# CHEM 101

# Chapter 1

# Units, Quantities, and Measurement

## SI System

The **SI system** is the standard system of units used in science.
It consists of 7 **base units** and various **derived units** formed from them.
The 7 base units and their corresponding quantities are:

| | |
|---|---|
| **meter (m)** | length ($l$) |
| **kilogram (kg)** | mass ($m$) |
| **second (s)** | time ($t$) |
| **ampere (A)** | electric current ($I$) |
| **kelvin (K)** | thermodynamic temperature ($T$) |
| **mole (mol)** | amount of substance ($n$) |
| **candela (cd)** | luminous intensity ($I_v$) |

### Celsius Units

Celsius (°C) is not an SI unit but is commonly used for temperature measurements. It is derived from the Kelvin scale as:

$$T(^\circ\mathrm{C}) = T(\mathrm{K}) - 273.15$$

### Imperial Units

Common imperial units can be converted from SI units as follows:

$$1\ \mathrm{in} = 2.54\ \mathrm{cm}$$

$$1\ \mathrm{lb} = 0.453592\ \mathrm{kg}$$

$$^\circ\mathrm{F} = \tfrac{9}{5}{}^\circ\mathrm{C} + 32$$

### Unit Prefixes

Prefixes indicate base-10 multiples and fractions of units.

| | |
|---|---|
| ***tera-*** **(T)** | $10^{12}$ |
| ***giga-*** **(G)** | $10^{9}$ |
| ***mega-*** **(M)** | $10^{6}$ |
| ***kilo-*** **(k)** | $10^{3}$ |
| ***deci-*** **(d)** | $10^{-1}$ |
| ***centi-*** **(c)** | $10^{-2}$ |
| ***milli-*** **(m)** | $10^{-3}$ |
| ***micro-*** **($\mu$)** | $10^{-6}$ |

| | |
|---|---|
| ***nano-* (n)** | $10^{-9}$ |
| ***pico-* (p)** | $10^{-12}$ |

For example, one milligram equals $10^{-3}$ grams.

## Derived Units

Common derived units include volume, density, speed, acceleration, force, energy, and work.

### Volume

Volume ($V$) is the amount of 3-dimensional space occupied by a substance.
The SI unit for volume is the cubic meter ($\text{m}^3$).
The liter (L) is not an SI unit but is commonly used for volume measurements. It is equal to one cubic decimeter ($\text{dm}^3$).

$$1 \text{ L} = 1 \text{ dm}^3 = 1 \times 10^{-3} \text{ m}^3$$

A common imperial unit for volume is the quart (qt). It relates to the liter as follows:

$$1 \text{ qt} = 0.946353 \text{ L}$$

### Density

Density ($\rho$) is mass per unit volume.

$$\rho = \frac{m}{V}$$

The SI unit for density is kilograms per cubic meter ($\text{kg/m}^3$), though other units are commonly used. Liquids are typically expressed in grams per milliliter (g/mL), solids in grams per cubic centimeter ($\text{g/cm}^3$), and gases in grams per liter (g/L).

### Speed

Speed ($v$) is distance ($d$) traveled per unit time.

$$v = \frac{d}{t}$$

The SI unit for speed is meters per second (m/s).

### Acceleration

Acceleration ($a$) is the change in speed per unit time.
The symbol $\Delta$, the Greek uppercase delta, is used to represent change. $\Delta v$, read "delta v," is the change in speed.

$$a = \frac{\Delta v}{t}$$

The SI unit for acceleration is meters per second squared ($\text{m/s}^2$).

### Force

Force ($F$) represents a physical interaction that causes a mass to accelerate. Its magnitude is the product of the mass and its acceleration.

$$F = ma$$

The SI unit for force is the newton (N). One newton is the force required to accelerate a mass of one kilogram at a rate of one meter per second squared.

$$1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2$$

### Energy and Work

Energy ($E$) is the capacity to do work.

Work ($W$) is the transfer of energy that occurs when a force is applied over a distance.

The interaction described by force is not instantaneous, but extended over a distance through which the mass is continuously accelerated. Force gives the instantaneous magnitude of this interaction. Work describes its total accumulation.

This interaction transfers energy from the system applying the force to the mass being accelerated. The mass possesses this energy as kinetic energy, which represents its capacity to do work on another mass by using its motion to apply force.

Work's magnitude is the product of the applied force and the distance over which it is applied:

$$W = Fd$$

The SI unit for energy and work is the joule (J). One joule is the energy transferred when one newton of force is applied over a distance of one meter:

$$1\ \mathrm{J} = 1\ \mathrm{N} \cdot 1\ \mathrm{m} = 1\ \mathrm{kg} \cdot \mathrm{m}^2/\mathrm{s}^2$$

The calorie (cal) and Calorie (Cal) are commonly used non-SI units of energy. The first is written with a lowercase 'c', the second with an uppercase 'C'. The Calorie is primarily used in nutrition.

A calorie is defined as the amount of energy required to raise the temperature of one gram of water from 14.5 °C to 15.5 °C. It relates to the joule as follows:

$$1\ \mathrm{cal} = 4.184\ \mathrm{J}$$

A Calorie is equal to 1000 calories.

## Accuracy and Precision

**Accuracy** is how close a measurement is to the true value.

**Precision** is the smallest range within which a measurement is reliable. It is determined by the range within which repeated measurements fall.

All measurements must ultimately be confined to a range, since continuous values cannot be measured exactly. The true value almost never aligns precisely with a discrete unit; it is slightly more or less.

A reported measurement's precision is indicated by the decimal position of its last significant figure. For example, a value reported as 6500 is precise to the nearest hundred; one reported as 6563.2 is precise to the nearest tenth.

When multiple measurements are combined in a calculation, the result is limited by the least precise term. Different rules apply for different types of calculation. For addition and subtraction, round the result to the decimal place of the term with the least precise decimal place. For multiplication and division, round the result to the number of significant figures in the term with the fewest.

To improve accuracy and precision, it is standard practice to take repeated measurements and report the mean ± standard deviation.

## Dimensional Analysis

Dimensional analysis is the process of converting quantities between different units.

To convert a quantity from one unit to another, multiply it by a **conversion factor**.

A conversion factor is a fraction made from equal quantities expressed in different units. The quantity with the unit of the given value is placed in the denominator, and the quantity with the desired unit is placed in the numerator.

Multiplying a given value by the conversion factor algebraically cancels its unit and converts its value to the desired unit.

For example, to convert 5 inches to centimeters, arrange an inch-to-centimeter conversion factor with inches in the denominator and centimeters in the numerator. One inch is equal to 2.54 cm, so the conversion factor is $\frac{2.54\ \mathrm{cm}}{1\ \mathrm{in}}$. Multiply 5 inches by this conversion factor:

$$5\ \cancel{\text{in}} \times \frac{2.54\ \text{cm}}{1\ \cancel{\text{in}}} = 12.7\ \text{cm}$$

Multiple conversion factors can be combined in one calculation. For example, to convert 60 miles per hour to meters per second, include conversion factors for miles to kilometers, kilometers to meters, and hours to seconds:

$$\frac{60\ \cancel{\text{mi}}}{1\ \cancel{\text{h}}} \times \frac{1.60934\ \cancel{\text{km}}}{1\ \cancel{\text{mi}}} \times \frac{1000\ \text{m}}{1\ \cancel{\text{km}}} \times \frac{1\ \cancel{\text{h}}}{3600\ \text{s}} = 26.8\ \text{m/s}$$

# Chapter 2

# Matter and Atoms

## 2.1 Matter

### Classifications of Matter

**Matter** is anything that has mass and occupies space.

Matter takes the form of distinct **substances**, each with unique, observable properties. Examples include copper, tin, water, and salt.

A sample of matter is classified as a pure substance or a mixture.

**A pure substance** contains only one substance.

A **mixture** contains more than one. For example, bronze and saltwater are mixtures.

A distinct substance has a universal composition and set of properties. All pure samples of copper, tin, water, or salt are identical. In contrast, mixtures do not have a fixed composition. Two samples of bronze can contain different ratios of copper and tin, but both are bronze. Similarly, two samples of saltwater may have different ratios of salt to water.

Pure substances are classified as elements and compounds.

**Compounds** are substances that can be separated into simpler substances. For example, water is a compound because it can be separated into hydrogen and oxygen by electrolysis.

**Elements** are substances that cannot be separated into simpler substances. For example, hydrogen and oxygen are elements.

Although compounds are formed from elements, they are pure substances, not mixtures. All samples of a given compound have the same fixed ratio of elements by mass. This is known as the **law of definite proportions**, or the **law of constant composition**. For example, all samples of water contain exactly 11.188% hydrogen and 88.812% oxygen.

Mixtures are classified as homogeneous or heterogeneous.

A **homogeneous mixture** has a uniform composition. Its components are not visually distinguishable and are difficult to separate. For example, saltwater and bronze are homogeneous mixtures. A given sample contains multiple substances that are evenly mixed, resulting in a uniform composition.

A **heterogeneous mixture** has a non-uniform composition. Its components are visually distinguishable and relatively easy to separate. For example, saltwater in which the salt is not fully dissolved, or a copper–tin mosaic, are heterogeneous mixtures.

**Chemistry** is the study of matter's composition, how composition determines properties, and the changes matter undergoes.

### States of Matter

There are 3 common **states of matter**: gas, liquid, and solid.

A **gas** has neither fixed volume nor fixed shape. It takes both the volume and shape of its container. Its particles do not hold one another. They move rapidly and collide frequently with each other and the container walls.

A **liquid** has fixed volume but no fixed shape. Its particles hold one another at fixed distances but not in fixed orientation, allowing them to move freely around one another. An overall volume is maintained, but not an overall shape.

A **solid** has both fixed volume and fixed shape. Its particles hold one another at fixed distances and in fixed orientations. They are held rigidly in place, maintaining both volume and shape.

Different states of a substance are not different substances.

Changes between states are called **phase changes**. Phase changes are caused by changes in temperature or external pressure.

### Properties and Changes of Matter

Pure substances are often referred to as **chemicals**, particularly when considering their composition and how it can change.

Changes of matter are classified as physical or chemical.

A **physical change** does not alter chemical identity. The substance remains the same. For example, mixing salt and water, or melting solid tin, are physical changes.

**Chemical changes** alter chemical identity and produce a new substance. For example, combining hydrogen and oxygen to form water is a chemical change.

Properties of matter are classified as physical or chemical.

**Physical properties** are characteristics of a substance in its current chemical state. Examples include color, hardness, and melting point.

**Chemical properties** describe how a substance can undergo chemical change. For example, oxygen's capacity to combine with hydrogen is a chemical property.

Properties are also classified as intensive or extensive.

**Intensive properties** do not depend on the amount of matter. Examples include color, melting point, and temperature.

**Extensive properties** depend on the amount of matter. Examples include mass, volume, and total energy.

## 2.2 Atomic Theory

**John Dalton** proposed 4 postulates of **atomic theory** in 1803:

1. All matter is composed of atoms.
2. All atoms of an element are identical; atoms of different elements are different.
3. Compounds are formed by the combination of atoms of different elements in fixed, small whole-number ratios.
4. Chemical reactions affect the ways atoms are combined, but the atoms themselves are neither created, destroyed, nor altered by chemical reactions.

These postulates are supported by the law of definite proportions and the law of multiple proportions.

As previously established, the law of definite proportions states that all samples of a given compound have the same fixed ratio of elements by mass. If matter were not composed of discrete units, there would be no explanation for this consistent equality.

For example, just as saltwater can contain varying ratios of salt to water, water itself should show varying ratios of hydrogen to oxygen.

This supports the conclusion that matter is composed of discrete atoms, that compounds are formed from fixed combinations of atoms, and that all atoms of a given element have identical mass. As a result, each compound has a fixed ratio of elements.

The **law of multiple proportions** applies to two elements that can combine in different ratios to form different compounds. It compares the mass of one element that would combine with a fixed mass of the other to form each compound, and states that these masses form a small whole-number ratio.

For example, hydrogen and oxygen combine in different ratios to form water and hydrogen peroxide. These ratios are determined by separating each compound into its elements and measuring the relative masses of hydrogen and oxygen.

Separating 10 grams of water and 10 grams of hydrogen peroxide gives 1.119 grams of hydrogen and 8.881 grams of oxygen for water, and 0.593 grams of hydrogen and 9.407 grams of oxygen for hydrogen peroxide. The two ratios are compared by fixing the mass of one component. For 1 unit of hydrogen, water contains 7.94 units of oxygen, and hydrogen peroxide contains 15.86. These masses form a 2:1 ratio.

This law supports the postulate that compounds are formed from small, whole-number ratios of atoms.

For a given mass of one element, corresponding to a specific number of atoms, the other must be present in a small, whole-number ratio of atoms. This results in small, whole-number ratios of mass.

## 2.3 Discovery of the Atomic Structure

### The Electron

**J. J. Thomson** discovered the **electron** in 1897 through the **cathode ray tube** experiment.

A cathode ray tube is a vacuum tube with a negatively charged cathode and positively charged anode inside. When a voltage is applied, a beam appears between them.

If the anode is perforated, part of the beam passes through. This confirms that the ray originates at the cathode, not the anode. Also, if an object is placed between the cathode and anode in the path of the ray, a shadow appears on the side of the tube opposite the cathode, further confirming that the ray originates at the cathode.

Thomson observed that the beam was deflected away from negative electric and magnetic fields and toward positive ones, indicating that the ray consists of negatively charged particles. These must originate from the cathode.

The beam behaved the same regardless of the material used for the cathode, indicating that all matter contains these negatively charged particles.

Atoms are electrically neutral. If atoms were fundamental, indivisible particles, their emission of negative particles could not be explained. Thomson concluded that the atom has internal structure and contains both positive and negative components, which together result in a neutral charge. The negative components are the particles emitted in the cathode ray. These particles were later named electrons.

Thomson then calculated the electron's charge-to-mass ratio. Although he could not determine the individual charge or mass of the electron, he was able to determine their ratio.

Thomson first determined the electron's velocity. He applied opposing electric and magnetic fields and adjusted their strengths until the beam was not deflected in either direction, indicating that the forces were balanced. He then calculated the velocity by comparing the strengths of the fields.

The electric force on a charged particle depends only on the electric field strength. The magnetic force, by contrast, is the product of the magnetic field strength and the particle's velocity. Since the forces were equal in magnitude, the velocity of the particle equals the electric field strength divided by the magnetic field strength.

Once the velocity was known, Thomson used the curvature of the beam in a magnetic field to determine the charge-to-mass ratio. The curvature of a charged particle's path in a magnetic field is proportional to the magnetic field strength, the particle's velocity, and its charge, and inversely proportional to its mass. Since the field strength and velocity were known, the charge-to-mass ratio could be calculated.

He measured the charge-to-mass ratio to be $1.76 \times 10^8$ coulombs per gram. Coulombs (C) are the SI unit of electric charge.

### Electron Mass and Charge

**Robert Millikan** determined the charge and mass of individual electrons in 1909 using the **oil-drop experiment**.

Small oil droplets are sprayed into a chamber. X-rays are then used to cause the air molecules in the chamber to release free electrons. Some of these electrons attach to the droplets, giving them a negative charge.

The chamber contains two charged plates, creating an upward electric field. The field strength is adjusted until the upward electric force balances the downward gravitational force, suspending the droplet.

Gravitational force is proportional to the droplet's mass. Electric force is proportional to the droplet's charge and the strength of the electric field. If the mass is known, the charge can be calculated from the field strength.

To determine a droplet's mass, Millikan first calculated its radius from its terminal velocity.

As an object falls through air, gravity pulls it downward and air drag pushes upward. Drag is proportional to speed. When the object first begins falling, its speed is low, so gravity exceeds drag and it accelerates downward. As its speed increases, drag increases, reducing downward acceleration. Eventually, drag equals gravity. At that point, the object stops accelerating and falls at constant speed. This is the object's terminal velocity.

An oil droplet's terminal velocity is proportional to its radius. By measuring terminal velocity, Millikan determined the droplet's radius. From its radius, he calculated its volume. From its volume, he calculated its mass using the known density of oil. With the mass known, he calculated the droplet's charge from the strength of the electric field that balanced gravity.

Millikan found that each droplet's charge was always a whole-number multiple of $1.602 \times 10^{-19}\,\mathrm{C}$. This pattern can only be explained if that value is the charge of a single electron. Using this charge and Thomson's charge-to-mass ratio, he calculated the electron's mass to be approximately $9.10 \times 10^{-28}\,\mathrm{g}$.

## Radiation

Radiation was discovered by **Henri Becquerel** in 1896. Photographic plates contain compounds that react when exposed to light. Becquerel placed a photographic plate and uranium compounds in a dark drawer. The plate reacted, even though no light was present. This showed that the uranium compound emitted radiation that affected the plate like light.

It was not clear from Becquerel's work what the precise source of the emitted radiation was. In 1898, **Marie Curie** tested uranium compounds in many chemical forms and found that the radiation's intensity depended only on the number of uranium atoms, regardless of chemical form. This showed that radiation is an intrinsic property of the atoms. She tested additional elements and discovered that other elements were also radioactive.

In 1899, **Ernest Rutherford** discovered distinct types of radiation. He placed radioactive material behind a lead plate with a small hole, so that the radiation emerged from the hole as a narrow beam. The beam's path was shown by detector screens placed opposite the hole. When he applied an electric field to the beam, it split into three parts: one was positive and deflected with the field, one was negative and deflected against it, and one was unaffected. He named them $\alpha$, $\beta$, and $\gamma$, respectively.

Further experiments showed that the types of radiation differed in their penetrative abilities. $\alpha$ radiation was the least penetrative and could be blocked by paper. $\beta$ radiation could be blocked by a thin metal sheet. $\gamma$ radiation was the most penetrative and required a thick metal block.

These findings did not confirm subatomic structure in all atoms, as radiation was observed only in certain elements. However, they did confirm that some atoms contain internal charged components. Once the universal presence of subatomic particles was discovered, radiation was understood to be the emission of particles present in all atoms.

## Plum Pudding Model

The mass of an electron, determined by Millikan, is $9.10 \times 10^{-28}\,\mathrm{g}$, which is thousands of times smaller than the mass of an atom. Hydrogen, the lightest element, was known to have a mass of approximately $1.67 \times 10^{-24}\,\mathrm{g}$.

Since the atom is electrically neutral, the rest of the atom must carry a positive charge equal in magnitude to the negative charge of the electrons.

J.J. Thomson proposed a model in which the positive charge and most of the atom's mass are spread uniformly throughout the atom. The much smaller, negatively charged electrons are embedded within this diffuse positive background. This is called the **plum pudding model**, where the positive background is the "pudding" and the electrons are like "raisins" embedded in it.

## Nuclear Model

Ernest Rutherford proposed the nuclear model in 1911 based on the **gold foil experiment**.

A beam of $\alpha$ particles was directed at a thin gold foil, and their deflections were measured. Most particles passed straight through, while a small number were deflected at large angles.

This contradicted the Thomson plum pudding model. If mass and positive charge were uniformly distributed, all particles would experience similar slight deflections.

Rutherford concluded that atoms are mostly empty space, with nearly all mass and positive charge concentrated in a small, dense nucleus. Most $\alpha$ particles passed through empty space, while a few that approached a nucleus were strongly deflected.

### Proton and Neutron

The proton was discovered by Rutherford in 1919, and the neutron by **James Chadwick** in 1932.

They were discovered by bombarding atoms with $\alpha$ particles, which caused the emission of nuclear particles.

The proton and neutron have nearly identical masses. The proton carries a positive charge, while the neutron is neutral. They compose the atom's nucleus and account for nearly all its mass.

## 2.4 Atomic Properties

### Atomic Units

Atomic-scale quantities are measured in specialized units.

#### Charge

The **elementary charge** ($e$) is the magnitude of the charge on a single electron.

$$e = 1.602 \times 10^{-19} \text{ C}$$

A proton has a charge of $+1e$. An electron has a charge of $-1e$.

#### Length

The **angstrom** (Å) is a common unit for atomic distances.

$$1 \text{ Å} = 10^{-10} \text{ m} = 0.1 \text{ nm} = 100 \text{ pm}$$

Atomic diameters typically range from 1 to 5 Å.

The atomic nucleus has a diameter of about $10^{-4}$ Å, or $10^{-14}$ m.

#### Mass

The **atomic mass unit** (amu) is one-twelfth the mass of a $^{12}$C atom.

$$1 \text{ amu} = 1.66054 \times 10^{-24} \text{ g}$$

A proton has a mass of 1.0073 amu, a neutron 1.0087 amu, and an electron $5.486 \times 10^{-4}$ amu.

### Atomic Number and Isotopes

An element is defined by the number of protons in its atoms' nuclei. This number is called the element's **atomic number**.

Each element has a designated name and symbol. For example, the element with six protons in its atoms' nuclei is called carbon and has the symbol C.

Atoms of the same element can have different numbers of neutrons. These are called **isotopes**. Isotopes have mostly similar properties.

An atom's **mass number** is the total number of protons and neutrons in its nucleus.

An isotope is notated by placing the mass number as a superscript before the element's symbol. For example, $^{12}C$ refers to the carbon-12 isotope, which has six protons and six neutrons.

Elements cannot be assigned fixed masses because their isotopes have different masses.

The average atomic mass of an element is called its **atomic weight**. It is calculated by averaging the masses of all isotopes, weighted by their relative natural abundances.

## The Periodic Table

When the elements are arranged by increasing atomic number, their chemical properties follow a distinct sequence that repeats periodically. This is called the **periodic law**.

The **periodic table** lists all known elements in order of increasing atomic number. It organizes the elements in rows, with each row reflecting a repeating sequence of chemical properties. These rows are called **periods**. Elements with similar properties align vertically in columns, called **groups**.

Most periodic tables include each element's name, symbol, atomic number, and atomic mass.

Elements are classified as metals, nonmetals, or metalloids. Metalloids have both metallic and nonmetallic properties. These categories are discussed in detail in a later chapter.

Metals occupy the left and lower regions of the periodic table. Nonmetals are in the upper right. They are separated by a step-like line that runs from between boron and aluminum to between polonium and astatine. Metalloids lie along this line.

