$ and OH^- (aq).
  - For example, $HCl(g)$ in water *ionizes* to form $H^+(aq)$ and Cl^- (aq).

Strong and Weak Electrolytes
- Compounds whose aqueous solutions conduct electricity well are called **strong electrolytes**.
  - These substances exist only as ions in solution.

- Example: NaCl

$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$
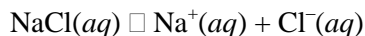
- The single arrow indicates that the Na^+ and Cl^- ions have no tendency to recombine to form NaCl molecules.
- In general, soluble ionic compounds are strong electrolytes.
- Compounds whose aqueous solutions conduct electricity poorly are called **weak electrolytes**
  - These substances exist as a mixture of ions and un-ionized molecules in solution.
    - The predominant form of the solute is the un-ionized molecule.
  - Example: acetic acid, $HC_2H_3O_2$

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

  - The double arrow means that the reaction is significant in both directions.
  - It indicates that there is a balance between the forward and reverse reactions.
  - This balance produces a state of chemical equilibrium.

4.2 Precipitation Reactions

- Reactions that result in the formation of an insoluble product are known as **precipitation reactions**.
- A **precipitate** is an insoluble solid formed by a reaction in solution.
  - Example: $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$

Solubility Guidelines for Ionic Compounds

- The **solubility** of a substance at a particular temperature is the amount of that substance that can be dissolved in a given quantity of solvent at that temperature.
- A substance with a solubility of less than 0.01 mol/L is regarded as being *insoluble*.
- Experimental observations have led to empirical guidelines for predicting solubility.
- Solubility guidelines for common ionic compounds in water:
  - Compounds containing alkali metal ions or ammonium ions are soluble.
  - Compounds containing NO_3^- or $C_2H_3O_2^-$ are soluble.
  - Compounds containing Cl^-, Br^- or I^- are soluble.
    - Exceptions are the compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}.
    - Compounds containing SO_4^{2-} are soluble.
      - Exceptions are the compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}.
    - Compounds containing S^{2-} are insoluble.
      - Exceptions are the compounds of NH_4^+, the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}.
    - Compounds of CO_3^{2-} or PO_4^{3-} are insoluble.
      - Exceptions are the compounds of NH_4^+ and the alkali metal cations.
    - Compounds of OH^- are insoluble.
      - Exceptions are the compounds of NH_4^+, the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}.

Exchange (Metathesis) Reactions

- **Exchange reactions**, or **metathesis reactions**, involve swapping ions in solution:

$$AX + BY \rightarrow AY + BX.$$

- Many precipitation and acid-base reactions exhibit this pattern.

Ionic Equations

- Consider $2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$.
- Both $KI(aq) + Pb(NO_3)_2(aq)$ are colorless solutions. When mixed, they form a bright yellow precipitate of PbI_2 and a solution of KNO_3.
- The final product of the reaction contains solid PbI_2, aqueous K^+, and aqueous NO_3^- ions.
- Sometimes we want to highlight the reaction between ions.
- The **molecular equation** lists all species in their molecular forms:

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

- The **complete ionic equation** lists all strong soluble electrolytes in the reaction as ions:

$$Pb^{2+}(aq) + 2NO_3^-(aq) + 2K^+(aq) + 2I^-(aq) \longrightarrow PbI_2(s) + 2K^+(aq) + 2NO_3^-(aq)$$
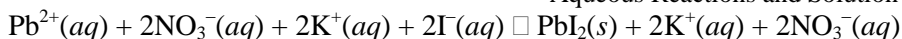
- Only strong electrolytes dissolved in aqueous solution are written in ionic form.
- Weak electrolytes and nonelectrolytes are written in their molecular form.
- The **net ionic equation** lists only those ions which are not common on both sides of the reaction:

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$

- Note that **spectator ions**, ions that are present in the solution but play no direct role in the reaction, are omitted in the net ionic equation.

