

Chapter 4. Aqueous Reactions and Solution Stoichiometry

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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.
- Students often confuse the symbols \rightleftharpoons (equilibrium) and \rightleftharpoons (resonance).
- Students often do not see that the net ionic equation for the reaction between strong acids and strong bases is always $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$.
- 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 smallest amount.
- Solutions in which water is the solvent are called **aqueous solutions**.

Electrolytic Properties¹

- All aqueous solutions can be classified in terms of whether or not they conduct electricity.
- If a substance forms ions in solution, the substance is an **electrolyte**, and the solution conducts electricity. Example: NaCl.
- If a substance does not form ions in solution, the substance is a **nonelectrolyte**, and the solution does not conduct electricity. Example: sugar.

Ionic Compounds in Water

- When an ionic compound dissolves in water, the ions *dissociate*.^{2,3}
 - 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 water molecules.
 - This tends to stabilize the ions in solution and prevent cations and anions from recombining.
 - The positive ions have the surrounding oxygen atoms of water pointing toward the ion; the negative ions have the surrounding hydrogen atoms of water pointing toward the ion.
 - The transport of ions through the solution causes electric current to flow through the solution.

Molecular Compounds in Water⁴

- When a molecular compound (e.g., CH₃OH) dissolves in water there are no ions formed.

¹ “Electrolytes and Nonelectrolytes” Movie from Student CD

² “Dissolution of NaCl in Water” from Matter

³ “Dissolution of KMnO₄” from Matter

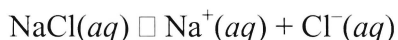
⁴ Figure 4.3 from Matter

- 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, $\text{NH}_3(g)$ reacts with water to form $\text{NH}_4^+(aq)$ and $\text{OH}^-(aq)$.
 - For example, $\text{HCl}(g)$ in water ionizes to form $\text{H}^+(aq)$ and $\text{Cl}^-(aq)$.

Strong and Weak Electrolytes⁵

- Compounds whose aqueous solutions conduct electricity well are called **strong electrolytes**.⁶

- 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.
- 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.
 - Example: acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$.

$$\text{HC}_2\text{H}_3\text{O}_2(aq) \text{---} \text{H}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$$
 - 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.⁷
 - Example: $\text{Pb}(\text{NO}_3)_2(aq) + 2\text{KI}(aq) \square \text{PbI}_2(s) + 2\text{KNO}_3(aq)$

Solubility Guidelines for Ionic Compounds^{8,9}

- The **solubility** of a substance is the amount of that substance that can be dissolved in a given quantity of solvent.
- 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:¹⁰
 - 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: compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+} .
 - Compounds containing SO_4^{2-} are soluble.
 - Exceptions: compounds of Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+} .
 - Compounds containing S^{2-} are insoluble.
 - Exceptions: compounds of NH_4^+ , the alkali metal cations, and Ca^{2+} , Sr^{2+} , and Ba^{2+} .

⁵ “Strong and Weak Electrolytes” from Matter

⁶ “Conductivity and Extent of Dissociation of Acids in Aqueous Solution” from Literature Demonstrations

⁷ “Name That Precipitate” from Literature Demonstrations

⁸ “Ionic Compounds” Activity from Student CD

⁹ “An Analogy for Solubility: Marbles and Magnets” from Further Readings

¹⁰ Table 4.1 from Matter and Transparency Pack

- Compounds of CO_3^{2-} or PO_4^{3-} are insoluble.
 - Exceptions: compounds of NH_4^+ and the alkali metal cations.
- Compounds of OH^- are insoluble.
 - Exceptions: compounds of the alkali metal cations, and Ca^{2+} , Sr^{2+} , and Ba^{2+} .

Exchange (Metathesis) Reactions

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



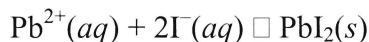
- Many precipitation and acid-base reactions exhibit this pattern.