Elements are further classified by group. Groups 1, 2, and 13–18 are called the **representative elements**. Groups 3–12 are called the **transition metals**.

Some groups have specific names:

| | |
|---|---|
| **Group 1** | Alkali metals |
| **Group 2** | Alkaline earth metals |
| **Group 16** | Chalcogens |
| **Group 17** | Halogens |
| **Group 18** | Noble gases |

# Chapter 3

# Ions and Molecules

## 3.1 Ionization and Covalent Bonds

### Electron Instability

A neutral atom has an equal number of protons and electrons. For example, a neutral carbon atom has 6 protons and 6 electrons.

Atoms are only stable when they contain certain numbers of electrons. These stable numbers correspond to the electron counts of the noble gases. The electron counts found in neutral atoms of all other elements are not stable.

As a result, atoms of elements other than noble gases do not exist as isolated atoms. They become stable by forming ions or covalent bonds.

### Valence Shells

The instability of most electron counts, and the stability of those found in the noble gases, is explained by **Bohr's atomic model**. The model is discussed in detail in a later chapter.

The model posits that an atom's electrons are arranged in distinct **energy shells**. Each successive shell is farther from the nucleus and has higher electrostatic potential energy.

Electrons fill the lower-energy shells first. Each shell can hold a maximum number of electrons. Once the lower-energy shells are filled, additional electrons enter higher-energy shells.

The electrons in the outermost shell of an atom are called **valence electrons**. The outermost shell is called the **valence shell**. Inner electrons are called **core electrons**; inner shells are called **core shells**.

Electrons are only stable when they are part of a complete shell. Core shells are by definition filled. The only shell that can be incomplete is the valence shell. The only stable configuration is one where the valence shell is complete.

The noble gases are the only neutral atoms with filled valence shells.

The first shell can hold a maximum of two electrons. The first noble gas, helium (He), has two protons and two electrons.

Each row in the periodic table corresponds to a new valence shell being filled. For example, a neutral lithium (Li) atom has three protons and three electrons. Two electrons fill the first shell, and the third electron enters the second shell.

The second shell can hold a maximum of eight electrons. The second noble gas, neon (Ne), has ten protons and ten electrons. Two electrons fill the first shell, and eight fill the second.

This pattern continues for all shells and noble gases. Higher energy shells are more complex, and are discussed in a later chapter.

All valence shells, except for the first, are complete when they contain eight electrons. This is called the **octet rule**.

All neutral atoms other than the noble gases have a partially filled valence shell. This is why these atoms are unstable. Atoms modify their electron configuration through ionization or covalent bonding to achieve a full valence shell.

## Ionization

An **ion** is a particle with an electric charge.

An atom can gain or lose electrons and become an ion. This process is called **ionization**.

Ions have distinct chemical and physical properties from their parent atoms.

Many atoms achieve stability by gaining or losing enough electrons to result in the quantity of the nearest noble gas.

An atom that loses electrons becomes positively charged and is called a **cation**. An atom that gains electrons becomes negatively charged and is called an **anion**.

Cations and anions can be created in pairs, where the cation donates electrons to the anion.

For example, sodium (Na) has one more electron than neon (Ne), and chlorine (Cl) has one less than argon (Ar). In an ionization reaction between sodium and neon, sodium donates one electron to chlorine. Sodium becomes a cation with a charge of $^{1+}$, and chlorine becomes an anion with a charge of $^{1-}$.

## Covalent Bond Formation

In a **covalent bond**, two atoms share electrons. The shared electrons contribute to the electron configuration of both atoms and hold the atoms together. The atoms remain neutral but achieve stability by sharing enough electrons to reach the configuration of the next noble gas.

For example, two fluorine (F) atoms may form a covalent bond. Each has 9 protons and, when neutral, 9 electrons. The next noble gas is neon, with 10 electrons. To reach this configuration, each atom needs 1 more electron. Each shares 1 electrons with the other, and both reach a configuration with 10 electrons. The two shared electrons are called a **bonding pair**.

Atoms can share more than 1 bonding pair, forming a **multiple bond**.

For example, two oxygen (O) atoms may form a double bond, with 2 bonding pairs. A neutral oxygen atom has 8 electrons, and needs 2 more to reach a noble gas configuration. In the double bond, each oxygen atom shares 2 electrons with the other.

## Metals, Nonmetals, and Electronegativity

An element's **electronegativity** is how strongly its atoms attract electrons.

An element's **ionization energy** is the amount of energy required to remove an electron from its atoms. Elements with lower ionization energy lose electrons more readily.

Metals have only a few more electrons than the nearest noble gas configuration, as shown by their position on the left side of the periodic table. They have low electronegativity and low ionization energy, and tend to lose electrons to form cations.

Nonmetals have only a few fewer electrons than the nearest noble gas configuration, as shown by their position on the right side of the periodic table. They have high electronegativity and high ionization energy, and tend to gain electrons to form anions or share electrons in covalent bonds.

An electron transfer occurs when two atoms with a large difference in electronegativity interact. This typically happens between a metal and a nonmetal. Electrons are transferred from the atom with lower electronegativity to the one with higher electronegativity, forming oppositely charged ions.

A covalent bond forms when two atoms with high electronegativity interact. This typically occurs between two nonmetals. Neither is sufficiently more electronegative to remove electrons from the other, so the electrons are shared.

In a **polar covalent bond**, one atom attracts the shared electrons more strongly than the other. The difference in electronegativity is not great enough to cause electron transfer, but is sufficient to cause the electrons to be unevenly shared. This unequal sharing gives the more electronegative atom a partial negative charge, and the less electronegative atom a partial positive charge. These partial charges are denoted by $\delta^{-}$ and $\delta^{+}$.

## 3.2 Ionic Compounds and Covalent Molecules

### Ionic Compounds

The **electrostatic force** is the attraction between oppositely charged particles and the repulsion between particles with the same charge.

Oppositely charged ions attract each other due to electrostatic forces. This attraction forms an **ionic bond**.

An **ionic compound** consists of many oppositely charged ions held together by ionic bonds. The ions are present in a fixed ratio that results in an overall neutral charge.

For example, sodium chloride, or table salt, is an ionic compound formed from sodium ions and chloride ions in a 1:1 ratio.

The ions in an ionic compound arrange themselves to maximize attraction between oppositely charged ions and minimize repulsion between ions with the same charge. This results in a fixed, repeating three-dimensional lattice, with each ion held rigidly in place. The exact arrangement depends on the sizes and relative numbers of the ions.

Because of their lattice structure, ionic compounds are typically hard and brittle solids.

### Molecules

A **molecule** is a discrete group of atoms held together by covalent bonds.

For example, a water molecule contains 1 oxygen atom and 2 hydrogen atoms. Each hydrogen forms a covalent bond with the oxygen. In each bond, both atoms share 1 electron. Initially, the oxygen atom has 2 fewer electrons than a noble gas, and each hydrogen atom has 1 fewer. With the shared electrons, each hydrogen's configuration gains 1 electron, and oxygen's gains 2.

Ionic compounds have a fixed ratio of each type of ion but are not limited in size. More ions can be added, simply extending the lattice. In contrast, a molecule contains a fixed number of atoms of each element.

For example, if 2 oxygen atoms and 4 hydrogen atoms react to form water, they will produce 2 separate water molecules. Each molecule contains 1 oxygen atom and 2 hydrogen atoms. The atoms do not combine into a single large molecule with 2 oxygen and 4 hydrogen atoms, even though the ratio is the same.

Ionic compounds form because of electrostatic attraction between charged ions. Each ion continues to attract others of opposite charge, resulting in a continuous lattice. In contrast, covalent bonds form when atoms share electrons to achieve the configuration of a noble gas. Once this configuration is reached, there is no need for additional atoms, and the molecule remains a discrete unit.

### Polar Molecules

Molecules carry a net neutral charge.

In a **polar molecule**, the charge is unevenly distributed due to polar covalent bonds. It has partially positive and partially negative regions.

The separation of charge within a single particle is called a **dipole**. Polar molecules have a **permanent dipole**.

### Intermolecular Forces

Molecules are attracted to one another. These attractions are called **intermolecular forces**.

Intermolecular forces are caused by a region of partial positive charge in one molecule being attracted to a region of partial negative charge in another. These forces are weaker than ionic bonds, where each ion carries a full positive or negative charge.

In polar molecules, these regions of partial charge are permanent. In nonpolar molecules, they are temporary, formed by the constant motion of shared electrons. The attractions between nonpolar molecules are called **van der Waals forces**.

Intermolecular forces hold adjacent molecules at a fixed distance but not in fixed positions. As a result, molecular substances generally have low melting and boiling points. In solid form, they are soft and bendable, since the molecules can shift around each other.

Polar molecules form stronger intermolecular forces than nonpolar molecules. Water is a highly polar molecule and forms strong intermolecular attractions known as **hydrogen bonds**. These forces are responsible for many of water's properties, such as surface tension.

## 3.3 Ionic and Molecular Formulas

### Ionic Formulas

A **monatomic ion** is the ion of a single atom.

A **polyatomic ion** is a group of covalently bonded atoms that carry an electric charge. These generally form through acid-base chemistry, as explained in a later chapter.

A substance's **chemical formula** denotes its chemical composition and charge.

The chemical formula for an ion includes the element symbol and the charge. The charge is written as a superscript after the symbol. The magnitude of the charge precedes the sign. If the charge is 1, the number is omitted.

For example, a sodium ion that lost one electron has a charge of $^{1+}$ and is denoted: $Na^+$. An oxygen atom that gained two electrons has a charge of $^{2-}$ and is denoted $O^{2-}$.

The chemical formula for a polyatomic ion includes the element symbols of the atoms present, the number of each atom, and the overall charge. The number of atoms of each element is written as a subscript after the symbol. The overall charge is written as a superscript at the end.

For example, the ion formed from one nitrogen and three oxygens with the overall charge of $^{1-}$ is denoted $NO_3{}^-$.

In an ionic compound, ions are present in a ratio that results in a net neutral charge. Such compounds are called **salts**, although in common usage the term refers specifically to *table salt*, a salt of sodium and chloride ions.

The chemical formula of an ionic compound gives the element symbols of the ions and the ratio between them. The cation is listed before the anion. The number of each ion is written as a subscript after its symbol. Charges are not shown.

For example, the compound formed from $Na^+$ and $Cl^-$ is NaCl. The compound formed from $Al^{3+}$ and $Cl^-$ is $AlCl_3$. The compound formed from $Al^{3+}$ and $O^{2-}$ is $Al_2O_3$.

When a polyatomic ion is part of an ionic compound, its atoms retain their covalent bonds and are collectively present in the compound as a discrete unit. It is denoted by placing the formula of the ion, without its charge, in parentheses, followed by a subscript indicating the number present.

For example, the compound formed from $Al^{3+}$ and $NO_3{}^-$ is $Al(NO_3)_3$.

### Molecular Formulas

A **diatomic molecule** contains two atoms. A **polyatomic molecule** contains more than two atoms.

A **molecular compound** is a molecule that contains atoms of more than one element.

Molecules can be represented using two types of chemical formulas. The **molecular formula** indicates the number of atoms of each element present, while the **empirical formula** gives the simplest whole-number ratio of atoms.

For example, glucose contains 6 carbon, 12 hydrogen, and 6 oxygen atoms. Its molecular formula is $C_6H_{12}O_6$, and its empirical formula is $CH_2O$.

More complex representations provide additional details about a molecule's structure. A molecule's **structure** is its specific arrangement of which atoms are bonded to which, and the three-dimensional arrangement of its bonds and electrons. **Isomers** are molecules with the same molecular formula but different structures.

A molecule's **structural representation** shows which atoms are bonded to which. Other models, such as the ball-and-stick or space-filling models, show the three dimensional arrangement. These are not covered here.

## 3.4 Table of Common Elements and Ions

| Group/Element | Elemental State | Monatomic Ions | Polyatomic Ions |
|---|---|---|---|
| **Hydrogen** | | | |
| H | Diatomic Gas | $H^+$ | $H_3O^+$, $HSO_3{}^-$, $HSO_4{}^-$ |
| **Group 1: Alkali Metals** | | | |
| Li | Solid Metal | $Li^+$ | |
| Na | | $Na^+$ | |
| K | | $K^+$ | |
| **Group 2: Alkaline Earth Metals** | | | |
| Be | Solid Metal | $Be^{2+}$ | |
| Mg | | $Mg^{2+}$ | |
| Ca | | $Ca^{2+}$ | |
| Sr | | $Sr^{2+}$ | |
| Ba | | $Ba^{2+}$ | |
| **Transition Metals** | | | |
| Cr | Solid Metal | $Cr^{2+}$, $Cr^{3+}$ | $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$ |
| Mn | | $Mn^{2+}$, $Mn^{4+}$ | $MnO_4{}^-$ |
| Fe | | $Fe^{2+}$, $Fe^{3+}$ | |
| Co | | $Co^{2+}$, $Co^{3+}$ | |
| Ni | | $Ni^{2+}$ | |
| Cu | | $Cu^+$, $Cu^{2+}$ | |
| Zn | | $Zn^{2+}$ | |
| Ag | | $Ag^+$ | |
| Cd | | $Cd^{2+}$ | |
| Hg | Liquid Metal | $Hg_2{}^{2+}$, $Hg^{2+}$ | |
| **Post-Transition Metals** | | | |
| Sn | Solid Metal | $Sn^{2+}$, $Sn^{4+}$ | |
| Pb | | $Pb^{2+}$, $Pb^{4+}$ | |
| **Group 13: Aluminum** | | | |
| Al | Solid Metal | $Al^{3+}$ | |
| **Metalloids** | | | |
| B | Solid Metalloid | | |
| Si | | | |
| **Group 14: Carbon Group** | | | |
| C | Solid Nonmetal | | $CO_3{}^{2-}$, $HCO_3{}^-$, $C_2O_4{}^{2-}$, $CH_3COO^-$ |
| **Group 15: Nitrogen Group** | | | |
| N | Diatomic Gas | $N^{3-}$ | $NO_3{}^-$, $NO_2{}^-$, $NH_4{}^+$, $CN^-$ |
| P | Solid Nonmetal ($P_4$) | $P^{3-}$ | $PO_4{}^{3-}$, $HPO_4{}^{2-}$, $H_2PO_4{}^-$ |
| **Group 16: Chalcogens** | | | |
| O | Diatomic Gas | $O^{2-}$, $O_2{}^{2-}$ | $OH^-$ |
| S | Solid Nonmetal ($S_8$) | $S^{2-}$ | $SO_4{}^{2-}$, $SO_3{}^{2-}$ |
| **Group 17: Halogens** | | | |
| F | Diatomic Gas | $F^-$ | |
| Cl | Diatomic Gas | $Cl^-$ | $ClO_4{}^-$, $ClO_3{}^-$, $ClO_2{}^-$, $ClO^-$ |
| Br | Liquid Nonmetal | $Br^-$ | |
| I | Solid Nonmetal ($I_2$) | $I^-$ | |
| **Group 18: Noble Gases** | | | |
| He | Monatomic Gas | | |
| Ne | | | |
| Ar | | | |

# Chapter 4

# Chemical Nomenclature

## Covered Topics

Organic compounds contain both carbon and hydrogen. They use a separate system of nomenclature from inorganic compounds. This course covers only inorganic compounds, so organic naming conventions are not included.

**IUPAC** is the international authority responsible for standardizing chemical nomenclature. Many substances have both a **systematic name**, based on IUPAC rules, and a **common name**, derived from historical usage. Both types of names are explained in this chapter.

## Cations

Most cations are metals. They form when metal atoms lose electrons.

The only common nonmetal cation is **ammonium** (${NH_4}^+$). It is formed from ammonia ($NH_3$) accepting a proton.

Metal cation nomenclature retains the name of the element and appends *ion*. For example, $Na^+$ is named *sodium ion*.

Alkali metals always form $^{1+}$ ions, and alkaline earth metals always form $^{2+}$ ions. Their charges are fixed and do not need to be specified.

Many transition metals have more than one possible cation, each with a different charge. An individual cation's charge cannot be inferred from the element alone and must be specified. In systematic nomenclature, the ion's charge is shown in parentheses as a Roman numeral after the name.

For example, iron (Fe) forms $Fe^{2+}$ and $Fe^{3+}$. These are named *iron(II) ion* and *iron(III) ion*.

An older naming convention specifies the ions of an element by using the suffix *-ic* for the ion with the higher charge and *-ous* for the ion with the lower charge. These suffixes are typically applied to the Latin name of the element, not its modern name.

For example, the Latin name for iron is *ferrum*. In this system, $Fe^{3+}$ is called *ferric ion*, and $Fe^{2+}$ is called *ferrous ion*. Similarly, copper's Latin name is *cuprum*. $Cu^{2+}$ is *cupric ion*, and $Cu^+$ is *cuprous ion*.

## Anions

Most anions are nonmetals. They can be either **monatomic** or **polyatomic**.

Monatomic anions and some polyatomic anions are named with the suffix *-ide*.

Common anions include:

| | |
|---|---|
| $\mathbf{H^-}$ | Hydride ion |
| $\mathbf{Cl^-}$ | Chloride ion |
| $\mathbf{O^{2-}}$ | Oxide ion |
| $\mathbf{OH^-}$ | Hydroxide ion |
| $\mathbf{CN^-}$ | Cyanide ion |

## Oxoanions

**Oxoanions** are polyatomic anions that contain oxygen. In older texts, they may be referred to as *oxyanions*.

The atom bonded to the oxygen is called the **central element**. It is usually a nonmetal or a metalloid.

Many elements have more than one possible oxoanion, each with a different number of oxygen atoms.

Oxoanions follow a distinct naming system and do not use the *-ide* suffix. This system identifies them as oxygen-containing anions and distinguishes among different forms of the same element.

The system designates one form as the reference point and names the others relative to it, based on the number of oxygen atoms they contain.

The reference form is named *-ate*. The form with one fewer oxygen atom is named *-ite*. A form with one more oxygen atom than the *-ate* is named *per-ate*. A form with one fewer than the *-ite* is named *hypo-ite*.

In order, the four names are: *hypo–ite* < *-ite* < *-ate* < *per–ate*.

For example, the oxoanions of chlorine are:

| | |
|---|---|
| $\mathbf{ClO^-}$ | Hypochlorite ion |
| $\mathbf{ClO_2{}^-}$ | Chlorite ion |
| $\mathbf{ClO_3{}^-}$ | Chlorate ion |
| $\mathbf{ClO_4{}^-}$ | Perchlorate ion |

The *-ate* form usually contains three or four oxygen atoms. However, there is no consistent rule to determine which form is designated as the *-ate*. The correct reference form must be memorized for each element.

Common *-ate* anions include:

| | |
|---|---|
| $\mathbf{CO_3{}^{2-}}$ | Carbonate ion |
| $\mathbf{NO_3{}^-}$ | Nitrate ion |
| $\mathbf{PO_4{}^{3-}}$ | Phosphate ion |
| $\mathbf{SO_4{}^{2-}}$ | Sulfate ion |

## Hydrogen-Containing Anions

Hydrogen-containing anions are formed when a polyatomic anion, typically an oxoanion, gains one or more protons ($H^+$), but not enough to fully neutralize its negative charge. The bond formed with the added hydrogen is covalent rather than ionic.

In systematic nomenclature, an anion that has gained one proton is named using the prefix *hydrogen*, and an anion that has gained two protons uses the prefix *dihydrogen*.

Examples of systematic names include:

| | |
|---|---|
| $\mathbf{HCO_3{}^-}$ | Hydrogen carbonate ion |
| $\mathbf{HSO_4{}^-}$ | Hydrogen sulfate ion |
| $\mathbf{H_2PO_4{}^-}$ | Dihydrogen phosphate ion |

In common nomenclature, the prefix *bi-* is used for the single-hydrogen form.

Examples of common names include:

| | |
|---|---|
| $\mathbf{HCO_3{}^-}$ | Bicarbonate ion |
| $\mathbf{HSO_4{}^-}$ | Bisulfate ion |

## Inorganic Acids

**Inorganic acids** are neutral molecules consisting of an anionic group covalently bonded to enough protons to fully neutralize its charge.

**Binary acids** consist of hydrogen and one other element, typically a nonmetal. They are derived from *-ide* anions and are named using the prefix *hydro-* and the suffix *-ic*.

**Oxoacids** contain oxygen, hydrogen, and another element. In older texts, they may be referred to as *oxyacids*.

They are formed from oxoanions. Acids from *-ate* anions use the suffix *-ic*, and those from *-ite* use *-ous*. The prefixes *per-* and *hypo-* are retained from the anion when present.

