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 $M_{\text{initial}}V_{\text{initial}} = M_{\text{final}}V_{\text{final}}$.
- 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 $\leftrightarrows$ (equilibrium) and $\leftrightarrow$ (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 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$.
- ***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 **non-electrolyte** 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, $HC_2H_3O_2$

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

  - 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:

$$A\mathbf{X} + B\mathbf{Y} \rightarrow \mathbf{AY} + BX.$$

- 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:

$$Pb^{2+}(aq) + 2NO_3^-(aq) + 2K^+(aq) + 2I^-(aq) \rightarrow PbI_2(s) + 2K^+(aq) + 2NO_3^-(aq)$$

  - 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:

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

- 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.

Write the Net Ionic Eqn for $Ag_2SO_4\ (aq) + K_3PO_4\ (aq) \rightarrow$

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:

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

- 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

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

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:

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

- **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:

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

Identifying Strong and Weak Electrolytes

- Compounds can be classified as strong electrolytes, weak electrolytes, or non-electrolytes 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:
$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + \mathbf{H_2CO_3}(aq) \rightarrow H_2O(l) + CO_2(g) + NaCl(aq)$$
    - Net ionic equation:
$$H^+(aq) + HCO_3^-(aq) \rightarrow H_2O(l) + CO_2(g)$$

Also NH_4OH, H_2SO_3 will decompose to a gas

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:

$$Cu(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$
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:

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

- 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 39.9 g of copper sulfate, $CuSO_4$ (***how do we convert to moles?***) 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:

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:

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

- An alternate form of this equation is:

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

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.