

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 \rightleftharpoons (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 $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$.
- **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

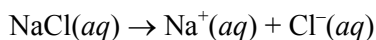
- When an ionic compound dissolves in water, the ions are said to *dissociate*.
 - This means that in solution, the solid no longer exists as a well-ordered arrangement of ions in contact with one another.
 - Instead, each ion is surrounded by a shell of water molecules.
 - This tends to stabilize the 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, $\text{NH}_3(\text{g})$ reacts with water to form $\text{NH}_4^+(\text{aq})$ and $\text{OH}^-(\text{aq})$.
 - For example, $\text{HCl}(\text{g})$ in water *ionizes* to form $\text{H}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$.

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



- 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, $\text{HC}_2\text{H}_3\text{O}_2$

$$\text{HC}_2\text{H}_3\text{O}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$$
- 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: $\text{Pb}(\text{NO}_3)_2(aq) + 2\text{KI}(aq) \rightarrow \text{PbI}_2(s) + 2\text{KNO}_3(aq)$

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 $\text{C}_2\text{H}_3\text{O}_2^-$ 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:

$$\text{AX} + \text{BY} \rightarrow \text{AY} + \text{BX}.$$
- Many precipitation and acid-base reactions exhibit this pattern.

Ionic Equations

- Consider $2\text{KI}(aq) + \text{Pb}(\text{NO}_3)_2(aq) \rightarrow \text{PbI}_2(s) + 2\text{KNO}_3(aq)$.
- Both $\text{KI}(aq)$ and $\text{Pb}(\text{NO}_3)_2(aq)$ 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:

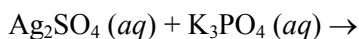
$$\text{Pb}(\text{NO}_3)_2(aq) + 2\text{KI}(aq) \rightarrow \text{PbI}_2(s) + 2\text{KNO}_3(aq)$$
- The **complete ionic equation** lists all strong soluble electrolytes in the reaction as ions:

$$\text{Pb}^{2+}(aq) + 2\text{NO}_3^-(aq) + 2\text{K}^+(aq) + 2\text{I}^-(aq) \rightarrow \text{PbI}_2(s) + 2\text{K}^+(aq) + 2\text{NO}_3^-(aq)$$
 - 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:

$$\text{Pb}^{2+}(aq) + 2\text{I}^{-}(aq) \rightarrow \text{PbI}_2(s)$$
- 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



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 $\text{HC}_2\text{H}_3\text{O}_2$ (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:

$$\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$$
- Common bases are NH_3 (ammonia), Drano, 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

$$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$$

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, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, and $\text{Sr}(\text{OH})_2$.
 - Strong acids include: HCl , HBr , HI , HClO_3 , HClO_4 , H_2SO_4 , and HNO_3 .
 - We write the ionization of HCl as:

$$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$$
- **Weak acids** and **weak bases** are weak electrolytes.
 - Therefore, they are partially ionized in solution.
- $\text{HF}(aq)$ is a weak acid; most acids are weak acids.
- We write the ionization of HF as:



Identifying Strong and Weak Electrolytes

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- 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:
 - $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{NaCl}(aq)$
 - (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.
 - $\text{Mg}(\text{OH})_2$ (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:
$$\text{Mg}(\text{OH})_2(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + 2\text{H}_2\text{O}(l)$$
 - Net ionic equation:
$$\text{Mg}(\text{OH})_2(s) + 2\text{H}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + 2\text{H}_2\text{O}(l)$$
 - Note that the magnesium hydroxide is an insoluble solid; it appears in the net ionic equation.

Acid-Base Reactions with Gas Formation

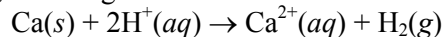
- There are many bases besides OH^- that react with H^+ to form molecular compounds.
 - Reaction of sulfides with acid gives rise to $\text{H}_2\text{S}(g)$.
 - Sodium sulfide (Na_2S) reacts with HCl to form $\text{H}_2\text{S}(g)$.
 - Molecular equation:
$$\text{Na}_2\text{S}(aq) + 2\text{HCl}(aq) \rightarrow \text{H}_2\text{S}(g) + 2\text{NaCl}(aq)$$
 - Net ionic equation:
$$2\text{H}^+(aq) + \text{S}^{2-}(aq) \rightarrow \text{H}_2\text{S}(g)$$
 - Carbonates and hydrogen carbonates (or bicarbonates) will form $\text{CO}_2(g)$ when treated with an acid.
 - Sodium bicarbonate (NaHCO_3 ; baking soda) reacts with HCl to form bubbles of $\text{CO}_2(g)$.
 - Molecular equation:
$$\text{NaHCO}_3(s) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{CO}_3(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) + \text{NaCl}(aq)$$
 - Net ionic equation:
$$\text{H}^+(aq) + \text{HCO}_3^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g)$$

Also NH_4OH , H_2SO_3 will decompose to a gas

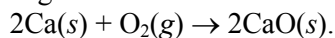
4.4 Oxidation-Reduction Reactions

Oxidation and Reduction

- **Oxidation-reduction**, or *redox*, reactions involve the transfer of electrons between reactants.
- When a substance loses electrons, it undergoes **oxidation**:



- 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**:



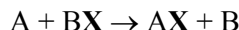
- In this reaction the neutral O_2 has gained electrons from the Ca to become O^{2-} in CaO.
- We say O_2 has been reduced to O^{2-} .
- In all redox reactions, one species is reduced at the same time as another is oxidized.

Oxidation Numbers

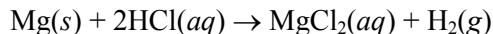
- Electrons are not explicitly shown in chemical equations.
- **Oxidation numbers** (or *oxidation states*) help us keep track of electrons during chemical reactions.
- Oxidation numbers are assigned to atoms using specific rules.
 - For an atom in its *elemental form*, the oxidation number is always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

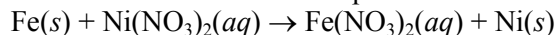
- The reaction of a metal with either an acid or a metal salt is called a **displacement reaction**.
- The general pattern is:



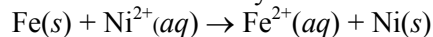
- Example: It is common for metals to produce hydrogen gas when they react with acids. Consider the reaction between Mg and HCl:



- 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:



- The net ionic equation shows the redox chemistry well:

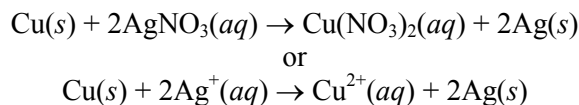


- In this reaction iron has been oxidized to Fe^{2+} , while the Ni^{2+} has been reduced to Ni.
- Always keep in mind that whenever one substance is oxidized, some other substance *must* be reduced.

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:



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 $M = \text{mol/L}$.
 - 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 $M = \text{mol/L}$.

Titration

- 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 $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$.
 - Therefore, we know moles of HCl.
 - Can we finish?
 - Knowing mol (HCl) and volume of HCl, we can calculate the molarity.