For example, the inorganic acids of chlorine are:

| | |
|---|---|
| **$HCl$** | Hydrochloric acid |
| **$HClO$** | Hypochlorous acid |
| **$HClO_2$** | Chlorous acid |
| **$HClO_3$** | Chloric acid |
| **$HClO_4$** | Perchloric acid |

## Ionic Compounds

In ionic compound names, the cation is listed first, followed by the anion. The word *ion* is not included in the name. The ratio of ions is not shown in the name.
Examples include:

| | |
|---|---|
| **$Al(NO_3)_3$** | Aluminum nitrate |
| **$CaCl_2$** | Calcium chloride |

## Binary Molecular Compounds

**Binary molecular compounds** are molecules that contain two nonmetal elements.
Both elements are named in the compound. The element farther to the left on the periodic table is named first. If both elements are in the same group, the lower one is named first. Oxygen is an exception and is always named second, except when combined with fluorine.
The second element is given the suffix *-ide*.
Greek prefixes indicate the number of atoms of each element. If the first element has one atom, the prefix *mono-* is omitted.
The Greek prefixes for one through ten are:

| | |
|---|---|
| ***mono-*** | 1 |
| ***di-*** | 2 |
| ***tri-*** | 3 |
| ***tetra-*** | 4 |
| ***penta-*** | 5 |
| ***hexa-*** | 6 |
| ***hepta-*** | 7 |
| ***octa-*** | 8 |
| ***nona-*** | 9 |
| ***deca-*** | 10 |

Examples include:

| | |
|---|---|
| **$NF_3$** | Nitrogen trifluoride |
| **$N_2O_4$** | Dinitrogen tetroxide |
| **$Cl_2O$** | Dichlorine monoxide |

## List of Common Substances and Names

| Formula | Name |
|---|---|
| **Monatomic Cations** | |
| $H^+$ | Hydrogen ion |
| $Li^+$ | Lithium ion |
| $Na^+$ | Sodium ion |
| $K^+$ | Potassium ion |
| $Mg^{2+}$ | Magnesium ion |
| $Ca^{2+}$ | Calcium ion |
| $Ba^{2+}$ | Barium ion |
| $Al^{3+}$ | Aluminum ion |
| $Cr^{3+}$ | Chromium(III) ion |
| $Mn^{2+}$ | Manganese(II) ion |
| $Fe^{2+}$ | Iron(II) ion |
| $Fe^{3+}$ | Iron(III) ion |
| $Ni^{2+}$ | Nickel(II) ion |
| $Cu^+$ | Copper(I) ion |
| $Cu^{2+}$ | Copper(II) ion |
| $Zn^{2+}$ | Zinc ion |
| $Ag^+$ | Silver ion |
| $Sn^{2+}$ | Tin(II) ion |
| $Sn^{4+}$ | Tin(IV) ion |
| $Pb^{2+}$ | Lead(II) ion |
| $Pb^{4+}$ | Lead(IV) ion |
| $Hg_2{}^{2+}$ | Mercury(I) ion |
| $Hg^{2+}$ | Mercury(II) ion |
| **Monatomic Anions** | |
| $F^-$ | Fluoride ion |
| $Cl^-$ | Chloride ion |
| $Br^-$ | Bromide ion |
| $I^-$ | Iodide ion |
| $O^{2-}$ | Oxide ion |
| $S^{2-}$ | Sulfide ion |
| **Polyatomic Ions** | |
| $CH_3COO^-$ | Acetate ion |
| $C_2O_4{}^{2-}$ | Oxalate ion |
| $CO_3{}^{2-}$ | Carbonate ion |
| $HCO_3{}^-$ | Hydrogen carbonate (bicarbonate) ion |
| $NO_2{}^-$ | Nitrite ion |
| $NO_3{}^-$ | Nitrate ion |
| $NH_4{}^+$ | Ammonium ion |
| $PO_4{}^{3-}$ | Phosphate ion |
| $H_2PO_4{}^-$ | Dihydrogen phosphate ion |
| $SO_3{}^{2-}$ | Sulfite ion |
| $HSO_3{}^-$ | Hydrogen sulfite (bisulfite) ion |
| $SO_4{}^{2-}$ | Sulfate ion |
| $HSO_4{}^-$ | Hydrogen sulfate (bisulfate) ion |
| $MnO_4{}^-$ | Permanganate ion |
| $OH^-$ | Hydroxide ion |
| **Diatomic Elements** | |
| $H_2$ | Hydrogen |
| $N_2$ | Nitrogen |
| $O_2$ | Oxygen |
| $F_2$ | Fluorine |
| $Cl_2$ | Chlorine |
| $Br_2$ | Bromine |
| $I_2$ | Iodine |

| Formula | Name |
|---|---|
| **Acids** | |
| $HF$ | Hydrofluoric acid |
| $HCl$ | Hydrochloric acid |
| $HBr$ | Hydrobromic acid |
| $HI$ | Hydroiodic acid |
| $HNO_3$ | Nitric acid |
| $H_2CO_3$ | Carbonic acid |
| $CH_3COOH$ | Acetic acid |
| $HClO_4$ | Perchloric acid |
| $H_2SO_4$ | Sulfuric acid |
| $H_3PO_4$ | Phosphoric acid |
| **Ionic Compounds** | |
| $NaCl$ | Sodium chloride |
| $NaOH$ | Sodium hydroxide |
| $NaHCO_3$ | Sodium bicarbonate |
| $Na_2CO_3$ | Sodium carbonate |
| $Na_2SO_4$ | Sodium sulfate |
| $KCl$ | Potassium chloride |
| $KOH$ | Potassium hydroxide |
| $K_2CO_3$ | Potassium carbonate |
| $Mg(OH)_2$ | Magnesium hydroxide |
| $CaCl_2$ | Calcium chloride |
| $Ca(OH)_2$ | Calcium hydroxide |
| $CaCO_3$ | Calcium carbonate |
| $Ca_3(PO_4)_2$ | Calcium phosphate |
| $BaCl_2$ | Barium chloride |
| $BaSO_4$ | Barium sulfate |
| $FeCl_2$ | Iron(II) chloride |
| $Fe(NO_3)_2$ | Iron(II) nitrate |
| $FeS$ | Iron(II) sulfide |
| $Fe_2O_3$ | Iron(III) oxide |
| $CuO$ | Copper(II) oxide |
| $Cu(NO_3)_2$ | Copper(II) nitrate |
| $CuSO_4$ | Copper(II) sulfate |
| $CuS$ | Copper(II) sulfide |
| $ZnCl_2$ | Zinc chloride |
| $ZnSO_4$ | Zinc sulfate |
| $ZnS$ | Zinc sulfide |
| $AgNO_3$ | Silver nitrate |
| $AgCl$ | Silver chloride |
| $Pb(NO_3)_2$ | Lead(II) nitrate |
| $PbCl_2$ | Lead(II) chloride |
| $NH_4NO_3$ | Ammonium nitrate |
| $NH_4Cl$ | Ammonium chloride |
| **Molecular Gases** | |
| $NH_3$ | Ammonia |
| $H_2S$ | Hydrogen sulfide |
| $CO$ | Carbon monoxide |
| $CO_2$ | Carbon dioxide |
| $NO$ | Nitric oxide |
| $NO_2$ | Nitrogen dioxide |
| $SO_2$ | Sulfur dioxide |

# Chapter 5

# Chemical Reactions and Stoichiometry

## 5.1 Chemical Reactions and Equations

### Classes of Chemical Reactions

There are many classes of chemical reactions. Three basic types are introduced here. Additional classes are covered in later chapters on acid–base and oxidation–reduction reactions.
In a **combination reaction**, two or more substances react to form a single product.
In a **decomposition reaction**, a single compound breaks down into two or more products. This is often the result of heating.
In a **combustion reaction**, a substance reacts rapidly with molecular oxygen ($O_2$), usually from the air, and releases heat and light. Combustion reactions are often used as sources of energy and light.

### Chemical Equations

Chemical reactions convert **reactants** into **products**.
A classic example is hydrogen and oxygen reacting to form water. The reactants are hydrogen and oxygen, and the product is water. This reaction will be used as an example throughout this chapter.
**Chemical equations** represent chemical reactions. Reactants are written on the left, products on the right, and an arrow points from reactants to products.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

The physical states of substances are often indicated by **phase symbols**: (s) for solid, (l) for liquid, and (g) for gas.

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O\,(l)$$

### Chemical Equation Coefficients

The chemical equation gives the number of particles of each substance involved in the reaction by placing a coefficient before the substance:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O;$$

2 molecules of $H_2$ react with 1 molecule of $O_2$ to produce 2 molecules of $H_2O$.
The coefficients reflect the smallest number of particles that can react, and the number of product particles formed. The smallest possible water reaction requires 2 molecules of $H_2$, 1 of $O_2$, and forms 2 molecules of $H_2O$.

It is important to distinguish the chemical equation coefficient from the chemical formula subscript. The subscript in $H_2$ indicates the identity of the substance — a diatomic hydrogen molecule. Without it, H would refer to a hydrogen atom, which is a different substance. The coefficient placed before $H_2$ indicates the number of particles involved in the reaction, not their identity.

## 5.2 Balancing Equations and Stoichiometry

### Balancing Chemical Equations

A fundamental postulate of atomic theory is that chemical reactions do not create, destroy, or change the identity of atoms. They only change interatomic bonds or redistribute electrons. Therefore, the number of atoms of each element must be the same in the reactants and the products.

A chemical equation with the same number of atoms of each element on both sides is called **balanced**. Once the substances involved in a reaction are identified, their coefficients must be adjusted to ensure that the equation is balanced. This process is called **balancing** the equation.

It is important to make sure, while balancing a chemical equation, to adjust only the coefficients and not the subscripts. This ensures that only the number of particles is changed, not their identity.

To balance the water reaction, we first determine that the reactants are $H_2$ and $O_2$, and the product is $H_2O$. The equation can then be balanced as follows:

1. The product, $H_2O$, contains 1 oxygen atom, while the reactant $O_2$ contains 2.
2. To balance oxygen, we place a 2 in front of $H_2O$.
3. We now check hydrogen. The product, 2 $H_2O$, contains 4 hydrogen atoms, while the reactant $H_2$ has 2.
4. To balance hydrogen, we place a 2 in front of $H_2$.

### Stoichiometric Ratios

**Stoichiometry** is the study of the quantitative relationships between substances in a chemical reaction. Balancing an equation determines the ratio of particles involved in the reaction and defines the reaction's stoichiometry.

The ratio of particles in a balanced equation is called a **stoichiometric ratio**. In the water reaction, the ratio of hydrogen, oxygen, and water particles is 2 : 1 : 2. The corresponding amounts of substance are called **stoichiometrically equivalent quantities**. 2 molecules of hydrogen, 1 molecule of oxygen, and 2 molecules of water are stoichiometrically equivalent.

The stoichiometric ratio applies at any scale. The numbers of particles involved always follow the same ratio. In the water reaction, any number of particles will follow the 2 : 1 : 2 ratio of hydrogen, oxygen, and water.

Because stoichiometrically equivalent quantities are equal in ratio, they can be expressed as fractions equal to one and used as conversion factors in dimensional analysis. For example, to determine the amount of water produced in a reaction involving 300 molecules of $O_2$:

$$300\ \cancel{O_2} \times \frac{2\ H_2O}{1\ \cancel{O_2}} = 600\ H_2O$$

## 5.3 The Mole, Molar Mass, and Quantitative Analysis of Composition

### Formula Weight, Percent Composition, and Elemental Composition

A substance's **formula weight** is the weight in atomic mass units (amu) of one unit of the substance, as given in its chemical formula. It is calculated by summing the atomic weights of the atoms in the chemical formula. Atomic weights are provided in most periodic tables.

The chemical formula for water is $H_2O$. The atomic weight of hydrogen is 1.008, and that of oxygen is 15.999.

$$1.008 + 1.008 + 15.999 = 18.015$$

An element's **percent composition** in a compound is its percentage of the formula weight. To calculate it, multiply the element's atomic weight by the number of atoms of that element in the formula, divide by the formula weight, and multiply by 100.
To determine hydrogen's percent composition in water:

$$\frac{1.008 \times 2}{18.015} \approx 11.191\%$$

A compound's **elemental composition** is the mass percent of each element in the compound.
The elemental composition of water is 88.809% oxygen and 11.191% hydrogen.

## The Mole

Most reactions involve a vast number of particles, each with negligible mass. Quantitative chemistry cannot be studied at the level of individual particles.
The **mole (mol)** is a unit that represents a quantity of $6.02 \times 10^{23}$ particles. This number is called **Avogadro's number**.
Chemical quantities are typically measured in moles.
Since the stoichiometric ratio given by a chemical equation's coefficients holds regardless of scale, the equation can be directly interpreted in terms of moles instead of individual particles. Two moles of $H_2$ react with one mole of $O_2$ to form two moles of $H_2O$.

## Molar Mass

A substance's **molar mass** is the mass in grams of one mole of the substance. It has the same numerical value as the substance's formula weight, but is expressed in grams per mole instead of atomic mass units. This simplifies scaling between microscopic and macroscopic quantities. The units involved — g, mol, and amu — are defined in a coordinated way so that this numerical equality holds.
For example, water has a formula weight of 18.015 amu, and its molar mass is 18.015 g/mol.
Molar mass can be directly calculated by dividing a substance's mass by its amount in moles:

$$\text{molar mass} = \frac{\text{mass of substance}}{\text{moles of substance}}$$

For example, if 6.5 moles of water have a mass of 117.0975 grams, the molar mass is:

$$\frac{117.0975\ \text{g H}_2\text{O}}{6.5\ \text{mol H}_2\text{O}} = 18.015\ \text{g/mol H}_2\text{O}$$

## Mass–Mole Conversions

Molar mass is a conversion factor between a substance's mass and its amount in moles. If either the mass or the amount in moles is known, the other can be calculated using the molar mass.
If the amount in moles is known, multiply by the molar mass to determine the mass.
For example, to find the mass of 8.25 moles of water:

$$8.25\ \cancel{\text{mol H}_2\text{O}} \times \frac{18.015\ \text{g H}_2\text{O}}{1\ \cancel{\text{mol H}_2\text{O}}} = 148.624\ \text{g H}_2\text{O}$$

If the mass is known, divide by the molar mass to determine the amount in moles.
For example, to find the amount in moles of 150 g of water:

$$150\ \cancel{\text{g H}_2\text{O}} \times \frac{1\ \text{mol H}_2\text{O}}{18.015\ \cancel{\text{g H}_2\text{O}}} = 8.326\ \text{mol H}_2\text{O}$$

## Experimental Determination of Elemental Composition

Previously, elemental composition was determined from a chemical formula.
It can also be calculated directly from experimental data.

1. Separate the compound into its component elements and measure the mass of each.
2. Convert the relative masses of the elements to percentages.

For example, to determine the elemental composition of water:

1. Separate 500 g $H_2O$ into its component elements via electrolysis.
2. Measure the mass of hydrogen and oxygen at approximately 55.955 g $H_2$ and 444.045 g $O_2$.
3. Convert the measured masses to percent composition. For hydrogen:
   $\frac{55.955}{55.955+444.045} \times 100 = 11.191\%$
4. For oxygen:
   $\frac{444.045}{55.955+444.045} \times 100 = 88.809\%$

### Empirical Formula from Elemental Composition

As established earlier, a molecular compound has 2 types of chemical formulas: the molecular formula gives the actual number of atoms of each element, while the empirical formula gives the smallest whole-number ratio. For example, the molecular formula of glucose is $C_6H_{12}O_6$, and the empirical formula is $CH_2O$.

If the chemical formula of a compound is unknown and the elemental composition is determined experimentally, the empirical formula can be calculated from it.

Elemental composition and empirical formula both express ratios between elements, but in different forms. Elemental composition gives the ratio by mass, while the empirical formula gives the ratio by number of particles or moles. Using molar mass, the mass ratio can be converted to the mole ratio.

1. Convert the mass percentage of each element into moles by dividing by the element's molar mass.
2. Find the simplest whole-number ratio of moles. This is the empirical formula.

For example, to determine the empirical formula of water from its elemental composition:

1. $11.191\ \cancel{\text{g}\,\text{H}_2} \times \frac{1\ \text{mol}\,\text{H}_2}{2.016\ \cancel{\text{g}\,\text{H}_2}} \approx 5.55\ \text{mol}\,\text{H}_2$
2. $88.809\ \cancel{\text{g}\,\text{O}_2} \times \frac{1\ \text{mol}\,\text{O}_2}{31.998\ \cancel{\text{g}\,\text{O}_2}} \approx 2.78\ \text{mol}\,\text{O}_2$
3. $\text{mol}\,\text{H}_2 : \text{mol}\,\text{O}_2 = 5.55 : 2.78 \approx 2 : 1$
4. Empirical formula: $H_2O$.

### Molecular Formula from Empirical Formula and Molar Mass

A compound's molecular formula can be determined from its empirical formula if the molar mass is known.

1. Calculate the empirical formula weight.
2. Divide the molar mass by the empirical formula weight.
3. The result should be an integer.
4. Multiply the empirical formula by this integer to obtain the molecular formula.

For example, if the empirical formula of glucose is $CH_2O$, and its molar mass is 180.156 g/mol:

1. The empirical formula weight of $CH_2O$ is 30.026 g/mol.
2. $\frac{180.156}{30.026} = 6$
3. Multiply $CH_2O$ by 6 to obtain the molecular formula: $C_6H_{12}O_6$.

## 5.4 Reaction Mass Stoichiometry

### Mass Stoichiometry

Previously, stoichiometric ratios were used to determine the amount in moles of one substance in a reaction from the amount in moles of another.

By combining stoichiometric ratios with molar mass, the mass of one substance in a reaction can be determined from the mass of another.

1. Divide the mass of the known substance by its molar mass to obtain its amount in moles.
2. Multiply by the stoichiometric ratio to determine the amount in moles of the unknown substance.
3. Multiply the moles of the unknown substance by its molar mass to find its mass.

For example, to determine the mass of water produced by a reaction that consumes 10 g of $O_2$:

$$10\ \cancel{\mathrm{g}\ \mathrm{O}_2} \times \frac{1\ \cancel{\mathrm{mol}\ \mathrm{O}_2}}{31.998\ \cancel{\mathrm{g}\ \mathrm{O}_2}} \times \frac{2\ \cancel{\mathrm{mol}\ \mathrm{H}_2\mathrm{O}}}{1\ \cancel{\mathrm{mol}\ \mathrm{O}_2}} \times \frac{18.015\ \mathrm{g}\ \mathrm{H}_2\mathrm{O}}{1\ \cancel{\mathrm{mol}\ \mathrm{H}_2\mathrm{O}}} = 11.26\ \mathrm{g}\ \mathrm{H}_2\mathrm{O}$$

## Limiting Reactants

If reactants are not present in stoichiometrically equivalent quantities, one will be consumed before the other, and the reaction will stop. The reactant that is fully consumed is the **limiting reactant**. The other is the **excess reactant**.

To determine which reactant is limiting and which is excess, calculate the amount of one substance that is stoichiometrically equivalent to the other.

For example, if there are 10 g of $O_2$ and 5 g of $H_2$, calculate the amount of $H_2$ that is stoichiometrically equivalent to 10 g of $O_2$:

$$10\ \cancel{\mathrm{g}\ \mathrm{O}_2} \times \frac{\cancel{\mathrm{mol}\ \mathrm{O}_2}}{31.998\ \cancel{\mathrm{g}\ \mathrm{O}_2}} \times \frac{2\ \cancel{\mathrm{mol}\ \mathrm{H}_2}}{1\ \cancel{\mathrm{mol}\ \mathrm{O}_2}} \times \frac{2.016\ \mathrm{g}\ \mathrm{H}_2}{1\ \cancel{\mathrm{mol}\ \mathrm{H}_2}} = 1.26\ \mathrm{g}\ \mathrm{H}_2$$

10 g of $O_2$ is stoichiometrically equivalent to 1.26 g of $H_2$. Since there are 5 g of $H_2$, the $O_2$ will be consumed while $H_2$ remains. Oxygen is the limiting reactant, and hydrogen is the excess reactant.

## Theoretical and Actual Yields

A reaction's **theoretical yield** is the amount of product that is stoichiometrically equivalent to the limiting reactant.

For the above example, the theoretical yield is the amount of water produced by 10 g of $O_2$:

$$10\ \cancel{\mathrm{g}\ \mathrm{O}_2} \times \frac{\cancel{\mathrm{mol}\ \mathrm{O}_2}}{31.998\ \cancel{\mathrm{g}\ \mathrm{O}_2}} \times \frac{2\ \cancel{\mathrm{mol}\ \mathrm{H}_2\mathrm{O}}}{1\ \cancel{\mathrm{mol}\ \mathrm{O}_2}} \times \frac{18.015\ \mathrm{g}\ \mathrm{H}_2\mathrm{O}}{1\ \cancel{\mathrm{mol}\ \mathrm{H}_2\mathrm{O}}} = 11.26\ \mathrm{g}\ \mathrm{H}_2\mathrm{O}$$

The theoretical yield can also be calculated by summing the mass of the limiting reactant and the amount of excess reactant that was consumed. We previously determined the amount of consumed $H_2$ to be 1.26 g:

$$10\ \mathrm{g}\ \mathrm{O}_2 + 1.26\ \mathrm{g}\ \mathrm{H}_2 = 11.26\ \mathrm{g}\ \mathrm{H}_2\mathrm{O}$$

In practice, reactions are not perfectly efficient, and the actual amount produced is usually less than the theoretical yield. This is called the **actual yield**.

The **percent yield** is the actual yield as a percentage of the theoretical yield:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

# Chapter 6

# Solvation and Precipitation Reactions

## 6.1 Solvation

### Solvents, Solutes and Solvation

A **solution** is a homogeneous mixture in which the components are uniformly distributed and visually indistinguishable.

In a solution, one substance is present in a much greater amount than the others. This substance is called the **solvent**. The others are called **solutes**.

The uniformity of a solution is due to **solvation**, the process by which solvent particles attract and surround solute particles. Solvated solute particles are completely enveloped by solvent. Properties of the solution that depend on attractive interactions, such as melting point, are determined by the solvent, since the solutes are isolated and do not participate in further interactions.

Most common solvents are molecular liquids.

Water is a particularly strong and versatile solvent, since it is highly polar and forms strong intermolecular attractions.

A solution in which water is the solvent is called an **aqueous solution**. Dissolved substances in aqueous solutions are denoted with the (aq) phase symbol. For example, solvated sodium ions are written as $Na^+(aq)$.

Many ions, especially those of transition metals, gain partial stability by losing electrons and forming cations, but do not achieve noble gas configurations. They often do not form stable ionic compounds but can be stabilized in aqueous solution through solvation. Their electrostatic potential energy is reduced through strong interactions with the polar regions of surrounding water molecules.

### Solubility

Since each solvated solute particle is individually surrounded by solvent, there is a maximum amount of solute that can dissolve in a fixed amount of a given solvent. If more solute is added, there is not enough solvent to fully solvate the additional particles.

Solubility is affected by temperature. The maximum amount of a solute that can dissolve in a given amount of solvent at a specific temperature is called its **solubility**.

For example, the solubility of NaCl in water at 25°C is 36 g per 100 mL.

When a substance's solubility is referenced without specifying the solvent or temperature, it typically refers to its solubility in water at room temperature.

A solubility below 0.01 mol/L is considered insoluble.

In a transparent solvent, solubility can often be inferred from **turbidity**, which is a solution's cloudiness. A soluble solute may cause a color change, but the solution will remain transparent. Turbidity indicates that some of the solute is not dissolved.

In general, small polar molecules are soluble in water, while nonpolar or large molecules are not. Nonpolar molecules are insoluble because they cannot form hydrogen bonds with water. Large molecules are insoluble because their size and surface complexity prevent solvent particles from interacting with them uniformly.