4.3 Acid-Base Reactions

Acids

- **Acids** are substances that are able to ionize in aqueous solution to form H^+.
  - Ionization occurs when a neutral substance forms ions in solution.
    An example is $HC_2H_3O_2$ (acetic acid).
- Since H^+ is a naked proton, we refer to acids as proton donors and bases as proton acceptors.
- Common acids are HCl, HNO_3, vinegar, and vitamin C.
- Acids that ionize to form *one* H^+ ion are called *monoprotic* acids.
- Acids that ionize to form *two* H^+ ions are called *diprotic acids*.

Bases

- **Bases** are substances that accept or react with the H^+ ions formed by acids.
- Hydroxide ions, OH^-, react with the H^+ ions to form water:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

- Common bases are NH_3 (ammonia), Draino, and milk of magnesia.
- Compounds that do not contain OH^- ions can also be bases.
  - Proton transfer between NH_3 (a weak base) and water (a weak acid) is an example of an acid–base reaction.
  - Since there is a mixture of NH_3, H_2O, NH_4^+, and OH^- in solution, we write

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

Strong and Weak Acids and Bases

- **Strong acids** and **strong bases** are strong electrolytes.
  - They are completely ionized in solution.
  - Strong bases include: Group 1A metal hydroxides, $Ca(OH)_2$, $Ba(OH)_2$, and $Sr(OH)_2$.
  - Strong acids include: HCl, HBr, HI, $HClO_3$, $HClO_4$, H_2SO_4, and HNO_3.
  - We write the ionization of HCl as:

$$HCl \longrightarrow H^+ + Cl^-$$

- **Weak acids** and **weak bases** are weak electrolytes.
  - Therefore, they are partially ionized in solution.
- $HF(aq)$ is a weak acid; most acids are weak acids.
- We write the ionization of HF as:

$$HF \longrightarrow H^+ + F^-$$

Identifying Strong and Weak Electrolytes

- Compounds can be classified as strong electrolytes, weak electrolytes, or nonelectrolytes by looking at their solubility.
- Strong electrolytes:
  - Ionic compounds are usually strong electrolytes.
  - Molecular compounds that are strong acids are strong electrolytes.
- Weak electrolytes:
  - Weak acids and bases are weak electrolytes.
- Nonelectrolytes:
  - All other compounds.

   Neutralization Reactions and Salts
- A **neutralization reaction** occurs when an acid and a base react:
  - $HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$
  - (acid)   +   (base) $\rightarrow$ (water) + (salt)
- In general an acid and a base react to form a **salt**.
- A salt is any ionic compound whose cation comes from a base and anion from an acid.
- The other product, H_2O, is a common weak electrolyte.
- A typical example of a neutralization reaction is:
  - the reaction between an acid and a metal hydroxide.
    - $Mg(OH)_2$ (milk of magnesia) is a suspension.
    - As HCl is added, the magnesium hydroxide dissolves, and a clear solution containing Mg^{2+} and Cl^- ions is formed.
    - Molecular equation:
    $$Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$$
    - Net ionic equation:
    $$Mg(OH)_2(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + 2H_2O(l)$$
      - Note that the magnesium hydroxide is an insoluble solid; it appears in the net ionic equation.

Acid-Base Reactions with Gas Formation

- There are many bases besides OH^- that react with H^+ to form molecular compounds.
  - Reaction of sulfides with acid gives rise to $H_2S(g)$.
    - Sodium sulfide (Na_2S) reacts with HCl to form $H_2S(g)$.
    - Molecular equation:
    $$Na_2S(aq) + 2HCl(aq) \rightarrow H_2S(g) + 2NaCl(aq)$$
    - Net ionic equation:
    $$2H^+(aq) + S^{2-}(aq) \rightarrow H_2S(g)$$
  - Carbonates and hydrogen carbonates (or bicarbonates) will form $CO_2(g)$ when treated with an acid.
    - Sodium bicarbonate ($NaHCO_3$; baking soda) reacts with HCl to form bubbles of $CO_2(g)$.
    - Molecular equation:
    $$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g) + NaCl(aq)$$
    - Net ionic equation:
    $$H^+(aq) + HCO_3^-(aq) \rightarrow H_2O(l) + CO_2(g)$$