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:

$$\text{Pb}^{2+}(aq) + 2\text{NO}_3^-(aq) + 2\text{K}^+(aq) + 2\text{I}^-(aq) \rightarrow \text{PbI}_2(s) + 2\text{K}^+(aq) + 2\text{NO}_3^-(aq)$$
- **The net ionic equation** lists only those ions that are not common on both sides of the reaction:



- 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^+ .¹¹
 - Ionization occurs when a neutral substance forms ions in solution. Example: $\text{HC}_2\text{H}_3\text{O}_2$ (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.¹²
- 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 react with the H^+ ions formed by acids.¹³
- 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, milk of magnesia.¹⁴

¹¹ "Introduction to Aqueous Acids" from Matter and Student CD

¹² Figure 4.601 from Matter

¹³ "Introduction to Aqueous Bases" from Matter and Student CD

¹⁴ Table 4.4 from Matter

- 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.¹⁵
 - Since there is a mixture of NH_3 , H_2O , NH_4^+ , and OH^- in solution, we write

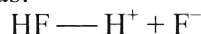
$$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$$

Strong and Weak Acids and Bases¹⁶

- **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:



- **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^{17, 18, 19, 20, 21}

- Compounds can be classified as strong electrolytes, weak electrolytes, or nonelectrolytes from their solubility.
- Strong electrolytes:
 - If a compound is water soluble and ionic, then it is probably a strong electrolyte.
 - If a compound is water soluble and not ionic, and is a strong acid, then it is a strong electrolyte.
 - Similarly, if a compound is water soluble and not ionic, but is a strong base, then it is a strong electrolyte.
- Weak electrolytes:
 - If a compound is water soluble and not ionic, and is a weak acid or weak base, then it is a weak electrolyte.
- Nonelectrolytes:
 - Otherwise, the compound is probably a nonelectrolyte.

Neutralization Reactions and Salts

- A **neutralization reaction** occurs when an acid and a base react:^{22, 23}
 - $\text{HCl}(aq) + \text{NaOH}(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{NaCl}(aq)$
 - (acid) + (base) \rightleftharpoons (water) + (salt)
- In general, an acid and base react to form a **salt**.

¹⁵ Figure 4.6 from Matter

¹⁶ Table 4.2 from Matter

¹⁷ Table 4.3 from Matter

¹⁸ Figure 4.7 from Matter and Transparency Pack

¹⁹ “Significance, Concentration Calculations, Weak and Strong Acids,” from Further Readings

²⁰ “Pictorial Analogies X: Solutions of Electrolytes” from Further Readings

²¹ “When Is a Strong Electrolyte Strong?” from Further Readings

²² “Demonstrations with Red Cabbage Indicator” from Literature Demonstrations

²³ “Reinforcing Net Ionic Equation Writing” from Further Readings

- A salt is any ionic compound whose cation comes from a base, and anion from an acid.
- The other product, H₂O, is a common weak electrolyte.
- Typical examples of neutralization reactions:
 - Reaction between an acid and a metal hydroxide:²⁴
 - Mg(OH)₂ (milk of magnesia) is a suspension.
 - As HCl is added, the magnesium hydroxide dissolves, and a clear solution containing Mg²⁺ and Cl⁻ ions is formed.
 - Molecular equation:

$$\text{Mg(OH)}_2(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + 2\text{H}_2\text{O}(l)$$
 - Net ionic equation:

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

Acid-Base Reactions with Gas Formation²⁵

- There are many bases besides OH⁻ that react with H⁺ to form molecular compounds.
 - Carbonates and hydrogen carbonates (or bicarbonates) will form CO₂(g) when treated with an acid.²⁶
 - Sodium hydrogen carbonate (NaHCO₃; baking soda) reacts with HCl to form bubbles of CO₂(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:

$$\text{H}^+(aq) + \text{HCO}_3^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g)$$
 - Reaction of sulfides with acid gives rise to H₂S, the substance that gives rotten eggs their foul odor.
 - Sodium sulfide (Na₂S) reacts with HCl to form H₂S(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:

$$2\text{H}^+(aq) + \text{S}^{2-}(aq) \rightarrow \text{H}_2\text{S}(g)$$

4.4 Oxidation-Reduction Reactions

Oxidation and Reduction^{27, 28, 29}

- When a substance loses electrons, it undergoes **oxidation**:³⁰

$$\text{Ca}(s) + 2\text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{H}_2(g)$$
- The neutral Ca has lost two electrons to 2H⁺ to become Ca²⁺.
- We say Ca has been oxidized to Ca²⁺.
- When a substance gains electrons, it undergoes **reduction**:

$$2\text{Ca}(s) + \text{O}_2(g) \rightarrow 2\text{CaO}(s)$$

²⁴ “Dissolution of Mg(OH)₂ by Acid” from Matter

²⁵ “A Handheld Reaction: Production of Ammonia Gas” from Literature Demonstrations