For example, ammonia ($NH_3$) is small, polar, and soluble. Molecular oxygen ($O_2$) is nonpolar and insoluble. Cellulose is polar but insoluble due to its large size. A typical cellulose molecule contains several thousand atoms.

It is important to note that soluble molecules do not dissociate into their component atoms when dissolved. They remain intact molecules, but the intermolecular attractions between them are overcome, and each is individually solvated.

Individual ions are always soluble in water. However, the solubility of ionic compounds is more complex. It cannot be reliably predicted using simple rules and must be learned from empirical solubility tables.

Soluble ionic compounds dissociate into individual ions when dissolved. Each ion is separately solvated by surrounding water molecules.

### Solubility Table

The solubility table categorizes ions into three groups: those whose compounds are always soluble, those that are generally soluble with exceptions, and those that are generally insoluble with exceptions.

If a compound is not covered by the solubility rules, it should be assumed to be insoluble.

#### Always Soluble

Group 1 ions
$NH_4^+$
$NO_3^-$
$CH_3COO^-$
$ClO_4^-$

#### Generally Soluble

Group 17 ions
    *Except with:* $Pb^{2+}$, $Hg_2^{2+}$, $Ag^+$

$SO_4^{2-}$
    *Except with:* $Pb^{2+}$, $Hg_2^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$

#### Generally Insoluble

$CO_3^{2-}$, $PO_4^{3-}$, $SO_3^{2-}$
    *Except with:* Group 1 ions, $NH_4^+$

$S^{2-}$
    *Except with:* Group 1 ions, Group 2 ions, $NH_4^+$

$OH^-$
    *Except with:* Group 1 ions, $NH_4^+$
    *Slightly soluble with:* $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$

## 6.2 Precipitation Reactions

### Precipitation

A **precipitate** is an insoluble solid formed from dissolved ions.

Many ions form soluble compounds with some ions and insoluble compounds with others. A precipitate forms when two ions that produce an insoluble compound are each initially dissolved as part of separate soluble compounds. When their solutions are mixed, the two ions react to form a precipitate.

For example, lead(II) nitrate ($Pb(NO_3)_2$) and potassium iodide (KI) are both soluble, but lead(II) iodide ($PbI_2$) is not. When their solutions are mixed, $Pb^{2+}$ and $I^-$ form a precipitate of $PbI_2$, while $K^+$ and $NO_3^-$ remain in solution.

The reaction is represented by the following equation:

$$\mathrm{Pb(NO_3)_2(aq) + 2\,KI(aq) \longrightarrow PbI_2(s) + 2\,KNO_3(aq)}$$

## Metathesis Reactions

Precipitation is a type of **metathesis reaction**, also known as a **double displacement reaction**. In these reactions, two compounds exchange components. The general form is:

$$\mathrm{AX + BY \longrightarrow AY + BX}$$

These reactions generally occur between two compounds dissolved in solution.

Precipitation reactions differ from other metathesis reactions that produce soluble products. When the product remains dissolved, the reaction does not go to completion because a small fraction of product particles are always converting back to reactants. When the rate of this reverse reaction equals the rate at which reactants form product, the system reaches a **dynamic equilibrium**, and the relative concentrations of reactants and products remain constant.

For example, solvated acetate ions ($CH_3COO^-$) and hydrogen ions ($H^+$) react to form acetic acid ($CH_3COOH$), a more energetically favorable species. However, not all ions convert, since some acetic acid molecules continuously dissociate back into acetate and hydrogen ions.

The energetic favorability of the product influences the rate of the forward reaction, but there is still a small rate of reverse reaction. When the ratio of products to reactants corresponds to the ratio of the forward and reverse reaction rates, the number of particles undergoing forward and reverse reactions is equal, and the system is at equilibrium.

This reversibility occurs primarily because the product remains dissolved and is fully solvated. Its components are already interacting with the solvent and are in an environment where they can readily form stable ions. In contrast, when a product is not solvated, as in precipitation, its components are not interacting with the solvent and cannot readily dissociate to form stable ions. In these situations, the reverse reaction does not occur, and the reaction proceeds to completion.

There are three common situations in which a product leaves the solution and drives the reaction to completion. The first is precipitation, where an insoluble ionic solid forms. The second occurs when a nonpolar, insoluble molecule forms. The third occurs when a gas is produced and escapes the solution. The latter two cases typically result from acid–base or redox reactions and are discussed later in the course.

## Ionic Equations

There are several ways to represent reactions involving soluble ionic compounds.

The **molecular equation** shows soluble ionic compounds as intact compounds, even though they dissociate into ions in solution. This identifies the original compounds that produce the ions.

For the precipitation reaction between lead(II) nitrate and potassium iodide, which produces lead(II) iodide, the molecular equation is:

$$\mathrm{Pb(NO_3)_2(aq) + 2\,KI(aq) \longrightarrow PbI_2(s) + 2\,KNO_3(aq)}$$

The **complete ionic equation** represents soluble ionic compounds as separate ions in solution and shows all ions present in the solution:

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

Ions that appear in identical form on both sides of the complete ionic equation did not participate in the reaction. These are called **spectator ions**.

The **net ionic equation** removes spectator ions and shows only the ions that participate in the reaction:

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

# Chapter 7

# Electrolytes, Acids and Bases

## 7.1 Electrolytes

### Strong and Weak Electrolytes

The principles of ionic compound solubility were discovered by studying the electrical conductivity of their solutions. Neutral water does not conduct electricity. Solutions containing some ionic compounds conduct electricity, while others do not. This led to the discovery that certain ionic compounds dissociate into individual ions in water, causing the solution to conduct electricity.

Substances whose aqueous solutions conduct electricity due to the formation of ions are called **electrolytes**. Those that do not are called **nonelectrolytes**.

Electrolytes are further classified as **strong** or **weak**, based on how strongly their solutions conduct electricity. This reflects whether the reaction that produces ions in solution is driven to completion.

The reaction of a strong electrolyte is driven to completion. The reaction of a weak electrolyte is not; it reaches a dynamic equilibrium.

Reactions that are driven to completion are represented in chemical equations with a single arrow. For example:

$$\mathrm{HCl(aq)} \longrightarrow \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)}$$

Reactions that reach an equilibrium are represented in chemical equations with a double half-arrow. For example:

$$\mathrm{CH_3COOH(aq)} \rightleftharpoons \mathrm{CH_3COO^-(aq)} + \mathrm{H^+(aq)}$$

### Ionic and Molecular Electrolytes

The criteria for determining whether a substance is an electrolyte differ between ionic and molecular compounds.

For ionic compounds, solubility determines whether a compound is an electrolyte, since those that are soluble dissociate into their component ions in solution. A fully soluble ionic compound is a strong electrolyte. A partially soluble one is a weak electrolyte. An insoluble compound is a nonelectrolyte.

For molecular compounds, solubility is not sufficient to determine electrolyte behavior. Even when soluble, molecular compounds remain as intact molecules in solution and do not dissociate into ions. Neutral molecular compounds are nonelectrolytes, even if they are soluble.

The only molecular compounds that are electrolytes are acids and bases. They increase the concentration of $H^+$ or $OH^-$ ions in solution. Their electrolyte strength depends on whether they are strong or weak acids or bases. This will be explained in the next section.

It is important to note that some molecular acids and bases do not directly release $H^+$ or $OH^-$, but react with water to produce these ions. They are still classified as electrolytes because they increase the ion concentration in solution.

## 7.2 Acids and Bases

### Acidity, Acids and Bases

**Acidity** refers to the concentration of hydrogen ions ($H^+$) in a solution. Because a neutral hydrogen atom has one proton and one electron, the $H^+$ ion consists of only the proton, and is commonly called a proton.

**Acids** are substances that increase a solution's acidity when added to it. They are molecular compounds that contain hydrogen atoms, which dissociate as $H^+$ ions when the compound is dissolved in solution.

Before dissociation, each hydrogen atom is covalently bonded to an atom in the acid and shares two electrons. When the hydrogen dissociates, it does not take any bonding electrons. Only the proton separates. The two electrons remain with the other atom and form a non-bonding electron pair.

A non-bonding pair of valence electrons is called a **lone pair**.

Most molecules do not dissociate in solution because the undissociated form is more thermodynamically stable than the separated components. The dissociation of hydrogen from acids results from the particular properties of hydrogen and its bonds in acidic molecules, where the $H^+$ ion and the remains of the acid are more thermodynamically stable than the original acid. The underlying reasons for this exception are not addressed at this level.

**Bases** are substances that decrease a solution's acidity when added to it. They accept the protons by forming covalent bonds with them.

A base has a full valence shell but contains a lone pair of electrons. It donates this lone pair to the proton, completing the hydrogen's valence shell and forming a covalent bond.

Typically, covalent bonds form between atoms that both need electrons to complete their valence shells. In contrast, a base already has a complete valence shell but still forms a bond with the proton.

A covalent bond in which both bonding electrons are supplied by one atom, rather than one from each atom, is called a **coordinate covalent bond**.

### Strong and Weak Acids and Bases

When an acid loses a proton, the species that remains is called its **conjugate base**. When a base gains a proton, the resulting species is called its **conjugate acid**. These species form a **conjugate acid–base pair**, which differ by one proton.

Acids and bases are classified as **strong** or **weak** based on the extent of their acid–base reactions.

A strong acid dissociates completely in solution; all acid molecules donate their protons. Its conjugate base that is typically neutral and does not act as a base. Similarly, a strong base reacts completely by accepting protons. Its conjugate acid is typically neutral and does not act as an acid.

In contrast, weak acids and weak bases do not fully react in solution. The conjugate base of a weak acid is a weak base, and the conjugate acid of a weak base is a weak acid. In a weak acid, not all acid molecules dissociate. Those that do form weak bases, some of which accept protons and revert to the acid form. Similarly, in a weak base, not all particles accept protons. Those that do form weak acids, some of which donate protons and revert to the base form.

The weak conjugate acid–base pair exists together in solution. The reaction proceeds in both directions and eventually reaches a dynamic equilibrium, where the forward and reverse reaction rates are equal and the concentrations of both species remain constant.

Although a weak acid does not dissociate fully in neutral solution, it reacts completely with a strong base. The base accepts any available protons and does not release them, driving the reaction to completion.

Similarly, a weak base reacts completely with a strong acid. The high proton concentration from the strong acid forces all base molecules to accept protons.

### Strong and Weak Bases

The only strong base is the hydroxide ion ($OH^-$). Its conjugate acid is water, a neutral molecule.

Weak bases slightly decrease the hydrogen ion concentration by partially accepting protons. In aqueous solution, they not only accept free protons but can also remove protons from water molecules. The base forms its conjugate acid, and the water molecules that lose a proton become hydroxide ions.

Bases can form in solution when a weak acid dissociates and releases a proton. They can also be introduced as the anions of soluble ionic compounds.

A compound containing a basic anion is considered a strong base only if both the base itself is strong and the compound is soluble. If the base is strong but the compound is insoluble, it behaves as a weak base due to limited dissociation. However, even in this case, the base reacts completely with strong acids because the acid drives its dissociation.

### Monoprotic and Polyprotic Acids

Some acids can donate more than one proton per molecule. Acids that donate only one proton are called **monoprotic** acids. Those that donate two are called **diprotic**, and those that donate more than two are called **polyprotic**.

Some diprotic or polyprotic acids are strong acids, but only the first ionization is strong. Subsequent ionizations are weak.

A diprotic acid that has lost one proton and has one remaining can act as either an acid or a base. It can donate the second proton or accept one back.

A species that can act as both an acid and a base is called **amphiprotic**. Its behavior depends on the acidity or basicity of its chemical environment.

## 7.3 Classes of Acids and Bases

### Common Classes of Acids and Bases

There are several common classes of acids and bases. These categories are not exhaustive; many acids and bases do not fit neatly into a specific class.

Five common classes are: binary acids, oxoacids, carboxylic acids, amines, and hydroxide.

The first three are molecular acids, and their conjugate bases are anions. Some are strong acids, and some are weak. None of their conjugate bases are strong.

Neutral amines are the only molecular bases. Their conjugate acids are protonated amines, which are the only common cationic acids. Both amine acids and bases are weak.

Hydroxide, discussed in the previous section, is the only strong base. Its conjugate acid is water, a neutral molecule.

As a general rule, any molecule whose formula begins with hydrogen, excluding those that contain only hydrogen, or only hydrogen and oxygen, is an acid, either strong or weak.

The only common acids whose formulas do not begin with hydrogen are carboxylic acids and protonated amines.

Many acids are gases under standard conditions and act as acids only when dissolved in solution. Some dissolve readily; others do not, and may evaporate without dissociating.

### Binary Acids

**Binary acids** are molecular compounds composed of hydrogen and one other element. They are gases under standard conditions but act as acids when dissolved in water. Their conjugate bases are anions that may remain solvated or form salts with cations.

All nonmetals in groups 16 and 17 form binary acids, except for oxygen. Oxygen does not form a binary acid because its bond with hydrogen is too strong for the hydrogen ion to dissociate.

The binary acids of group 17 are hydrogen fluoride ($HF$), hydrogen chloride ($HCl$), hydrogen bromide ($HBr$), and hydrogen iodide ($HI$). All are strong acids except for HF, which is weak.

The binary acids of group 16 are hydrogen sulfide ($H_2S$) and hydrogen selenide ($H_2Se$). Both are weak acids.

The conjugate bases of strong binary acids are neutral. The conjugate bases of weak binary acids are weak bases.

The strength of a binary acid depends on the stability of its conjugate base. A stable conjugate base does not readily attract protons, so the acid is strong. An unstable conjugate base attracts protons, making the acid weak.

An anion is more stable if it is both large and highly electronegative. A larger size allows the negative charge to be distributed over a greater volume. Higher electronegativity helps stabilize the negative charge.

Most halide ions are sufficiently large and electronegative to be stable, so their binary acids are strong. Fluoride ion ($F^-$) is too small, and sulfide ($S^{2-}$) and selenide ($Se^{2-}$) are not sufficiently electronegative.

Group 17 binary acids are monoprotic. Group 16 binary acids are diprotic because the central atom requires two additional electrons to complete its valence shell. Their intermediate forms, hydrogensulfide ion ($HS^-$) and hydrogenselenide ion ($HSe^-$), are amphiprotic.

$$HF \rightleftharpoons H^+ + F^-$$
$$HCl \longrightarrow H^+ + Cl^-$$
$$HBr \longrightarrow H^+ + Br^-$$
$$HI \longrightarrow H^+ + I^-$$
$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{2-}$$
$$H_2Se \rightleftharpoons H^+ + HSe^-$$
$$HSe^- \rightleftharpoons H^+ + Se^{2-}$$

## Oxoacids

**Oxoacids** are molecular compounds composed of hydrogen, a nonmetal, and oxygen. They are typically solids or liquids in their pure form and act as acids when dissolved in water. Their conjugate bases are oxoanions, which may remain dissolved or form salts with cations.

Most oxoanions form oxoacids when a hydrogen ion is added. Some oxoacids are strong, and others are weak. Several weak oxoacids are unstable and readily decompose into water and other products rather than dissociating.

Many oxoacids are associated with corresponding nonmetal oxides, called **anhydrides**, which react with water to form the acid.

The following is an overview of common oxoacids and their conjugate bases for most nonmetals:

### Carbon (C)

The oxoacid of carbon is **carbonic acid** ($H_2CO_3$). It is a weak, diprotic, and unstable acid. Its conjugate bases are bicarbonate ($HCO_3{}^-$) and carbonate ($CO_3{}^{2-}$). It decomposes to carbon dioxide ($CO_2$) and water. Its anhydride is $CO_2$.

Dissociation reactions:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3{}^-$$
$$HCO_3{}^- \rightleftharpoons H^+ + CO_3{}^{2-}$$

Decomposition reaction:

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

Anhydride reaction:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

### Nitrogen (N)

The oxoacids of nitrogen are **nitric acid** ($HNO_3$) and **nitrous acid** ($HNO_2$).

$HNO_3$ is a strong, monoprotic acid. Its conjugate base is nitrate ($NO_3{}^-$).

Dissociation reaction:

$$HNO_3 \longrightarrow H^+ + NO_3{}^-$$

$HNO_2$ is a weak, monoprotic, and unstable acid. Its conjugate base is nitrite ($NO_2^-$). It decomposes to nitric oxide (NO), nitrogen dioxide ($NO_2$), and water.
Dissociation reaction:

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

Decomposition reaction:

$$3\,HNO_2 \longrightarrow HNO_3 + 2\,NO + H_2O$$

### Phosphorus (P)

The common oxoacid of phosphorus is **phosphoric acid** ($H_3PO_4$). It is a weak, triprotic acid. Its conjugate bases are dihydrogen phosphate ($H_2PO_4^-$), hydrogen phosphate ($HPO_4^{2-}$), and phosphate ($PO_4^{3-}$).
Dissociation reactions:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

### Sulfur (S)

The oxoacids of sulfur are **sulfuric acid** ($H_2SO_4$) and **sulfurous acid** ($H_2SO_3$).
$H_2SO_4$ is a strong, diprotic acid. Only the first ionization is strong; the second is weak. Its conjugate bases are hydrogen sulfate ($HSO_4^-$) and sulfate ($SO_4^{2-}$). Its anhydride is sulfur trioxide ($SO_3$).
Dissociation reactions:

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

Anhydride reaction:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$H_2SO_3$ is a weak, diprotic, and unstable acid. Its conjugate bases are hydrogen sulfite ($HSO_3^-$) and sulfite ($SO_3^{2-}$). It decomposes into sulfur dioxide ($SO_2$) and water. Its anhydride is $SO_2$.
Dissociation reactions:

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$
$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$$

Decomposition reaction:

$$H_2SO_3 \longrightarrow H_2O + SO_2$$

Anhydride reaction:

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

### Fluorine (F)

Fluorine does not form any oxoacids or oxoanions, because it is more electronegative than oxygen.

### Chlorine (Cl)

The common oxoacids of chlorine are **perchloric acid** ($HClO_4$) , **chloric acid** $HClO_3$, and **hypochlorous acid** HClO. The first two are strong acids; the last is weak and unstable. All are monoprotic. Their respective conjugate bases are perchlorate ($ClO_4^-$), chlorate ($ClO_3^-$), and hypochlorite ($ClO^-$).
Dissociation reactions:

$$HClO_4 \longrightarrow H^+ + ClO_4^-$$
$$HClO_3 \longrightarrow H^+ + ClO_3^-$$
$$HClO \rightleftharpoons H^+ + ClO^-$$

Decomposition reaction for $ClO^-$:

$$2\,HClO \longrightarrow 2\,HCl + O_2$$

### Iodine (I)

The common oxoacid of iodine is **iodic acid** ($HIO_3$). It is a strong, monoprotic acid. Its conjugate base is iodate ($IO_3^-$).
Dissociation reaction:

$$HIO_3 \longrightarrow H^+ + IO_3^-$$

### Manganese (Mn)

Manganese is the only metal that forms a stable oxoacid and oxoanion. The reason for this is not discussed at this level. Its oxoacid is **permanganic acid** ($HMnO_4$). It is a strong, monoprotic acid. Its conjugate base is permanganate ($MnO_4^-$). It is also a strong oxidizer; oxidation is discussed in a later chapter.
Dissociation reaction:

$$HMnO_4 \longrightarrow H^+ + MnO_4^-$$

## Carboxylic Acids

**Carboxylic acids** contain the carboxyl group ($-COOH$). They are typically solids or liquids in their pure form and act as acids when dissolved in water. Their conjugate bases are carboxylate anions, which may remain dissolved or form salts with cations.
All carboxylic acids are weak acids, and their conjugate bases are weak bases.
The most common example is acetic acid ($CH_3COOH$) and its conjugate base, acetate ($CH_3COO^-$).

## Amines

**Neutral amines** are uncharged molecules with a central nitrogen atom that contains a lone pair of electrons. They are the only common bases that are neutral molecules rather than anions.
Nitrogen has five valence electrons and requires three more to achieve a full octet. It forms three covalent bonds and retains a lone pair of nonbonding electrons. This lone pair allows it to accept a proton, making it a base.
Neutral amines are weak bases. Their conjugate acids are protonated amines, which are weak acids. Protonated amines are the only common acids that are cations.
Neutral amines are gases in their pure form and act as bases when dissolved in water. Their conjugate acids may remain solvated or form salts with anions.
The classic acid–base pair is ammonia ($NH_3$) and the ammonium ion ($NH_4^+$).
Dissociation reaction:

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

## Other Pairs

Some common acid–base pairs do not fall into the structural categories listed above. One example is hydrogen cyanide (HCN) and its conjugate base, cyanide ($CN^-$). HCN is a weak acid, and $CN^-$ is a weak base.

$$HCN \rightleftharpoons H^+ + CN^-$$

### Charged Metal Cations as Acids

Highly charged metal cations, such as $Fe^{3+}$ and $Al^{3+}$, can act as acids by forming **hydrated metal complexes** that release protons.

Many small, highly charged metal cations form coordinate covalent bonds with multiple water molecules. The cation accepts lone pairs from the oxygen atoms of the water molecules. The resulting compound is a hydrated metal complex. The bonded water molecules are called **ligands**.

These complexes typically consist of a central metal ion surrounded by six ligands arranged in an octahedral geometry. Additional details about the formation and structure of these compounds are not addressed at this level.

Hydrated metal complexes remain dissolved in solution. The O–H bonds in some of the water ligands become polarized due to the high charge of the central metal ion. This polarization can lead to the loss of a proton from the ligand. The deprotonated ligand remains bound to the metal as a hydroxide ligand.

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$$

These cations also react with hydroxide ions to form insoluble metal hydroxides, which precipitate out of solution.

$$Al^{3+} + 3\,OH^- \longrightarrow Al(OH)_3(s)$$

### Reactive Anions as Bases

Most bases dissolve in water and weakly accept free protons or pull them from water molecules.

Highly charged anions do not dissolve in water. Instead, they react immediately with water to remove a proton and generate hydroxide.

Such anions include the oxide ion ($O^{2-}$), sulfide ion ($S^{2-}$), nitride ion ($N^{3-}$), and phosphide ion ($P^{3-}$).