4.4 Oxidation-Reduction Reactions

Oxidation and Reduction

- **Oxidation-reduction**, or *redox*, reactions involve the transfer of electrons between reactants.
- When a substances loses electrons, it undergoes **oxidation**:
$$Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$$
  - The neutral Ca has lost two electrons to $2H^+$ to become Ca^{2+}.
  - We say Ca has been oxidized to Ca^{2+}.
- When a substance gains electrons, it undergoes **reduction**:
$$2Ca(s) + O_2(g) \rightarrow 2CaO(s).$$
  - In this reaction the neutral O_2 has gained electrons from the Ca to become O^{2-} in CaO.
  - We say O_2 has been reduced to O^{2-}.
- In all redox reactions, one species is reduced at the same time as another is oxidized.

Oxidation Numbers

- Electrons are not explicitly shown in chemical equations.
- **Oxidation numbers** (or *oxidation states*) help up keep track of electrons during chemical reactions.
- Oxidation numbers are assigned to atoms using specific rules.
  - For an atom in its *elemental form*, the oxidation number is always zero.

- For any *monatomic ion*, the oxidation number equals the charge on the ion.
- *Nonmetals* usually have negative oxidation numbers.
  - The oxidation number of *oxygen* is usually –2.
    - The major exception is in peroxides (containing the O_2^{2-} ion).
- The oxidation number of *hydrogen* is +1 when bonded to nonmetals and –1 when bonded to metals.
- The oxidation number of *fluorine* is –1 in all compounds. The other *halogens* have an oxidation number of –1 in most binary compounds.
- *The sum of the oxidation numbers* of all atoms in a neutral compound is zero.
- The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.
- The oxidation of an element is evidenced by its increase in oxidation number; reduction is accompanied by a decrease in oxidation number.

Oxidation of Metals by Acids and Salts

- The reaction of a metal with either an acid or a metal salt is called a **displacement reaction.**
- The general pattern is:

$$A + B\mathbf{X} \rightarrow A\mathbf{X} + B$$

  - Example: It is common for metals to produce hydrogen gas when they react with acids. Consider the reaction between Mg and HCl:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

    - In the process the metal is oxidized and the H^+ is reduced.
  - Example: It is possible for metals to be oxidized in the presence of a salt:

$$Fe(s) + Ni(NO_3)_2(aq) \rightarrow Fe(NO_3)_2(aq) + Ni(s)$$

    - The net ionic equation shows the redox chemistry well:

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

    - In this reaction iron has been oxidized to Fe^{2+}, while the Ni^{2+} has been reduced to Ni.
- Always keep in mind that whenever one substance is oxidized, some other substance *must* be reduced.

The Activity Series

- We can list metals in order of decreasing ease of oxidation.
  - This list is an **activity series**.
- The metals at the top of the activity series are called *active metals*.
- The metals at the bottom of the activity series are called *noble metals*.
- A metal in the activity series can only be oxidized by a metal ion below it.
- If we place Cu into a solution of Ag^+ ions, then Cu^{2+} ions can be formed because Cu is above Ag in the activity series:

$$Cu(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$
$$\text{or}$$
$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$
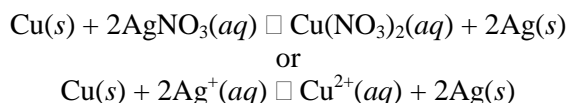
4.5 Concentrations of Solutions

- The term **concentration** is used to indicate the amount of solute dissolved in a given quantity of solvent or solution.