²⁶ “Alka Seltzer Poppers: An Interactive Exploration” Literature Demonstrations

²⁷ “Oxidation-Reduction Reactions — Part I” from Matter and Student CD

²⁸ “Formation of Silver Crystals” Movie from Student CD

²⁹ “Oxidation-Reduction Reactions II” Movie from Student CD

³⁰ “Oxidation and Reduction” from Further Readings

- 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 reduction-oxidation (redox) reactions, one species is reduced at the same time as another is oxidized.

Oxidation Numbers^{31, 32}

- 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 Salts³³

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

$$A + BX \rightarrow AX + B$$
 - 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^{34, 35}

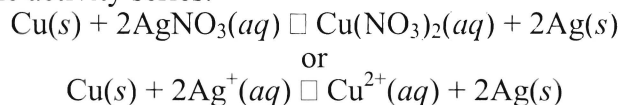
³¹ "Oxidation Numbers" from Further Readings

³² "Simple Method for Determination of Oxidation Numbers of Atoms in Compounds" from Further Readings

³³ "Oxidation-Reduction Reactions — Part II" from Matter

³⁴ Table 4.5 from Matter and Transparency Pack

- 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 be oxidized only 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:³⁶



4.5 Concentrations of Solutions

- The term **concentration** is used to designate 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** 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.³⁷
- 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 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 $0.250 \text{ mol CuSO}_4 / 0.250 \text{ L solution} = 1.00 \text{ M}$.

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.³⁸
- 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^{39, 40, 41}

³⁵ “What Makes Gold Such a Noble Metal?” from Further Readings

³⁶ “Formation of Silver Crystals” from Matter

³⁷ “Solution Formation from a Solid” from Matter and Student CD

³⁸ “A Cyclist’s Guide to Ionic Concentration” from Further Readings

³⁹ “Solution Formation by Dilution” from Matter and Student CD

⁴⁰ “Teaching Dilutions” from Further Readings

- 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 alternative 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 dilute forms of the solution, we can show:

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

- An alternative form of this equation is:

$$M_{concentrated}V_{concentrated} = M_{dilute}V_{dilute}$$

4.6 Solution Stoichiometry and Chemical Analysis

- In approaching stoichiometry problems:⁴²
 - 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 product.
 - ***This step requires the balanced chemical equation***
 - Convert the chemical 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**.^{43, 44, 45}
- 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.
 - First, let us examine what 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 (e.g., 20.0 mL) and measure the number of milliliters of 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.^{46, 47}

⁴¹ “On the Use of Intravenous Solutions to Teach Some Principles of Solution Chemistry” from Further Readings

⁴² Figure 4.20 from Matter and Transparency Pack

⁴³ Figure 4.22 from Matter

⁴⁴ “Titration” Movie from Student CD

⁴⁵ “Titration” Activity from Student CD

- 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?
 - Volume of NaOH. Since we already have the molarity of the NaOH, we can calculate moles of NaOH.
- 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 (20.0 mL above), we can calculate the molarity.

⁴⁶ “Natural Indicators” from Matter

⁴⁷ “Teas as Natural Indicators” from Literature Demonstrations

Further Readings:

1. Richard A. Kjonaas, "An Analogy for Solubility: Marbles and Magnets," *J. Chem. Educ.*, Vol. 61, **1984**, 765.
2. H. van Lubeck, "Significance, Concentration Calculations, Weak and Strong Acids," *J. Chem. Educ.*, Vol. 60, **1983**, 189.
3. Albert Kowalak, "When Is a Strong Electrolyte Strong?" *J. Chem. Educ.*, Vol. 65, **1988**, 607.
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