The products of their protonation vary. Oxide forms hydroxide ions. Others form polyatomic anions or neutral molecules, some of which are gases. $S^{2-}$ forms the hydrosulfide ion ($HS^-$), a weak base. $P^{3-}$ forms phosphine ($PH_3$), a neutral molecule. $N^{3-}$ forms ammonia gas ($NH_3$), a weak base.

$$O^{2-} + H_2O \longrightarrow 2\,OH^-$$
$$S^{2-} + H_2O \longrightarrow HS^- + OH^-$$
$$N^{3-} + 3\,H_2O \longrightarrow NH_3 + 3\,OH^-$$
$$P^{3-} + 3\,H_2O \longrightarrow PH_3 + 3\,OH^-$$

These anions are typically introduced to solution as the anion of an ionic compound. These compounds are not classified as *soluble* but rather as *reactive*, since they react immediately with water.

The hydroxide produced from the water molecule often replaces the reactive anion in the original ionic compound, forming a metal hydroxide. The solubility of the resulting metal hydroxide follows the standard solubility rules for hydroxides.

## 7.4 Neutralization Reactions

**Neutralization** is the reaction between an acid and a base that reduces the solution's acidity or basicity. These reactions go to completion when either the acid or the base is strong.

In a neutralization reaction, the acid donates a proton and becomes its conjugate base. The conjugate base is typically an anion, except in the case of protonated amines, where it is an uncharged molecule. Strong acids form neutral conjugate bases; weak acids form weak bases.

The base accepts a proton and becomes its conjugate acid. If the base is hydroxide ($OH^-$), the conjugate acid is water. For other bases, the conjugate acid is a weak acid. These weak acids may remain dissolved, may be gases that escape, or may be unstable species that decompose.

If the base was introduced as the anion of a soluble ionic compound, the conjugate base of the acid typically forms a salt with the cation originally paired with the base.

In the case of neutral amines, the conjugate acid is a cation. The conjugate base of the original acid bonds directly with the protonated amine, forming an ammonium salt.

As previously discussed, acid anhydrides are nonmetal oxides that react with water to form oxoacids by pulling hydroxide from water and releasing hydrogen ions. These oxides also react directly with hydroxide bases and often form salts with the cations originally paired with the base.

For example, carbon dioxide ($CO_2$) reacts with sodium hydroxide (NaOH) to form sodium carbonate ($Na_2CO_3$) and water:

$$CO_2(g) + 2\,NaOH\,(aq) \longrightarrow Na_2CO_3(aq) + H_2O\,(l)$$

This reaction is driven by the conversion of $CO_2$ into ${CO_3}^{2-}$. To do so, the $CO_2$ must gain one oxygen atom. It must also combine with two sodium ions to form a stable ionic compound. Since each unit of NaOH provides one $Na^+$, two units are required. This also provides two hydroxide ions. The oxygen atom from one hydroxide combines with $CO_2$ to form ${CO_3}^{2-}$. The remaining hydrogen from that hydroxide combines with the second hydroxide ion to form water.

# Chapter 8

# Oxidation-Reduction Reactions

## 8.1 Oxidation and Reduction

**Oxidation-reduction reactions**, or **redox reactions**, involve the transfer of electrons between reactants. The substance that loses electrons becomes more positively charged and is **oxidized**. The substance that gains electrons becomes more negatively charged and is **reduced**.

Oxidation and reduction always occur together. One reactant loses electrons and the other gains them.

The substance that is oxidized donates electrons and is the **reducing agent**. The substance that is reduced accepts electrons and is the **oxidizing agent**.

A common redox reaction is the electron transfer between an elemental metal and a nonmetal. The metal loses electrons and is oxidized to form a cation. The nonmetal gains electrons and is reduced to form an anion.

## 8.2 Displacement Reactions

A common class of redox reactions is **displacement reactions**. These follow the pattern:

$$\mathrm{A} + \mathrm{BX} \longrightarrow \mathrm{B} + \mathrm{AX}$$

where A is an elemental substance and B is the cation of the ionic compound BX. A transfers electrons to B. B is reduced to its elemental form and displaced from the compound. A is oxidized to a cation and forms an ionic compound with X.

There are two common classes of displacement reactions. In both, the reducing agent is an elemental metal. In the first, the oxidizing agent is a metal cation. In the second, it is hydrogen.

In the first class, an elemental metal reacts with the metal cation of an ionic compound. The elemental metal transfers electrons to the metal cation. The cation is reduced to its elemental form and displaced from the compound. The elemental metal is oxidized to a cation and replaces the original cation in the compound For example, zinc (Zn) reacts with copper sulfate ($CuSO_4$) to form copper (Cu) and zinc sulfate ($ZnSO_4$). Zinc is oxidized, and copper is reduced.

$$\mathrm{Zn(s)} + \mathrm{CuSO_4(aq)} \longrightarrow \mathrm{Cu(s)} + \mathrm{ZnSO_4(aq)}$$

In the second class, an elemental metal reacts with hydrogen from an acid or water. The metal transfers electrons to the hydrogen. The hydrogen is reduced to form hydrogen gas ($H_2$), which typically escapes from the solution. The metal is oxidized to a cation and typically forms an ionic compound with the anion from the acid or water.

For example, calcium (Ca) reacts with hydrochloric acid (HCl) to form hydrogen gas and calcium chloride ($CaCl_2$), and with water to form hydrogen gas and calcium hydroxide ($Ca(OH)_2$). In both reactions, calcium is oxidized and hydrogen is reduced.

$$\mathrm{Ca(s)} + 2\,\mathrm{HCl(aq)} \longrightarrow \mathrm{CaCl_2(aq)} + \mathrm{H_2(g)}$$

$$\mathrm{Ca(s)} + 2\,\mathrm{H_2O(l)} \longrightarrow \mathrm{Ca(OH)_2(aq)} + \mathrm{H_2(g)}$$

### Activity Series

**Ease of oxidation** is a substance's tendency to lose electrons and be oxidized.
A redox reaction occurs only if the reducing agent has a higher ease of oxidation than the oxidizing agent.
The **activity series** ranks metals by ease of oxidation, from highest to lowest.
An elemental metal displaces metal cations that are lower than it in the activity series.
The series includes hydrogen. Metals higher than hydrogen are called **reactive metals**, and those lower are called **noble metals**.
For a metal to reduce hydrogen from an acid or water, it is not sufficient to have a higher ease of oxidation than hydrogen. Reducing hydrogen requires breaking its covalent bond, so the redox reaction must release enough energy to do so.
The hydrogen–oxygen bond in water is stronger than the hydrogen–anion bond in acids. All reactive metals reduce hydrogen from acids. Only the most reactive, such as Group 1 metals and some Group 2 metals, reduce it from water.

### Activity Series Table

| | |
|---|---|
| **Li** | Lithium |
| **K** | Potassium |
| **Ba** | Barium |
| **Ca** | Calcium |
| **Na** | Sodium |
| **Mg** | Magnesium |
| **Al** | Aluminum |
| **Mn** | Manganese |
| **Zn** | Zinc |
| **Cr** | Chromium |
| **Fe** | Iron |
| **Co** | Cobalt |
| **Ni** | Nickel |
| **Sn** | Tin |
| **Pb** | Lead |
| **$H_2$** | Hydrogen |
| **Cu** | Copper |
| **Ag** | Silver |
| **Hg** | Mercury |
| **Pt** | Platinum |
| **Au** | Gold |

## 8.3 Oxidation Numbers

When a redox reaction involves isolated atoms or ions, the transfer of electrons is readily apparent because it directly results in a change in charge.
For example, in the reaction between a sodium atom (Na) and a chlorine atom (Cl), sodium transfers an electron to chlorine, and both atoms become ions. The electron transfer is obvious because both atoms ionize:

$$\mathrm{Na} + \mathrm{Cl} \longrightarrow \mathrm{Na}^+ + \mathrm{Cl}^-$$

In contrast, atoms in covalent bonds do not have individual charges, because electrons are shared and the charge is distributed across the molecule. In redox reactions involving covalent species, electron transfer is not as apparent.
For example, in the combustion of methane ($CH_4$), methane reacts with oxygen to form carbon dioxide and water. Electrons are transferred from carbon to oxygen, but this is not apparent from the formulas:

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$$

To identify electron transfers in covalent compounds, atoms are assigned individual **oxidation numbers**. These are hypothetical charges assigned as if the atoms were not covalently bonded. In general, bonding electrons are assigned to the more electronegative atom. Specific rules follow in the next section.

For example, in water, oxygen is assigned an oxidation number of −2 and each hydrogen +1. In each O–H bond, both bonding electrons are assigned to oxygen because it is more electronegative than hydrogen. When water is dissociated, such as by electrolysis, oxygen indeed retains all bonding electrons and forms $O^{2-}$, while each hydrogen forms $H^+$.

To distinguish oxidation numbers from ionic charges, oxidation numbers are written with the sign first and ionic charges with the magnitude first:

Oxidation numbers: +1, −2

Ionic charges: $^{1+}$, $^{2-}$

## Oxidation Number Assignment Rules

The sum of the oxidation numbers in a compound must equal its total charge.

If a compound contains a species not covered by the following rules, sum the oxidation numbers of the known elements and subtract that total from the compound's charge. The remainder is the oxidation number of the unknown species.

### Elemental Atoms

For elemental atoms, the oxidation number is always 0.

### Monatomic Ions

For monatomic ions, the oxidation number equals the ionic charge.

Group 1 metals form $^{1+}$ ions, Group 2 metals form $^{2+}$ ions, and Group 13 metals form $^{3+}$ ions.

Group 15 nonmetals form $^{3-}$ ions, Group 16 nonmetals form $^{2-}$ ions, and Group 17 nonmetals form $^{1-}$ ions.

Hydrogen has two ionic forms. It bonds to metals as $H^-$ (hydride ion) and to nonmetals as $H^+$ (hydrogen ion). It has a charge of $^{1+}$ as $H^+$ and $^{1-}$ as $H^-$.

Most transition metals do not have a single ionic form. They can form one of several, each with a different charge. Their charge must be inferred from the context. For example, in $FeCl_3$, the iron must have a charge of $^{3+}$.

### Covalently Bonded Atoms

Hydrogen has an oxidation number of +1, except in $H_2$ and metal hydrides.

Fluorine always has an oxidation number of −1.

Oxygen generally has an oxidation number of −2. In peroxides it is −1, and in superoxides it is $-\frac{1}{2}$. Peroxides and superoxides are defined in a later chapter. In compounds with fluorine, oxygen has a positive oxidation number (+1 or +2), since fluorine is more electronegative.

Halogens generally have an oxidation number of −1, but may be positive in compounds with oxygen.

# 8.4 Oxidizing and Reducing Agents

## Common Classes of Oxidizing and Reducing Agents

There are several common classes of oxidizing and reducing agents, though many substances do not fit neatly into any one class.

Metal atoms and neutral hydrogen tend to lose electrons and oxidize to form cations. They typically act as reducing agents.

Metal cations and hydrogen ions can be reduced to their elemental form by stronger reducing agents.

Nonmetal atoms tend to gain electrons and reduce to form anions. They typically act as oxidizing agents.
Nonmetal anions can be oxidized to their elemental form by stronger oxidizing agents.
A final common class is the central atom in oxo compounds. These atoms form covalent bonds with oxygen and often have high oxidation numbers, since oxygen is assigned the bonding electrons. Each bonded oxygen increases the central atom's oxidation number by 2.
When highly oxidized, these central atoms typically act as oxidizing agents. They accept electrons to reduce their oxidation number. When not fully oxidized, they can act as reducing agents for species that are more highly oxidized.

## Reduction Potential

Reduction potential ($E°$) is a measure of a species' tendency to gain electrons and be reduced.
A redox reaction will occur only if the species gaining electrons has a higher reduction potential than the oxidized form of the species losing them.
For example, to determine if nitrate ion ($NO_3^-$) can oxidize bromide ($Br^-$), compare the reduction potential of nitrate with that of bromine ($Br_2$). Nitrate has a reduction potential of +0.96 V, while bromine is +1.07 V. Since bromine has the higher reduction potential, nitrate cannot oxidize bromide.
In contrast, iodine ($I_2$) has a reduction potential of +0.54 V, which is less than that of nitrate. Therefore, nitrate can oxidize iodide ($I^-$) to iodine.

## Nonmetal Atoms as Oxidizing Agents

The halogens are very electronegative and act as strong oxidizing agents. Their oxidizing strength decreases down the group. Fluorine (F) is the strongest.
Most other nonmetals, apart from oxygen, are relatively weak oxidizers.
Oxygen is a strong oxidizing agent due to its high electronegativity and its tendency to be reduced to oxidation number −2. However, it can only oxidize reactive metals, not noble metals.
Oxygen classically acts as an oxidizing agent in the formation of rust. Rust is a hydrated metal oxide produced when iron reacts with moist air. The oxygen in the air pulls electrons from the iron atoms. The iron is oxidized to iron(III) ions ($Fe^{3+}$). The oxygen is reduced to oxide ions ($O^{2-}$), which react with water in the air to form hydroxide ions ($OH^-$). The iron(III) ions then combine with hydroxide ions to form iron(III) hydroxide. Over time, this compound dehydrates to form rust.

$$4\,Fe + 3\,O_2 + 6\,H_2O \longrightarrow 4\,Fe(OH)_3 \longrightarrow 2\,Fe_2O_3 \cdot 3\,H_2O$$

In the term "$\cdot H_2O$" at the end of the equation, the dot is called a **hydrate dot**. It indicates that the water is physically integrated into the crystal lattice of the compound but not covalently bonded. Such a compound is called a **hydrate** and is not discussed further at this level.

## Central Atom of Oxo Compounds

Oxo compounds include oxoacids and oxoanions.
The central atom in oxo compounds is typically in a high oxidation state. Each bonded oxygen increases its oxidation number by 2. This high oxidation state gives the atom a strong tendency to gain electrons, making it a strong oxidizing agent.
For example, the permanganate ion ($MnO_4^-$) has a charge of −1 and contains four oxygen atoms, each with an oxidation number of −2. To balance the charge, the manganese (Mn) atom must have an oxidation number of +7.
When the central atom of an oxo compound is reduced, bonded oxygen atoms are often removed. This occurs because the reduced atom has gained electrons and no longer requires the bonding electrons from oxygen atoms to complete its valence shell. The different oxo compounds of the same element correspond to different oxidation states of that element.
Since reduction involves the removal of oxygen atoms, its extent depends not only on the reduction potential of the central atom but also on the stability of the released oxygen atoms. In acidic solution, oxygen atoms

are more stable because they can bond with $H^+$. Therefore, oxo compounds act as stronger oxidizing agents under acidic conditions.

For example, in neutral solution, $MnO_4{}^-$ can be reduced to $MnO_2$, gaining four electrons and losing two oxygen atoms. In acidic solution, it can be reduced further to $Mn^{2+}$, gaining two additional electrons and losing all oxygen atoms.

These central atoms are stronger oxidizing agents than elemental oxygen and can oxidize noble metals.

For example, nitric acid ($HNO_3$) can oxidize copper (Cu):

$$\mathrm{Cu(s) + 4\,HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2\,NO_2(g) + 2\,H_2O\,(l)}$$

In this reaction, copper loses two electrons and is oxidized to $Cu^{2+}$. Each nitrogen in nitrate initially has an oxidation number of +5. Two of the four nitrate ions act as oxidizing agents. Each of their nitrogen atoms is reduced to +4 and forms nitrogen dioxide ($NO_2$), releasing one oxygen atom in the process. The other two nitrate ions remain unchanged and combine with $Cu^{2+}$ to form $Cu(NO_3)_2$. The hydrogen ions from all four nitric acid molecules combine with the two released oxygen atoms to form water.

Some oxo compounds are strong enough to oxidize halide ions to halogens.

For example, permanganate in acidic solution oxidizes chloride ($Cl^-$) to chlorine gas ($Cl_2$):

$$\mathrm{2\,KMnO_4 + 16\,HCl \longrightarrow 2\,MnCl_2 + 5\,Cl_2 + 8\,H_2O + 2\,KCl}$$

## Molecular Redox Reactions

Most redox reactions previously discussed involved at least one ion and were driven by a species having a strong tendency to gain or lose electrons.

Another class involves only neutral molecules. In these reactions, oxidation and reduction occur through the redistribution of electrons during bond formation and breaking.

A classic molecular redox reaction is the combustion of methane.

The reactants are one molecule of methane ($CH_4$) and two molecules of oxygen ($O_2$). Since carbon is more electronegative than hydrogen, it is assigned both bonding electrons in each C–H bond, giving it an oxidation number of −4. The oxygen atoms in $O_2$ each have an oxidation number of 0.

The products are one molecule of carbon dioxide ($CO_2$) and two molecules of water. In carbon dioxide, each oxygen atom is assigned both electrons from the C=O double bond, giving each oxygen an oxidation number of −2 and carbon an oxidation number of +4. In water, the oxygen is assigned both bonding electrons in each O–H bond, giving it an oxidation number of −2, and each hydrogen +1.

Overall, the carbon atom is oxidized from −4 to +4, and each of the four oxygen atoms is reduced from 0 to −2.

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$$

# Chapter 9

# Solution Concentration and Stoichiometry

## Molarity

**Concentration** is the amount of solute dissolved in a given amount of solution. It is most commonly expressed in **molarity (M)**. Molarity is the number of moles of solute per liter of solution.

$$\mathrm{M} = \frac{\text{mol solute}}{\text{L solution}}$$

For example, a 1.0 M solution of HCl contains 1.0 mol of HCl per 1.0 L of solution.
For solutions of soluble ionic compounds, molarity can be expressed either as the molarity of the compound or as the molarity of the individual ions in solution.
For example, a 1.0 M $Na_2SO_4$ solution can be described as 1.0 M $Na_2SO_4$, 2.0 M $Na^+$, or 1.0 M ${SO_4}^{2-}$.

## Molarity as a Conversion Factor

Molarity can be used to convert between volume of solution in liters and amount of solute in moles:

$$\text{L solution} \times \mathrm{M} = \text{mol solute}$$
$$\tfrac{\text{mol solute}}{\mathrm{M}} = \text{L solution}$$

Molarity can also be used as a conversion factor in stoichiometric calculations.
For example, to find the volume of 5.0 M calcium hydroxide ($Ca(OH)_2$) solution required to neutralize 3.0 L of 2.5 M hydrochloric acid (HCl):

1. Convert volume of HCl to moles using its molarity.
2. Use the stoichiometric ratio to convert moles of HCl to moles of $Ca(OH)_2$.
3. Convert moles of $Ca(OH)_2$ to volume using its molarity.

This gives:

$$3.0\,\cancel{\text{L HCl solution}} \times \frac{2.5\,\cancel{\text{mol HCl}}}{1.0\,\cancel{\text{L HCl solution}}} \times \frac{1\,\cancel{\text{mol Ca(OH)}_2}}{2\,\cancel{\text{mol HCl}}} \times \frac{1.0\,\text{L Ca(OH)}_2\text{ solution}}{5.0\,\cancel{\text{mol Ca(OH)}_2}} = 0.15\,\text{L Ca(OH)}_2\text{ solution}$$

## Titration

A solution with a known concentration is called a **standard solution**. **Standardization** is the process of determining the concentration of a solution.
**Titration** is a common method of standardization. It determines concentration by reacting an unknown solution with a standard solution.

The standard solution is added gradually until the amount added is exactly sufficient to react completely with the unknown solution. This is called the **equivalence point**.

The equivalence point is often detected using an indicator. For example, phenolphthalein ($C_{20}H_{14}O_4$) is commonly used in acid–base titrations. It is colorless in acidic solution, pale pink in slightly basic solution, and vivid pink in strongly basic solution. A base is added slowly to the acid until the solution turns pale pink, indicating that the equivalence point has been reached.

Once the equivalence point is reached, the concentration of the unknown solution can be calculated from the volume and molarity of the standard solution:

1. Convert the volume of the standard solution to moles using its molarity.
2. Use the stoichiometric ratio to convert moles of standard solute to moles of unknown solute.
3. Divide moles of unknown solute by its volume to determine its molarity.

For example, if 1.0 L of an unknown HCl solution is neutralized by 2.8 L of 3.0 M $Ca(OH)_2$, then the molarity of the HCl solution is:

$$2.8\,\cancel{\mathrm{L\ Ca(OH)_2\ solution}} \times \frac{3.0\,\cancel{\mathrm{mol\ Ca(OH)_2}}}{1.0\,\cancel{\mathrm{L\ Ca(OH)_2\ solution}}} \times \frac{2\,\cancel{\mathrm{mol\ HCl}}}{1\,\cancel{\mathrm{mol\ Ca(OH)_2}}} \times \frac{1}{1.0\,\cancel{\mathrm{L\ HCl\ solution}}} = 16.8\,\mathrm{M\ HCl}$$

## Dilution

**Dilution** is the process of reducing a solution's concentration by adding water. The volume of solution increases, while the number of moles of solute remains constant.

The molarity and volume of the concentrated and diluted solutions are related by the equation:

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

where $M_{\text{conc}}$ and $V_{\text{conc}}$ are the molarity and volume of the concentrated solution, and $M_{\text{dil}}$ and $V_{\text{dil}}$ are the molarity and volume of the diluted solution.

When three of these four quantities are known, the fourth can be calculated.

For example, to determine the amount of water that must be added to 1.5 L of 7.5 M HCl to prepare a 3.0 M solution:

1. Calculate the total volume of the diluted solution using the dilution equation.
   $7.5\,\mathrm{M} \times 1.5\,\mathrm{L} = 3.0\,\mathrm{M} \times V_{\text{dil}}$
   $V_{\text{dil}} = \frac{7.5\times1.5}{3.0} = 3.75\,\mathrm{L}$
2. Subtract the volume of the concentrated solution.
   $3.75\,\mathrm{L} - 1.5\,\mathrm{L} = 2.25\,\mathrm{L}$
3. This gives the volume of water to add.