Molarity

- Solutions can be prepared with different concentrations by adding different amounts of solute to solvent.
- The amount (moles) of solute per liter of solution is the **molarity** (symbol *M*) of the solution:

$$\mathrm{Molarity} = \frac{\text{moles solute}}{\text{liters of solution}}$$

- By knowing the molarity of a quantity of liters of solution, we can easily calculate the number of moles (and, by using molar mass, the mass) of solute.

- Consider weighed copper sulfate, $CuSO_4$ (39.9 g, 0.250 mol) placed in a 250 ml volumetric flask. A little water is added and the flask is swirled to ensure that the copper sulfate dissolves. When all the copper sulfate has dissolved, the flask is filled to the mark with water.
  - The molarity of the solution is 0.250 mol $CuSO_4$ / 0.250 L solution = 1.00 M.

Expressing the Concentration of an Electrolyte

- When an ionic compound dissolves, the relative concentrations of the ions in the solution depend on the chemical formula of the compound.
  - Example: for a 1.0 M solution of NaCl:
    - The solution is 1.0 M in Na^+ ions and 1.0 M in Cl^- ions.
  - Example: for a 1.0 M solution of Na_2SO_4:
    - The solution is 2.0 M in Na^+ ions and 1.0 M in SO_4^{2-} ions.

Interconverting Molarity, Moles, and Volume

- The definition of molarity contains three quantities: molarity, moles of solute, and liters of solution.
  - If we know any two of these, we can calculate the third.
  - Dimensional analysis is very helpful in these calculations.

Dilution

- A solution in concentrated form (*stock solution*) is mixed with solvent to obtain a solution of lower solute concentration.
  - This process is called **dilution**.
- An alternate way of making a solution is to take a solution of known molarity and dilute it with more solvent.
- Since the number of moles of solute remains the same in the concentrated and diluted forms of the solution, we can show:

$$M_{conc}V_{conc} = M_{dil}V_{dil}$$

- An alternate form of this equation is:

$$M_{initial}V_{initial} = M_{final}V_{final}$$

4.6 Solution Stoichiometry and Chemical Analysis

- In approaching stoichiometry problems:
  - recognize that there are two different types of units:
    - laboratory units (the macroscopic units that we measure in lab) and
    - chemical units (the microscopic units that relate to moles).
  - Always convert the laboratory units into chemical units first.
    - Convert grams to moles using molar mass.
    - Convert volume or molarity into moles using M = mol/L.
  - Use the stoichiometric coefficients to move between reactants and products.
    - ***This step requires the balanced chemical equation.***
  - Convert the laboratory units back into the required units.
    - Convert moles to grams using molar mass.
    - Convert moles to molarity or volume using M = mol/L.

Titrations

- A common way to determine the concentration of a solution is via **titration**.
- We determine the concentration of one substance by allowing it to undergo a specific chemical reaction, of known stoichiometry, with another substance whose concentration is known (**standard solution**).
- Example: Suppose we know the molarity of an NaOH solution and we want to find the molarity of an HCl solution.
  - What do we know?
    - molarity of NaOH, volume of HCl

- What do we want?
  - molarity of HCl
- What do we do?
- Take a known volume of the HCl solution (i.e., 20.00 mL) and measure the number of mL of 0.100 M NaOH solution required to react completely with the HCl solution.
- The point at which stoichiometrically equivalent quantities of NaOH and HCl are brought together is known as the **equivalence point** of the titration.
- In a titration we often use an acid-base **indicator** to allow us to determine when the equivalence point of the titration has been reached.
  - Acid-base indicators change color at the *end point* of the titration.
  - The indicator is chosen so that the end point corresponds to the equivalence point of the titration.
- What do we get?
  - We get the volume of NaOH. Since we already have the molarity of the NaOH, we can calculate moles of NaOH.
- What is the next step?
  - We also know $HCl + NaOH \rightarrow NaCl + H_2O$.
  - Therefore, we know moles of HCl.
- Can we finish?
  - Knowing mol (HCl) and volume of HCl, we can calculate the molarity.