# Chapter 10

# Thermochemistry

## 10.1 Forms of Energy

### Kinetic and Potential Energy

**Energy** is the capacity to do work or transfer heat.
Energy is classified as **kinetic** or **potential**.
**Kinetic energy** is possessed by moving objects. It represents their capacity to do work by using their motion to apply force.
Kinetic energy is proportional to an object's mass and the square of its velocity:

$$E_k = \frac{1}{2}mv^2$$

**Potential energy** is the energy an object possesses due to its position or condition. The position or condition involves a force that is prevented from acting because the object is constrained. Potential energy represents the capacity for that force to do work when the constraint is removed.
For example, an object held at a height possesses **gravitational potential energy**. The gravitational force is prevented from acting because the object is held. Gravitational potential energy is the capacity for work to be done on the object when it is released.
Similarly, a compressed spring possesses **elastic potential energy**. The restoring force is prevented from acting because the spring is held in a compressed state. Elastic potential energy is the capacity for that force to do work when the spring is released.
The **first law of thermodynamics**, or the **law of conservation of energy**, states that energy cannot be created or destroyed. It can only be transferred between systems or transformed from one form to another.
For example, when a lifted object is dropped, its gravitational potential energy is transformed into kinetic energy. The kinetic energy is not created but results from this transformation. The gravitational potential energy was not created either, but transferred to the object through the work done by the system that lifted it.
**Thermodynamics** is the study of how energy is transferred between systems and transformed between forms.

### Temperature and Heat

All particles possess kinetic energy and are in constant motion. In gases and liquids, particles move freely around one another. In solids, particles are held in fixed positions but vibrate in place.
**Temperature** is the average kinetic energy of a substance's particles.
The **second law of thermodynamics** states that energy flows from regions of higher temperature to regions of lower temperature, resulting in an even distribution of temperature.
In systems governed by random processes, the statistically inevitable outcome over time is an even distribution. Because particles are in constant motion and frequently collide, energy becomes uniformly spread.
This transfer of energy from a region of higher temperature to one of lower temperature is called **heat**.

### Electrostatic Potential Energy and Coulomb's Law

The **electrostatic force** is the attractive force between opposite charges and the repulsive force between like charges.

**Electrostatic potential energy** is the energy a system of charged particles possesses due to the positions of the charges relative to one another. When two like charges are held close together, the system has electrostatic potential energy due to the repulsive force between them. If released, the charges accelerate away from each other. When two opposite charges are held apart, the system has electrostatic potential energy due to the attractive force between them. If released, the charges accelerate toward each other.

Electrostatic potential energy is quantified by **Coulomb's law**. It is directly proportional to the product of the charges and inversely proportional to the distance between them.

$$E_{\text{el}} = \frac{KQ_1Q_2}{d}$$

where $E_{\text{el}}$ is the electrostatic potential energy (J), $K$ is Coulomb's constant ($8.99 \times 10^9$ J $\cdot$ m/C$^2$), $Q_1$ and $Q_2$ are the charges (C), and $d$ is the distance between them (m).

The formula $E_{\text{el}} = \frac{KQ_1Q_2}{d}$ gives the energy of repulsion between two charges. When the charges have like signs, their product is positive and the energy is positive, indicating repulsion. When the charges have opposite signs, their product is negative and the energy is negative, indicating attraction.

### Energy in Chemical Reactions

Ionic and covalent bonds are electrostatic attractions. In an ionic bond, oppositely charged ions attract. In a covalent bond, both nuclei are attracted to the shared electrons.

Breaking an ionic or covalent bond requires energy, which overcomes the electrostatic forces holding the particles together. Because energy cannot be created, it must be transferred to the system. This energy increases the system's total energy.

Once separated, the particles possess electrostatic potential energy. When a bond forms, electrostatic potential energy is released. Because energy cannot be destroyed, it must be released from the system, often as a transfer of heat to the surroundings.

**Thermochemistry** is the study of the thermodynamics of chemical reactions.

Systems tend toward the configuration with the lowest potential energy, which involves the least constrained forces. Chemical systems tend toward the configuration with the lowest chemical potential energy.

## 10.2 Energy Transfer in Chemical Systems

### Changes in Internal Energy

The **internal energy** of a system ($E$) is the total of all kinetic and potential energies of the particles within the system.

Because energy is conserved, internal energy changes only when energy is transferred between the system and its surroundings.

Systems are classified by whether they can exchange energy or matter with their surroundings. An **open system** can exchange both matter and energy. A **closed system** can exchange energy but not matter. An **isolated system** can exchange neither.

The **change in internal energy ($\Delta E$)** is defined as the final internal energy minus the initial:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

When a system gains energy, $E_{\text{final}} > E_{\text{initial}}$ and $\Delta E$ is positive. When it loses energy, $E_{\text{initial}} > E_{\text{final}}$ and $\Delta E$ is negative.

Energy is transferred as heat ($q$) or work ($w$). Both $q$ and $w$ are defined as energy added to the system. When the system gains energy, $q$ and $w$ are positive. When the system loses energy, they are negative.

A system's change in internal energy equals the sum of the heat added and the work done on it:

$$\Delta E = q + w$$

## Energy Changes in Chemical Reactions

Breaking chemical bonds requires energy, and forming bonds releases energy. Most chemical reactions involve the breaking of some bonds and the formation of others.
The energy change of a chemical reaction equals the internal energy of the products minus that of the reactants.

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

If $E_{\text{products}} > E_{\text{reactants}}$, then $\Delta E$ is positive and the system has absorbed energy.
If $E_{\text{products}} < E_{\text{reactants}}$, then $\Delta E$ is negative and the system has released energy.

## State and Path Functions

A **state function** is a property that depends only on the current state of a system and is independent of the process used to reach that state.
The change in a state function is determined solely by the initial and final states of the system, not by the process taken between them.
For example, altitude is a state function. The change in altitude depends only on the starting and ending altitudes, not on the path taken between them.
Changes in state functions are denoted by the symbol $\Delta$.
In contrast, a **path function** quantifies the change that occurs during a process. Its value depends on the specific path taken from one state to another. It cannot be determined solely from the initial and final states.
For example, distance traveled during a change in altitude is a path function because it depends on the route taken.
Internal energy ($E$) is a state function. Its change, $\Delta E$, depends only on the initial and final energy values.
In contrast, heat ($q$) and work ($w$) are path functions. They do not describe the state of a system. Instead, they quantify energy transferred as heat or work during a specific process. Neither value can be determined solely from the initial and final states.

## Pressure–Volume Work

Systems exchange energy with their surroundings as heat or work.
In most chemical reactions, the only work involved is pressure–volume work. This is the work associated with the expansion or contraction of the system against an external pressure. It is quantified as:

$$w = -P_{\text{ext}}\Delta V$$

where $w$ is the work done on the system (J), $P_{\text{ext}}$ is the external pressure (N/m$^2$), and $\Delta V$ is the change in volume (m$^3$).
Under constant external pressure, pressure–volume work is directly proportional to the change in volume. When the volume increases and $\Delta V$ is positive, $w$ is negative. The system does work on the surroundings as it expands and loses energy. When the volume decreases and $\Delta V$ is negative, $w$ is positive. The surroundings do work on the system as it contracts, and the system gains energy.
Volume is a state function. Although pressure–volume work is a path function, under constant pressure its value can be calculated from the initial and final volumes.
This applies only when the external pressure is constant. If the external pressure changes during the process, the total pressure–volume work depends on the pressure at each stage. In such cases, it cannot be determined from the volume change alone and must be calculated from the full pressure–volume path.

## Enthalpy

**Enthalpy** ($H$) is a state function that is defined to track the energy exchanged as heat in processes that occur at constant pressure.
Enthalpy is defined as the internal energy of a system ($E$) plus the energy associated with the system occupying space under external pressure. This additional energy is equal to the product of the external pressure and the system's volume:

$$H = E + P_{\text{ext}}V$$

As a state function, the change in enthalpy ($\Delta H$) depends only on the initial and final states:

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

As established earlier, at constant pressure, the change in internal energy due to pressure–volume work is equal to the difference in $P_{\text{ext}}V$ between states. The state with the higher $P_{\text{ext}}V$ has a correspondingly lower internal energy. Because enthalpy is defined by adding $P_{\text{ext}}V$ to internal energy, any change in energy due to pressure–volume work is directly offset by the added term. As a result, the only energy change that affects enthalpy under constant pressure is heat exchange, and the change in enthalpy is equal to the heat exchanged:

$$\Delta H = q_P$$

where $q_P$ is the heat transferred at constant pressure.

An **endothermic** process is one that absorbs heat. An **exothermic** process is one that releases heat. When $\Delta H$ is positive, the process is endothermic. When $\Delta H$ is negative, the process is exothermic.

## Enthalpy of Reaction

The change in enthalpy associated with a chemical reaction is called the **enthalpy of reaction** ($\Delta H_{\text{rxn}}$).

$$\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$$

A **thermochemical equation** gives the enthalpy of reaction for the molar amounts of substances shown in the chemical equation.

For example, the enthalpy of reaction for 2 moles of hydrogen ($H_2$) reacting with 1 mole of oxygen ($O_2$) to form 2 moles of water is −483.6 kJ. The corresponding thermochemical equation is:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad \Delta H_{\text{rxn}} = -483.6\text{ kJ}$$

## Effect of Physical State on Enthalpy

$\Delta H_{\text{rxn}}$ depends on the physical states of the reactants and products.

For example, in the following combustion reactions, $\Delta H_{\text{rxn}}$ is more negative when the products include liquid water instead of water vapor:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad \Delta H_{\text{rxn}} = -802\text{ kJ}$$
$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H_{\text{rxn}} = -890\text{ kJ}$$

Forming liquid water releases more energy than forming water vapor, because the enthalpy of liquid water is lower. The difference in enthalpy between the two reactions corresponds to the enthalpy change for the condensation of water:

$$H_2O(g) \longrightarrow H_2O(l) \qquad \Delta H_{\text{rxn}} = -88\text{ kJ}$$

This energy is associated with the phase change itself. Even when a substance is at its melting or boiling point, energy is required for the phase change to occur.

# Chapter 11

# Determining Reaction Enthalpy

## 11.1 Calorimetry

### Heat Capacity

The amount of energy exchanged as heat is determined from the temperature change of a substance.
The amount of energy associated with a given temperature change varies between substances.
**Heat capacity** ($C$) is the amount of energy required to raise the temperature of a substance by 1 K. **Molar heat capacity** ($C_m$) is the heat capacity per mole of a substance. **Specific heat capacity** ($C_s$) is the heat capacity per gram of a substance. It is measured in J/g · °C (joules per gram-degree Celsius).
A substance's specific heat capacity is determined by applying a known amount of heat and measuring the resulting temperature change. The specific heat capacity is calculated by dividing the amount of heat by the product of the substance's mass and the temperature change.

$$C_s = \frac{q}{m\Delta T}$$

where $q$ is the heat exchanged (J), $m$ is the mass of the substance (g), and $\Delta T$ is the temperature change (°C).
For example, if 25 J of heat is applied to 65 g of a substance and the temperature increases by 5 °C, the specific heat capacity is:

$$C_s = \frac{25\,\mathrm{J}}{65\,\mathrm{g} \times 5\,{}^{\circ}\mathrm{C}} = 0.08\,\mathrm{J/g} \cdot {}^{\circ}\mathrm{C}$$

Tables of $C_s$ values list the specific heat capacities of common substances.
To calculate the heat exchanged from a temperature change, multiply the specific heat capacity by the substance's mass and the temperature change:

$$q = C_s m \Delta T$$

For example, the specific heat capacity of water is 4.184 J/g · °C. If the temperature of 25 g of water decreases by 8 °C, the heat lost is:

$$4.184\,\mathrm{J/g} \cdot {}^{\circ}\mathrm{C} \times 25\,\mathrm{g} \times (-8\,{}^{\circ}\mathrm{C}) = -838.6\,\mathrm{J}$$

### Calorimetry and Calorimeters

**Calorimetry** is the process of determining the amount of heat released or absorbed in a chemical reaction. The instrument used is a **calorimeter**.
A calorimeter consists of a reaction vessel surrounded by water. If the reaction releases or absorbs heat, that heat is exchanged primarily with the surrounding water. The change in the water's temperature is used to determine the amount of heat absorbed or released by the reaction.

The amount of heat gained or lost by the water is calculated by multiplying its mass, specific heat capacity (4.184 J/g · °C), and temperature change. This value is equal in magnitude and opposite in sign to the heat absorbed or released by the reaction.

$$q_{\text{soln}} = C_s \cdot m \cdot \Delta T$$
$$q_{\text{rxn}} = -q_{\text{soln}}$$

There are two common types of calorimeters: constant-pressure and bomb.

A **constant-pressure calorimeter** measures the change in enthalpy ($\Delta H$). The reaction occurs in an open vessel under atmospheric pressure.

A **bomb calorimeter** measures the change in internal energy ($\Delta E$). The vessel is sealed, so the reaction is isolated from atmospheric pressure and no pressure–volume work occurs.

## 11.2 Enthalpy Calculations

### Hess's Law

Complex reactions often consist of multiple individual steps that occur in sequence, forming a **reaction pathway**. Some reactions have multiple possible reaction pathways that lead from the same reactants to the same products.

**Hess's law**, stated by Germain Henri Hess in 1840, states that the enthalpy change ($\Delta H$) for a reaction is independent of the reaction pathway taken.

This is consistent with the thermodynamic classification of state and path functions, which was established in the late 1800s. Since enthalpy is a state function, its change depends only on the initial and final states, not on the path taken between them.

For example, there are two reaction pathways that convert 1 mole of nitrogen ($N_2$) and 2 moles of oxygen ($O_2$) to 2 moles of nitrogen dioxide ($NO_2$). In the first pathway, 1 mole of $N_2$ reacts directly with 2 moles of $O_2$ to form 2 moles of $NO_2$:

$$N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g) \quad \Delta H = +66.4 \text{ kJ}$$

In the second pathway, 1 mole of $N_2$ reacts with 1 mole of $O_2$ to produce 2 moles of nitric oxide (NO). Then, 2 moles of NO react with another mole of $O_2$ to form 2 moles of $NO_2$:

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \quad \Delta H = +180.5 \text{ kJ}$$
$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g) \quad \Delta H = -114.1 \text{ kJ}$$

The total enthalpy change is the same for both pathways:

$$\Delta H = 180.5 \text{ kJ} + (-114.1 \text{ kJ}) = +66.4 \text{ kJ}$$

### Standard Enthalpies of Formation

According to Hess's law, the enthalpy change of a reaction is equal to the sum of the enthalpy changes for decomposing the reactants into their elements and forming the products from those elements.

This simplifies the determination of reaction enthalpies. Instead of measuring a reaction's enthalpy directly, one can use tabulated values for the standard enthalpies of formation of the substances involved.

The enthalpy change involved in forming a compound from its elements is the compound's **enthalpy of formation** ($\Delta H_f$).

The enthalpy change for decomposing a compound into its elements is called the compound's **enthalpy of decomposition**. It is equal in magnitude and opposite in sign to the enthalpy of formation. The reverse of a state function change has the same magnitude and the opposite sign.

For example, the enthalpy of formation of 2 moles of water is the enthalpy change for reacting 2 moles of hydrogen ($H_2$) with 1 mole of oxygen ($O_2$), and is equal to $-483.6$ kJ. The enthalpy of decomposition has the opposite sign.

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \quad \Delta H_{\text{rxn}} = -483.6 \text{ kJ}$$
$$2\,H_2O(g) \longrightarrow 2\,H_2(g) + O_2(g) \quad \Delta H_{\text{rxn}} = +483.6 \text{ kJ}$$

The **standard enthalpy of formation** ($\Delta H_f^\circ$) is the enthalpy change for forming 1 mole of a compound from its elements in their standard states at 25°C and 1 atm. An atmosphere (atm) is a unit of pressure.
For elements in their standard state, $\Delta H_f^\circ = 0$ by definition.
A substance's $\Delta H_f^\circ$ depends on its physical state.
To determine the enthalpy change for a reaction using standard enthalpies of formation:

1. Multiply each substance's $\Delta H_f^\circ$ by its stoichiometric coefficient.
2. Add the results for the products.
3. Subtract the results for the reactants.

$$\Delta H_{\text{rxn}} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

For example, in the combustion of methane ($CH_4$), 1 mole of methane reacts with 2 moles of oxygen to produce 1 mole of carbon dioxide ($CO_2$) and 2 moles of water ($H_2O$):

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$$

To calculate the enthalpy change for the reaction:

1. Obtain the standard enthalpies of formation from tabulated values.
    $CH_4(g)$: $-74.8$ kJ/mol
    $O_2(g)$: 0 kJ/mol
    $CO_2(g)$: $-393.5$ kJ/mol
    $H_2O(l)$: $-285.8$ kJ/mol
2. Multiply the standard enthalpy of formation for each substance by its stoichiometric coefficient.
    $CH_4(g)$: $1 \times (-74.8) = -74.8$ kJ
    $O_2(g)$: $2 \times 0 = 0$ kJ
    $CO_2(g)$: $1 \times (-393.5) = -393.5$ kJ
    $H_2O(l)$: $2 \times (-285.8) = -571.6$ kJ
3. Add the results for the products.
    $-393.5 + (-571.6) = -965.1$ kJ
4. Add the results for the reactants.
    $-74.8 + 0 = -74.8$ kJ
5. Finally, subtract the total for the reactants from the total for the products.
    $\Delta H_{\text{rxn}} = -965.1 - (-74.8) = -890.3$ kJ

## Bond Enthalpies

Breaking a bond requires energy, and forming a bond releases energy.
For a given bond, the energy required to break one mole of bonded atoms in the gas phase is the **bond enthalpy**. Bond enthalpy is denoted $D(\text{X–Y})$ for the bond between atoms $X$ and $Y$.
For example, the energy required to break one mole of H–H bonds is 436 kJ/mol:

$$D(\text{H}-\text{H}) = 436 \text{ kJ/mol}$$

Single ($-$), double ($=$), and triple ($\equiv$) bonds have different bond enthalpies.
Except in diatomic molecules, most bonds occur within larger chemical species. The energy required to break a bond depends not only on the bond itself but also on the species it is part of. As a result, bond enthalpy values vary between substances.
The values listed in tables are average bond enthalpies derived from multiple species. These average values cannot be used for precise calculations but are useful for estimating reaction enthalpies, such as to determine

whether a reaction is endothermic or exothermic. However, even for estimations, they can only be applied to gaseous bonds, not liquid or solid.

To estimate $\Delta H_{\text{rxn}}$ using bond enthalpies, add the bond enthalpies of the bonds broken and subtract those of the bonds formed:

$$\Delta H_{\text{rxn}} = \sum D(\text{bonds broken}) - \sum D(\text{bonds formed})$$

For example, 1 mole of hydrogen ($H_2$) reacts with 1 mole of chlorine ($Cl_2$) to form 2 moles of hydrogen chloride (HCl). The bond enthalpy for H−H is 436 kJ/mol, for Cl−Cl is 243 kJ/mol, and for H−Cl is 431 kJ/mol. The reaction breaks one mole of H−H bonds and one mole of Cl−Cl bonds, and forms two moles of H−Cl bonds.

$$\Delta H_{\text{rxn}} = (436 + 243) - (2 \times 431) = -183 \text{ kJ}$$

# Chapter 12

# Light, Photons, and the Bohr Model

## 12.1 Light

### Waves

**Waves** are propagating, periodically oscillating disturbances of equilibrium. An initial oscillation at the source point affects the adjacent point, which affects the next, propagating the disturbance outward and forming a repeating pattern of peaks and troughs.

The distance between successive peaks or troughs is the wave's **wavelength ($\lambda$)**, measured in meters. The number of cycles that pass a point per second is the **frequency ($\nu$)**, measured in hertz (Hz). The wave's **velocity ($v$)** is the product of its wavelength and frequency:

$$\lambda\nu = v$$

**Interference** is a property of waves in which overlapping waves combine constructively or destructively.

### Wave Property of Electromagnetic Radiation

**Light** exhibits interference, as well as other wave properties, demonstrating that it behaves as a wave.

**James Clerk Maxwell** showed that light is composed of oscillating electric and magnetic fields that propagate through space and carry energy. Light is therefore a form of **electromagnetic radiation**.

Other forms of electromagnetic radiation include radio waves, microwaves, infrared, ultraviolet, X-rays, and gamma rays. All electromagnetic waves travel at the same speed in a vacuum, $2.998 \times 10^8$ m/s ($c$), but differ in wavelength and frequency. These quantities are inversely related, since their product is constant:

$$\lambda\nu = c$$

The **electromagnetic spectrum** organizes electromagnetic radiation by wavelength and frequency:

| **Region** | **Wavelength (m)** | **Frequency (Hz)** |
|---|---|---|
| Radio Waves | $> 0.1$ | $< 3 \times 10^9$ |
| Microwaves | $10^{-3}$ to $0.1$ | $3 \times 10^9$ to $3 \times 10^{11}$ |
| Infrared (IR) | $7 \times 10^{-7}$ to $10^{-3}$ | $3 \times 10^{11}$ to $4.3 \times 10^{14}$ |
| Visible Light | $4 \times 10^{-7}$ to $7 \times 10^{-7}$ | $4.3 \times 10^{14}$ to $7.5 \times 10^{14}$ |
| Ultraviolet (UV) | $1 \times 10^{-8}$ to $4 \times 10^{-7}$ | $7.5 \times 10^{14}$ to $3 \times 10^{16}$ |
| X-Rays | $1 \times 10^{-11}$ to $1 \times 10^{-8}$ | $3 \times 10^{16}$ to $3 \times 10^{19}$ |
| Gamma Rays | $< 1 \times 10^{-11}$ | $> 3 \times 10^{19}$ |

Visible light ranges from red, with a wavelength of approximately 700 nm and frequency of $4.3 \times 10^{14}$ Hz, to violet, with a wavelength of approximately 400 nm and frequency of $7.5 \times 10^{14}$ Hz.

## Blackbody Radiation and Planck's Constant

Temperature reflects the average kinetic energy of a substance's particles. This energy is called **thermal energy**. Since all matter possesses some thermal energy, charged particles within it oscillate, producing electromagnetic radiation. Most of this radiation lies outside the visible spectrum, typically at lower frequencies. However, when an object is heated, the thermal energy can become sufficient to generate radiation in the visible range.

In general, the frequency distribution of the radiation emitted by a heated object depends not only on its thermal energy but also on its atomic structure. A special case, known as **blackbody radiation**, occurs when radiation escapes through a small hole from the hollow interior of a heated object. In this setup, the emitted spectrum depends only on temperature, not on the object's composition.

According to classical physics, blackbody radiation should be predictable by analyzing the motion of thermally energized particles and the electromagnetic waves they produce. Classical theory assumed that thermal energy should be distributed continuously across all frequencies, including high ones. However, experimental data shows a sharp drop in radiation intensity at high frequencies. This cannot be explained with classical physics.

**Max Planck** explained this in 1900 by proposing that energy is absorbed and emitted in discrete quantities, called **quanta**, which are proportional to frequency. Higher frequencies require higher quanta of energy. At a given temperature, thermal energy is not sufficient to produce large numbers of high-frequency quanta, so intensity drops off sharply at higher frequencies.

Planck's formula relates frequency ($\nu$) to the energy of a quantum ($E$):

$$E = h\nu$$

$$h = 6.626 \times 10^{-34}\,\mathrm{J \cdot s}$$

where $E$ is the quantum of energy (J), $h$ is Planck's constant, and $\nu$ is the frequency (Hz). For a given frequency, energy is emitted or absorbed only in integer multiples of $h\nu$.

## Photoelectric Effect and Einstein's Introduction of the Photon

When metals are exposed to light, they emit electrons. This is the **photoelectric effect**. Each metal has a **threshold frequency** - the minimum light frequency needed to eject electrons. Light below this frequency cannot eject electrons, regardless of intensity.

According to classical physics, dislodging electrons should depend on the total light energy. Low-frequency light at sufficiently high intensity should eject electrons, and there should not be a threshold frequency.

**Albert Einstein** explained this in 1905 by extending Planck's idea of quantized energy. Planck's model gave discrete quanta by which energy is emitted, but allowed for large amounts of energy, as long as the total was an integer multiple of the quantum. Einstein proposed that light itself consists of discrete packets, called **photons**, each carrying a single quantum of energy proportional to its frequency, as given by Planck. Increasing the intensity of light increases the number of photons, but not the energy of each photon.

This explains the photoelectric effect. A single electron is ejected when struck by a single photon with enough energy to dislodge it; the energy must come from that one photon. If the frequency is below the threshold, no electrons are ejected, since no photons have sufficient energy, regardless of intensity.

The energy of a photon is:

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

At the beginning of this chapter, light's wave behavior was established. The photon model reveals its particle behavior. This paradox is called **wave-particle duality** and is not fully understood. Light behaves as a wave in some situations and as a particle in others. **Quantum mechanics** predicts which behavior will occur in a given context.

## 12.2 Bohr's Model of the Hydrogen Atom

### Line Spectra and the Rydberg Constant

Electromagnetic radiation with a single wavelength is **monochromatic**. **Polychromatic radiation** consists of multiple wavelengths. The distribution of wavelengths and intensities is the radiation's **spectrum**, and can be visualized using a spectrometer. In a **continuous spectrum**, all wavelengths within a range are present. In a **line spectrum**, only specific, discrete wavelengths appear.

Certain gases emit radiation when excited by an electric current. Each produces a distinct line spectrum. Classical physics cannot explain why the radiation is restricted to discrete wavelengths, or why those specific wavelengths appear.

**Johann Balmer** noted in 1855 that the wavelengths of the line spectrum emitted by hydrogen follow an integer-based pattern. This is described by the **Rydberg equation**:

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where $\lambda$ is the wavelength in meters, $n_1$ and $n_2$ are positive integers with $n_2 > n_1$, and $R_H$ is the **Rydberg constant**:

$$R_H = 1.096776 \times 10^7 \,\mathrm{m}^{-1}$$

### The Classical Electron Orbit Model

Once the proton and electron were discovered, it was proposed that the electron orbits the proton, similar to how a planet orbits a star.

Gravitational force follows an inverse-square law with distance. Planetary orbit is the result of gravitational attraction and the object's tangential velocity.

The electromagnetic force also follows an inverse-square law with distance, and can likewise result in orbital motion between charged particles.

However, this encounters a problem. Accelerating charges emit energy as electromagnetic radiation. Orbital motion involves constant centripetal acceleration. An electron orbiting a proton should continuously radiate energy, lose tangential velocity, and spiral into the nucleus.

This does not occur. Atoms have stable sizes, determined by the electron's distance from the nucleus. Additionally, if the electron continuously emitted energy, the radiation frequency should increase as the electron moves faster and approaches the nucleus. This would produce a continuous spectrum, not the observed line spectrum.

### Bohr's Quantized Orbit Model

To resolve these issues, **Niels Bohr** proposed in 1913 a model of the hydrogen atom that introduced quantized electron orbits, building on the concept of energy quantization from Planck and Einstein.

Bohr's model is based on three postulates:

1. The electron occupies only discrete, quantized energy levels. The lowest is the **ground state**.
2. While in an allowed energy level, the electron does not emit radiation.
3. Energy is absorbed or emitted only during transitions between energy levels.

Bohr showed that the energy of each allowed level corresponds to a positive integer $n$, called the **principal quantum number**, with the ground state corresponding to $n = 1$:

$$E_n = -hcR_H \left( \frac{1}{n^2} \right) = (-2.18 \times 10^{-18}) \left( \frac{1}{n^2} \right) \mathrm{J}$$

where $h$ is Planck's constant, $c$ is the speed of light, and $R_H$ is the Rydberg constant.

Energy is emitted or absorbed when the electron transitions between energy levels. The energy corresponds to the difference between the two levels:

$$\Delta E = E_f - E_i = (-2.18 \times 10^{-18}) \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ J}$$

where $\Delta E$ is the energy absorbed or emitted, and $n_f$ and $n_i$ are the final and initial quantum numbers. From this energy, the frequency and wavelength of the emitted or absorbed photon can be calculated:

$$\nu = \frac{E_{\text{photon}}}{h}$$
$$\lambda = \frac{hc}{E_{\text{photon}}}$$

Substituting the energy levels into these expressions yields the Rydberg equation from the previous section, the significance of which is now understood:

$$\nu = cR_H \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|$$
$$\lambda = \frac{1}{R_H \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|}$$

## Limitations of the Bohr Model

Although the Bohr model accurately explains the line spectrum of hydrogen or single-electron ions, it fails to explain the spectra of species with more than one electron. Additionally, its three postulates are assumed without explanation.

Extensive experimental evidence also shows that electrons do not move in fixed orbits. Instead, they exhibit wave-like and probabilistic behavior, as explored in the next section. This forms the basis of the quantum mechanical model.

However, two of Bohr's postulates are retained in the quantum model:

1. Electrons occupy discrete, quantized energy levels.
2. Energy is absorbed or emitted during transitions between levels.

# Chapter 13

# Wave Nature of Matter and Quantum Mechanics

## 13.1 Wave Property of Matter

### de Broglie Wavelength

As established earlier, electromagnetic radiation exhibits wave-particle duality; though classically a wave, it also behaves as a particle.

**Louis de Broglie** proposed in 1924 that matter also exhibits wave-particle duality; though classically a particle, it has wave-like properties.

Subsequent experiments confirmed that particles such as electrons exhibit wave behavior, including diffraction and interference.

The associated wavelength is called the **de Broglie wavelength**. De Broglie proposed that a particle's wavelength is inversely proportional to its momentum ($p$). Momentum is defined as the product of mass ($m$) and velocity ($v$).

$$\lambda = \frac{h}{mv}$$

This relation generalizes a result from Einstein's theory of relativity concerning photon momentum. According to relativity, although photons do not have mass, they carry momentum inversely proportional to their wavelength:

$$p = \frac{h}{\lambda}$$

De Broglie proposed that if matter has wave properties, its wavelength is inversely proportional to its momentum.

This equation was later verified experimentally.

For macroscopic objects, the de Broglie wavelength is negligibly small. However, for electrons, the wavelength is much larger than the particle itself and dominates its behavior. The electron's wavelength is on the scale of nanometers ($10^{-9}$ m), while its physical size is less than $10^{-19}$ m.

### Heisenberg's Uncertainty Principle

In 1927, **Werner Heisenberg** introduced the **uncertainty principle**, which states that it is impossible to precisely measure both the position and momentum of an electron.

The uncertainties in position and momentum vary inversely; their product is bounded by a minimum constant, so increasing precision in one decreases precision in the other.

$$\Delta x \times \Delta(mv_x) \geq \frac{h}{2\pi}$$

where $\Delta x$ is the uncertainty in position (in meters), and $\Delta(mv_x)$ is the uncertainty in momentum (in $\text{kg} \cdot \text{m/s}$).

That the electron does not spiral into the nucleus is explained by the uncertainty principle. If the electron were confined to the space of the nucleus, the certainty of its position would increase. This would require a corresponding increase in momentum uncertainty, resulting in high kinetic energy that prevents such confinement.

The uncertainty principle is a consequence of the wave nature of matter. It is not a result of insufficient means of measurement, but rather an inherent physical limit on the precision of the measurements. The nature of this limit is not fully understood.

## 13.2 Schrödinger's Wave Equation

The wave aspect of the electron describes the probability of finding it at a given location. This means the electron does not have a fixed position; instead, its location is described by a probability distribution. The wave represents the range of possible locations and their associated probabilities.

When an electron is near a proton, its wave is influenced by the proton's attraction. Describing this interaction involves complex mathematics. In 1926, **Erwin Schrödinger** proposed a **wave equation** to describe the electron's wave in such systems.

The wave is described by a set of **quantum numbers**. Only specific sets of quantum numbers solve Schrödinger's equation and correspond to valid electron waves. These quantum numbers, and the rules governing them, are described in the next section.

The spatial probability distribution given by a wave is called an **electron orbital**. Unlike Bohr's electron orbits, which follow fixed circular paths, orbitals are regions where the electron is likely to be found. The electron does not have a fixed location or defined path within an orbital. Orbitals are often described as an **electron cloud**.

## 13.3 Orbitals and Quantum Numbers

### Quantum Numbers

Orbitals are defined by three quantum numbers: the principal quantum number ($n$), the angular momentum quantum number ($\ell$), and the magnetic quantum number ($m_\ell$).

$n$, the **principal quantum number**, defines the **energy level**, or **shell**. As $n$ increases, the orbital becomes larger, the electron is on average farther from the nucleus, and the energy is higher.

$\ell$, the **angular momentum quantum number**, defines the orbital **subshell**; a given energy level can have multiple subshells.

$m_\ell$, the **magnetic quantum number**, specifies the orbital within the subshell; a given subshell can have multiple orbitals.

Each subshell contains a distinct set of $m_\ell$ orbitals, as described in the next sections.

### Allowed Values of Quantum Numbers

$n$ can be any positive integer, though basic chemistry typically involves orbitals with $n \leq 4$.

For the subshells within a given shell, $\ell$ must be an integer from 0 to $n - 1$. For example, the shell with $n = 3$ has three subshells, for $\ell = 0$, 1, and 2.

| **Shell** | **Allowed $\ell$ values** |
|---|---|
| $n = 1$ | 0 |
| $n = 2$ | 0, 1 |
| $n = 3$ | 0, 1, 2 |
| $n = 4$ | 0, 1, 2, 3 |

The subshells described by values of $\ell$ are denoted by letters:

| **Value of $\ell$** | **Subshell** |
|---|---|
| $\ell = 0$ | $s$ |
| $\ell = 1$ | $p$ |
| $\ell = 2$ | $d$ |
| $\ell = 3$ | $f$ |

Subshells are labeled by combining the value for $n$ and the letter for $\ell$. For example, the subshell with $n = 3$ and $\ell = 1$ is labeled $3p$.

For the orbitals within a given subshell, $m_\ell$ must be an integer from $-\ell$ to $\ell$. For example, the subshell with $\ell = 2$ has five orbitals, for $m_\ell = -2$, -1, 0, 1, and 2.

| **Value of $\ell$** | **Allowed $m_\ell$ values** |
|---|---|
| $\ell = 0$ | 0 |
| $\ell = 1$ | -1, 0, 1 |
| $\ell = 2$ | -2, -1, 0, 1, 2 |
| $\ell = 3$ | -3, -2, -1, 0, 1, 2, 3 |

### Orbital Shapes

$\ell$ determines an orbital's spatial distribution, while $m_\ell$ determines its spatial orientation around the nucleus. Each value of $\ell$ corresponds to a distinct form of spatial distribution for the electron's probability density. These forms can be visualized by imposing a shape over the region where most of the probability density is concentrated. For higher-$\ell$ subshells, the value of $m_\ell$ can affect the orbital's visual shape.

Every shell has an $s$ subshell. The $s$ subshell has a single orbital.

The $s$ orbital is spherical and centered around the nucleus.

The $s$ orbital's probability distribution is not uniform. The probability oscillates along the radial distance from the nucleus. Each crest is a **radial peak**. An $ns$ orbital has $n$ radial peaks. The outermost radial peak is the highest. Between each peak is a **spherical node**, where the probability is zero. There are $n - 1$ radial nodes.

Shells with $n > 1$ have a $p$ subshell. The $p$ subshell has three orbitals, for $m_\ell = -1, 0$, and 1.

$p$ orbitals are dumbbell-shaped, with two lobes on opposite sides of the nucleus. Each of the three is aligned along a different axis and labeled $p_x$, $p_y$, and $p_z$.

Each $p$ orbital has a **nodal plane** - a plane where the probability is zero. The plane passes through the nucleus and is perpendicular to the axis the orbital occupies: $yz$ for $p_x$, $xz$ for $p_y$, and $xy$ for $p_z$.

Shells with $n > 2$ have a $d$ subshell. The $d$ subshell has five orbitals, for $m_\ell = -2, -1, 0, 1$, and 2.

Four of the $d$ orbitals have a four-lobed shape. $d_{xy}$, $d_{xz}$, and $d_{yz}$ are oriented between the axes of their respective planes. $d_{x^2-y^2}$ is oriented along the axes of the $xy$ plane. $d_{z^2}$ has two lobes along the $z$ axis and a doughnut-shaped region in the $xy$ plane.

Each $d$ orbital has two nodal planes. These are simple for the four-lobed orbitals but more complex for the $d_{z^2}$ orbital.

Shells with $n > 3$ have an $f$ subshell. The $f$ subshell has seven orbitals, for $m_\ell = -3, -2, -1, 0, 1, 2$, and 3.

$f$ orbitals have complex shapes.

## 13.4 Electron Spin

### Spin Magnetic Quantum Number

Many spectral lines for multi-electron atoms are actually pairs of closely spaced lines. These are caused by two electrons in the same orbital having slightly different energies.

In 1925, George E. Uhlenbeck and Samuel A. Goudsmit proposed that electrons have a property called **spin**, which is associated with magnetism. All electrons have the same spin magnitude, but the spin can take one of two possible orientations relative to a magnetic field, referred to as **spin up** and **spin down**. These two states lead to slight energy differences, producing closely spaced spectral lines.

Spin is described by the fourth quantum number, the **spin magnetic quantum number** ($m_s$), which can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$, corresponding to spin up and spin down states.

## Pauli Exclusion Principle

**Wolfgang Pauli** proposed the **Pauli exclusion principle** in 1925. It states that no two electrons in an atom can have the same set of all four quantum numbers. Two electrons can only occupy the same orbital if they have opposite spins.

An electron alone in an orbital is called **unpaired**. When two electrons with opposite spins occupy the same orbital, they are called **paired**.

# Chapter 14

# The Periodic Table and Electron Configuration

## 14.1 The Periodic Table

### Development of the Periodic Table

#### Periodic Properties of the Elements

**Dmitri Mendeleev** introduced the **periodic table** in 1869. He observed that when elements are arranged by increasing atomic weight, their physical and chemical properties repeat periodically. The table organizes elements by placing each complete cycle of repeating properties in a row, called a **period**. Because each period follows the same pattern, elements with similar properties align vertically in **groups**.

In some positions, no known element with the properties of the group had the expected atomic weight. Mendeleev left these positions blank and predicted the existence and properties of the missing elements. These elements were later discovered and closely matched his predictions.

#### Atomic Number

**Henry Moseley** discovered the concept of **atomic number** in 1913. When atoms are bombarded with high-energy electrons, they emit X-rays. Each element emits a unique X-ray frequency. Moseley observed that these frequencies increased in a regular pattern corresponding to consecutive whole numbers. He proposed that these numbers represented the number of protons in the nucleus of each element. This was later confirmed experimentally and came to be known as the element's atomic number.

Following Moseley's discovery, the periodic table was reordered by atomic number instead of atomic weight. Although atomic number and atomic weight generally increase together, there are exceptions. In all such cases, the order based on atomic number aligns with the pattern of chemical properties in the table. An example is argon and potassium. Argon has a lower atomic number but a higher atomic weight than potassium. Based on their properties, argon comes first, which aligns with the atomic number ordering.

### Correlation Between the Periodic Table and Electron Configuration

#### Electron Configuration

An element's **electron configuration** describes how its electrons are distributed among orbitals.

The modern periodic law states that most chemical and physical properties of elements arise from their electron configurations and vary systematically with atomic number. The periodic table's structure reflects these configurations.

#### Periods and Shells

Each period corresponds to a new electron shell with a higher principal quantum number ($n$) and contains as many elements as needed to fill that shell.
Each element has one more electron than the last, because neutral atoms have equal numbers of protons and electrons. These electrons fill the shell associated with that period until it is complete. Noble gases, in the last column, have complete valence shells. The first element in the next period starts a new shell with one electron.

#### Valence and Core Electrons

Electrons in the outermost shell are called **valence electrons**. Electrons in filled inner shells are called **core electrons**.
Elements down a group share valence electron counts but differ in core electron number. Properties that repeat down a group are determined by valence electrons. Since chemical reactivity depends on valence electrons, elements in a group show similar chemical behavior. Noble gases are chemically inert because they have full valence shells.

#### Aufbau Principle

The **Aufbau principle** states that electrons fill orbitals in order of increasing energy. Lower-energy orbitals are filled before higher-energy ones. Within a shell, subshells are filled in order of increasing energy, generally corresponding to increasing angular momentum quantum number ($\ell$).

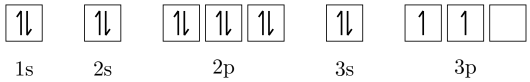
#### Subshell Blocks

The periodic table is divided into **blocks**, defined by the type of subshell being filled.
The first two columns, including helium, form the $s$ **block**. In each period, the first element adds one $s$ electron, the second adds a second. The $s$ subshell has one orbital and holds two electrons, so this block has two columns.
The last six columns form the $p$ **block**. The $p$ subshell has three orbitals and holds six electrons.
The ten columns between the $s$ and $p$ blocks, starting in the fourth period, form the $d$ **block**. The $d$ subshell has five orbitals and holds ten electrons.
The fourteen columns usually placed below the main table form the $f$ **block**. The $f$ subshell has seven orbitals and holds fourteen electrons.

## 14.2 Electron Configurations of the Elements

### Electron Configuration Notation

Electron configurations are written using orbital labels followed by superscripts indicating the number of electrons. Silicon, which has two electrons in its $1s$, $2s$, and $3s$ orbitals, six in $2p$, and two in $3p$, has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^2$.
**Orbital diagrams** represent electron configurations as half-arrows within boxes. Each box represents an orbital. If the orbital contains one electron, an upward-facing half-arrow is drawn in the box; if it contains two, one upward-facing and one downward-facing half-arrow are drawn.
The orbital diagram for silicon is as follows:

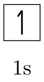


The **condensed electron configuration** abbreviates completed inner shells using the symbol of the previous noble gas in brackets, followed by the valence electrons. For silicon, the $n = 1$ and $n = 2$ shells are abbreviated as *[Ne]*. Only the $n = 3$ electrons are listed: $[\mathrm{Ne}]3s^2 3p^2$.

## Electron Configurations of Hydrogen Through Boron

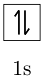
**Hydrogen** has one electron, which occupies the 1$s$ orbital.

Hydrogen (H): $1s^1$



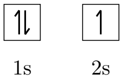
**Helium** has two electrons, which occupy the 1$s$ orbital with opposite spins. The $n = 1$ shell is complete.

Helium (He): $1s^2$



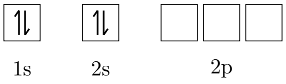
**Lithium** has three electrons. The first two fill the 1$s$ orbital. The third occupies the 2$s$ orbital and begins the $n = 2$ shell. It has significantly more energy and is, on average, farther from the nucleus than the first two electrons.

Lithium (Li): $[\text{He}]2s^1$



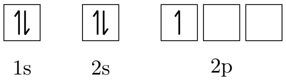
**Beryllium** has four electrons, which fill its 1$s$ and 2$s$ orbitals. Although both subshells are filled, the $n = 2$ shell is not complete, since the 2$p$ subshell is empty. A noble gas requires a complete valence shell; a complete subshell is not sufficient.

Beryllium (Be): $[\text{He}]2s^2$



**Boron** has five electrons. The first four fill the 1$s$ and 2$s$ orbitals. The fifth occupies one of the 2$p$ orbitals.

Boron (B): $[\text{He}]2s^22p^1$

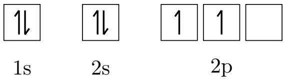


## Carbon and Hund's Law

**Carbon** has six electrons. The fifth and sixth electrons occupy the 2$p$ subshell.

Carbon (C): $[\text{He}]2s^22p^2$

In contrast to the 1$s$ and 2$s$ subshells, where electrons pair in the same orbital with opposite spins, the two 2$p$ electrons occupy separate orbitals with the same spin. Electrons in the same subshell that share the same spin are called **parallel**.

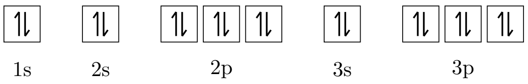


This is explained by **Hund's rule**, which states that a subshell with unpaired electrons having parallel spin is more stable than one with paired electrons of opposite spin. Electrons first occupy separate orbitals with parallel spins and pair only after all orbitals in the subshell contain one electron.

## Argon and the Noble Gases

Argon has 18 electrons. The first two fill the $n = 1$ shell, the next eight fill the $n = 2$ shell, and the remaining eight occupy the $n = 3$ shell. The $3s$ and $3p$ subshells are filled, but the $3d$ subshell is empty.

Argon (Ar): [Ne]$3s^2 3p^6$

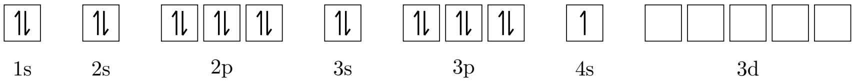


Even though the $3d$ subshell is empty, argon is a noble gas. All noble gases except helium have exactly eight electrons in their outer shell, filling the $s$ and $p$ orbitals, with no electrons in the $d$ orbital. This is called the **octet rule**. The reason for this is explained in the next section.

## Potassium, Calcium, the Aufbau Principle, and the Madelung Rule

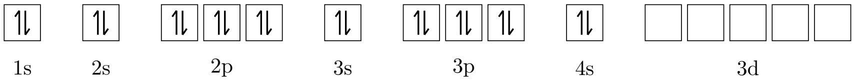
**Potassium** follows argon, with one additional electron. One might expect this electron to occupy the $3d$ orbital. However, potassium shares properties with lithium and sodium, both of which have an $ns^1$ valence configuration. This indicates that potassium's valence electron occupies the $4s$ orbital, not $3d$, giving it a $4s^1$ configuration.

Potassium (K): [Ar]$4s^1$



Similarly, **calcium** follows potassium and shares properties with beryllium and magnesium, which have $ns^2$ valence configurations. This indicates that calcium's valence electrons occupy the $4s$ orbital, giving it a $4s^2$ configuration.

Calcium (Ca): [Ar]$4s^2$



The Aufbau principle explains why the $4s$ subshell fills before $3d$: $4s$ has lower energy, even though $3d$ has a lower principal quantum number.
Orbital energies follow the **Madelung rule**, which ranks orbitals by increasing $n + \ell$. If two orbitals have the same $n + \ell$, the orbital with the lower $n$ has lower energy.
$3d$ has $n + \ell = 5$ $(3 + 2)$, while $4s$ has $n + \ell = 4$ $(4 + 0)$, so $4s$ has lower energy and is filled first.
$3d$ and $4p$ $(4 + 1)$ both have $n + \ell = 5$, but $3d$ has a lower $n$, so it lies below $4p$ in energy and is filled after $4s$ and before $4p$.
Orbitals with the same $n + \ell$ value, such as $4d$, $5f$, and $6p$, tend to have similar energies. However, $s$ orbitals are generally higher in energy than other orbitals with the same $n + \ell$, and closer in energy to orbitals with $n + \ell + 1$. This leads to the general order within a period: $ns < (n-2)f < (n-1)d < np$.
This explains why noble gases have filled $ns$ and $np$ subshells, but not $nd$. An incomplete valence shell causes chemical reactivity because orbitals of similar energy are unevenly filled. An orbital is considered part of the valence shell only if its energy is comparable to the other valence orbitals. Although $nd$ has the same principal quantum number as $ns$ and $np$, it has higher energy and is not part of the valence shell. Once the $ns$ and $np$ subshells are filled, the valence shell is complete, and the element is inert.

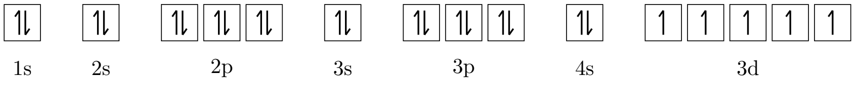
| **Period** | **Subshells** | **Explanation** |
|---|---|---|
| 1 | $1s$ | $n = 1$ allows $\ell < 1$ |
| 2 | $2s$ $2p$ | $n = 2$ allows $\ell < 2$ |

| | | |
|---|---|---|
| 3 | $3s$ $3p$ | $n = 3$ allows $\ell < 3$, but $3d$ is not filled until after $4s$ |
| 4 | $4s$ $3d$ $4p$ | $n = 4$ allows $\ell < 4$, but $4f$ is not filled until after $6s$ |
| 5 | $5s$ $4d$ $5p$ | |
| 6 | $6s$ $4f$ $5d$ $6p$ | |
| 7 | $7s$ $5f$ $6d$ $7p$ | |

### Transition Metals

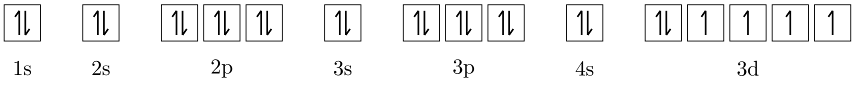
The elements in the $d$ block are called the **transition metals**.
For example, manganese has five $3d$ electrons. Each occupies a separate orbital.

Manganese (Mn): $[\mathrm{Ar}]4s^2 3d^5$



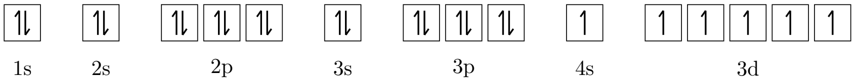
Iron has one more $3d$ electron, which pairs in one of the orbitals.

Iron (Fe): $[\mathrm{Ar}]4s^2 3d^6$



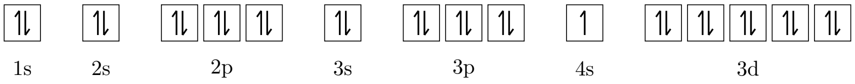
In some transition metals, the Aufbau principle is not followed. An $ns$ electron shifts to the $(n-1)d$ subshell to achieve a more stable half-filled or fully filled $d$ subshell.
For example, chromium has $[\mathrm{Ar}]\,4s^1\,3d^5$ instead of $[\mathrm{Ar}]\,4s^2\,3d^4$; a $4s$ electron moves to the $3d$ subshell to achieve a half-filled arrangement.

Chromium (Cr): $[\mathrm{Ar}]4s^1 3d^5$



Similarly, copper has $[\mathrm{Ar}]\,4s^1\,3d^{10}$ instead of $[\mathrm{Ar}]\,4s^2\,3d^9$; a $4s$ electron moves to the $3d$ subshell to fill it completely.

Copper (Cu): $[\mathrm{Ar}]4s^1 3d^{10}$



### Lanthanides and Actinides

The elements that fill the $4f$ orbitals are called the **lanthanides**, or **rare earth elements**. They have similar chemical properties and are typically found together in nature.
The elements that fill the $5f$ orbitals are called the **actinides**. All are radioactive, and most do not occur naturally.

## 14.3 Electron Configuration of Ions

### Order of Electron Removal and Addition in Ions

A neutral atom ionizes when it absorbs enough energy for an electron to transition to an energy level where its attraction to the nucleus becomes negligible. This is represented as a transition from a finite principal quantum number $n$ to $n = \infty$.

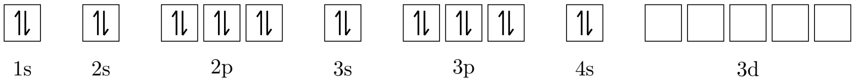
Electrons are removed from the orbital with the highest energy. This typically corresponds to the highest principal quantum number $n$. When multiple orbitals have the same $n$, electrons are removed from the orbital with the highest angular momentum quantum number $\ell$.

As previously established, the $4s$ orbital is filled before the $3d$ orbital because $4s$ has lower energy when both are unoccupied. One might then expect that electrons would be removed from the $3d$ orbital before $4s$. However, this is not the case - electrons are removed from $4s$ before $3d$. The explanation for this reversal is given in the following section.

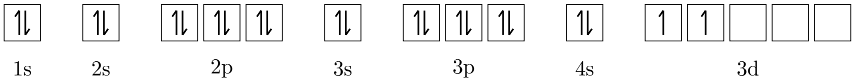
This difference between the orders of filling and removal is illustrated by comparing the electron configurations of neutral calcium and the titanium(II) ion. Both have 20 electrons, but differ in valence electron configuration.

Calcium has two valence electrons, both occupying the $4s$ orbital. Neutral titanium has four valence electrons, two in $4s$ and two in $3d$. When titanium ionizes to form $\mathrm{Ti}^{2+}$, the two $4s$ electrons are removed. This leaves two valence electrons, both in the $3d$ orbital.

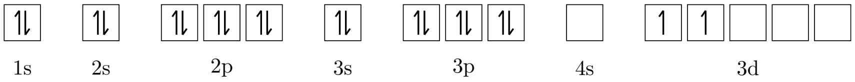
Calcium (Ca): $[\mathrm{Ar}]\,4s^2$



Titanium (Ti): $[\mathrm{Ar}]\,4s^2\,3d^2$



Titanium(II) Ion ($\mathrm{Ti}^{2+}$): $[\mathrm{Ar}]\,3d^2$



Anions, however, follow the same pattern as filling: electrons are added to the orbital with the lowest value of $n + \ell$, and where equal, to the one with lower $n$.

## Reversal of Orbital Energies Due to Occupancy

The $4s$ orbital is filled before the $3d$ orbital because it has lower energy. However, during ionization, electrons are removed from $4s$ before $3d$, implying that $4s$ has higher energy. These two facts appear to contradict each other.

The resolution is that orbital energy depends on orbital occupancy. When only one of the two orbitals is occupied, $4s$ has lower energy than $3d$. When both are occupied, this reverses: $3d$ becomes lower in energy than $4s$.

This reversal is caused by electron shielding. The $3d$ electrons shield the $4s$ orbital from the nucleus more effectively than the $4s$ electrons shield the $3d$ orbitals. As a result, although $4s$ initially has lower energy, once the $3d$ orbitals begin to fill, they reduce the effective nuclear charge felt by the $4s$ electrons, raising the energy of the $4s$ orbital above that of $3d$.

This seems counterintuitive. If $4s$ is initially lower in energy than $3d$, it is presumably closer to the nucleus. If it is closer, it should shield $3d$ more effectively than $3d$ shields it.

The explanation lies in the spatial distributions of the $4s$ and $3d$ orbitals, and how different types of averages affect energy and shielding.

Most of the time, the $3d$ electrons are closer to the nucleus than the $4s$ electrons, due to their lower principal quantum number. The bulk of the $3d$ electron density lies inside the bulk of the $4s$ electron density.

$d$ orbitals have a concentrated electron distribution. In contrast, $s$ orbitals are more diffuse, with electron density spread over a larger volume.

The shape of an orbital's distribution is determined by its angular momentum quantum number ($\ell$). The $3d$ orbital ($\ell = 2$) has higher angular momentum, which limits its penetration and keeps its radial distance more stable. The $4s$ orbital ($\ell = 0$) has no angular momentum barrier, allowing it to penetrate into inner regions. This results in some $4s$ electron density very close to the nucleus, despite its higher $n$ value. These occasional deep penetrations reduce its average energy and skew its average radius inward.

However, shielding is not governed by rare penetrations, but by where the electron density is located most of the time. Because the $3d$ electrons are more consistently closer to the nucleus, they shield the $4s$ orbital more effectively.

As a result, once the $3d$ orbitals begin to fill, they reduce the effective nuclear charge experienced by the $4s$ electrons. This raises the energy of the $4s$ orbital above that of $3d$, making $4s$ the first to lose electrons during ionization.

# Chapter 15

# Periodic Trends in Atomic Properties

## Effective Nuclear Charge

Many atomic properties depend on the magnitude of the electrostatic attraction between the nucleus and the valence electrons.

According to Coulomb's law, electrostatic attraction is proportional to the product of the charges and inversely proportional to the square of the distance between them

$$F \propto \frac{Z_1 Z_2}{r^2}$$

Therefore, the electrostatic attraction between the nucleus and a valence electron is proportional to the product of their charges and inversely proportional to the square of the electron's average distance from the nucleus.

The charge of an electron is constant. In contrast, the nuclear charge, denoted $Z$, varies between elements and equals the number of protons in the nucleus.

In multi-electron atoms, the electrostatic attraction between the nucleus and a given electron is reduced. Other electrons introduce negative charge into the electron's nuclear-facing region, reducing the net positive electrostatic field in that direction. As a result, the electron experiences less attraction toward the nucleus. This effect is called **screening**.

The total screening experienced by an electron is quantified by the **screening constant**, $S$. The **effective nuclear charge**, $Z_{\text{eff}}$, represents the net positive charge experienced by an electron after accounting for screening:

$$Z_{\text{eff}} = Z - S$$

Using $Z_{\text{eff}}$, the electrostatic attraction between the nucleus and a valence electron is given by:

$$F \propto \frac{Z_{\text{eff}}}{r^2}$$

Electrons in the same shell provide limited screening, but the most significant screening comes from electrons in lower-energy subshells. These electrons are consistently located closer to the nucleus and lie within the electron's nuclear-facing region. For valence electrons, the screening constant $S$ is often approximated as the number of core electrons.

### Periodic Trends in Effective Nuclear Charge

Across a period, $Z_{\text{eff}}$ increases. Each successive element has an additional proton, increasing $Z$. Although each added valence electron contributes some additional screening, the increase in $Z$ is greater than the increase in $S$, so $Z_{\text{eff}}$ increases.

Down a group, $Z_{\text{eff}}$ increases slightly. The relative amounts of $Z$ and $S$ remain approximately constant, since both increase. However, in lower elements of the group, core electrons occupy higher-energy shells, which are more diffuse and located farther from the nucleus. These electrons are less effective at screening the nuclear charge than those in lower-energy shells, leading to a slight increase in $Z_{\text{eff}}$.

Although $Z_{\text{eff}}$ increases down a group, the actual electrostatic force on the valence electrons decreases. This is because force is also inversely proportional to the square of the distance, and valence electrons are farther from the nucleus in larger atoms.

## Atomic Radii

According to the quantum mechanical model, electrons do not have precise locations. As a result, atoms do not have fixed boundaries and cannot be assigned a fixed size.

Atomic size is therefore not directly measurable for isolated atoms. Instead, it is based on the distance between the nuclei of two adjacent atoms, which is defined as the sum of both atoms' **atomic radii**.

When both atoms are the same element, the atomic radius is half the distance between their nuclei. When the atoms are from different elements, the individual radii cannot be determined from a single bond and must be estimated by comparing data from many compounds.

There are two types of atomic radii: the **van der Waals radius** and the **bonding radius**.

The van der Waals radius applies to atoms that are adjacent but not chemically bonded, such as colliding gas-phase atoms.

The bonding radius applies to covalently bonded atoms and is smaller than the van der Waals radius. It is more easily determined experimentally and has broader practical use. Unless specified otherwise, "atomic radius" refers to the bonding radius.

An atom's bonding radius is not fixed; it varies depending on the bonding partner and the species it is part of. Tabulated values are average bonding radii derived from multiple compounds and cannot be used for precise calculations.

### Periodic Trends in Atomic Radii

Across a period, atomic radius decreases as $Z_{\text{eff}}$ increases.

Down a group, atomic radius increases significantly with each additional electron shell.

## Ionic Radii

Similar to atomic radius, the **ionic radius** is based on the distance between the nuclei of two adjacent ions in an ionic compound.

Anions have larger radii than their neutral atoms due to increased electron–electron repulsion and greater shielding, which reduce $Z_{\text{eff}}$.

Cations have smaller radii than their neutral atoms because the loss of electrons reduces shielding and increases $Z_{\text{eff}}$. When the entire valence shell is removed, the resulting radius is significantly smaller than that of the neutral atom.

An **isoelectronic series** is a group of ions or atoms that have the same number of electrons but different nuclear charges.

For example, $\mathrm{O^{2-}, F^{-}, Na^{+}, Mg^{2+}, Al^{3+}}$ all have 10 electrons but different nuclear charges.

Across an isoelectronic series, ionic radius decreases as nuclear charge $(Z)$ increases.

## Ionization Energy

**Ionization energy** is the energy required to remove an electron from the ground state of a gas-phase species. It is expressed in kJ/mol.

Ionization energy is always positive, since energy is required to overcome the electrostatic attraction between the electron and the nucleus.

The **first ionization energy** $(I_1)$ is the energy required to remove an electron from a neutral atom. The **second ionization energy** $(I_2)$ is the energy required to remove an electron from a $+1$ ion. This pattern continues with the third ionization energy and beyond.

Each successive ionization requires more energy, because removing an electron increases $Z_{\text{eff}}$ for the remaining electrons.

Once all valence electrons are removed, the next ionization energy increases sharply, because the next electron must be removed from a core shell, where electrons are more tightly bound to the nucleus.

For example, sodium (Na) has one valence electron. Its first ionization energy is 496 kJ/mol, while its second ionization energy is 4562 kJ/mol:

$$\mathrm{Na(g)} \longrightarrow \mathrm{Na^{+}(g)} + \mathrm{e^{-}} \qquad \Delta H = +496\ \mathrm{kJ/mol}$$

$$\mathrm{Na^{+}(g)} \longrightarrow \mathrm{Na^{2+}(g)} + \mathrm{e^{-}} \qquad \Delta H = +4562\ \mathrm{kJ/mol}$$

Elements with low ionization energies tend to lose electrons and form cations.

### Periodic Trends in First Ionization Energies

Across a period, $I_1$ generally increases with increasing $Z_{\text{eff}}$ and decreasing distance from the nucleus. However, there are several exceptions.

Boron (B) and aluminum (Al), in group 13, lie to the right of beryllium (Be) and magnesium (Mg), in group 2, but have lower $I_1$. This is explained by the subshell model and was one of the key observations that led to its development.

Although B and Al have one more valence electron than Be and Mg, the additional electron occupies an *np* subshell, while all of Be and Mg's valence electrons are in an *ns* subshell. The *np* subshell is higher in energy than the *ns* subshell, and its electrons are more easily removed.

Another exception occurs between groups 15 and 16. Oxygen (O) and sulfur (S) lie to the right of nitrogen (N) and phosphorus (P), but have lower $I_1$. This is explained by Hund's rule, which states that unpaired electrons are more stable than paired ones.

N and P each have three *np* electrons. All three are unpaired. O and S have four *np* electrons. Two are unpaired, and two are paired. Paired electrons experience greater repulsion than unpaired electrons and are less stable, making them easier to remove.

Down a group, $I_1$ generally decreases. As noted earlier, the electrostatic attraction decreases with increasing distance from the nucleus.

These trends apply only to the representative elements. For transition metals, $I_1$ increases gradually across a period and shows no consistent trend down a group. An explanation of this behavior is beyond the scope of this level.

## Electron Affinity

**Electron affinity** ($EA$) is the energy change that occurs when a gas-phase atom accepts an electron to form an anion. It is expressed in kJ/mol.

In many atoms, gaining an additional electron increases stability and releases energy. Although the existing electrons repel the added one, the energy released is sufficient to overcome the repulsion. For these atoms, the process results in a net release of energy, and $EA$ is negative.

In others, the energy released is not sufficient to overcome electron repulsion. Energy must be supplied to overcome the repulsion and add the electron. For these atoms, $EA$ is positive.

For example, the halogens are highly electronegative, and the addition of a single electron completes their valence shell. The energy released by adding the electron far exceeds the repulsion from existing electrons, resulting in a highly negative $EA$.

In contrast, the noble gases have filled valence shells and gain no additional stability by accepting another electron. Energy must be supplied to cause the atom to accept the electron, resulting in a positive $EA$.

### Periodic Trends in Electron Affinity

There is no consistent trend in electron affinity across a period or down a group. It generally varies by group. Halogens have the most negative electron affinities.

Noble gases have positive electron affinities. Beryllium and magnesium also have positive electron affinities because their *ns* subshells are filled.

Nitrogen and phosphorus have less negative electron affinities than carbon (C) and silicon (Si). This is explained by Hund's rule. C and Si each have 2 *np* electrons, so an added electron can enter an empty orbital. N and P have 3 *np* electrons, so an added electron must pair with an existing one, increasing repulsion and decreasing stability. As a result, more energy is required, and the electron affinity is less negative.

# Chapter 16

# Metals, Nonmetals, and Element Groups

## 16.1 Metals, Nonmetals, and Metalloids

### Classification of Metals and Nonmetals

Elements are classified as **metals**, **nonmetals**, or **metalloids**.

Metals are defined as elements that exhibit metallic properties. These properties are described in the next section. Metalloids exhibit only some metallic properties. Nonmetals exhibit none.

### Metallic Properties

#### Physical Properties

Most metals are lustrous, malleable (can be hammered into thin sheets), ductile (can be drawn into wires), good conductors of heat and electricity, and have high melting points. All are solid at room temperature, except mercury (Hg), which is liquid.

#### Ionization Energy

All metals have low first ionization energies. This is the primary indicator of metallic character. All other metallic properties result from this readiness to lose valence electrons.

#### Ionic Charge

The *s*-block metals, Group 1 and Group 2, have *ns* valence electrons. They tend to lose these electrons to achieve a noble gas configuration. Group 1 metals have one *ns* electron and form $^{1+}$ ions. Group 2 metals have two *ns* electrons and form $^{2+}$ ions.

The *p*-block metals have *ns* and *np* valence electrons. Some lose only the *np* electrons. Others lose both the *np* and *ns* electrons. A third group can lose either only the *np* electrons or both, depending on the chemical environment.

For example, tin [Kr] $5s^2\,4p^2$ can lose only its $5p$ electrons to form $Sn^{2+}$, or lose both the $5p$ and $5s$ electrons to form $Sn^{4+}$.

Transition metals have a filled valence *ns* subshell, no valence *np* subshell, and a partially filled valence *nd* subshell. Their ionization patterns are complex. Many have multiple possible ionization states.

#### Chemical Properties

Metals react with nonmetals to form ionic compounds. They most readily react with halogens because of the halogens' high electronegativity.

Because oxygen is the most abundant element in Earth's crust, most naturally occurring metals are found in oxo compounds.

## Nonmetals

### Physical Properties

Nonmetals are not lustrous, are brittle in the solid state, are poor conductors of heat and electricity, and have lower melting and boiling points than metals.

### Elemental State

The noble gases exist as monatomic gases.
Seven nonmetals form diatomic molecules: $H_2$, $N_2$, $O_2$, $F_2$, and $Cl_2$ are gases; $Br_2$ is a liquid; $I_2$ is a volatile solid that sublimes.
The remaining nonmetals are solids. Some, such as carbon, are hard. Others, such as sulfur, are soft.

# 16.2 Element Groups

## Group 1: Alkali Metals

Alkali metals are soft, lustrous, good conductors of heat and electricity, and have low density and melting points.
They are very reactive and have the lowest $I_1$. Each has a single valence electron, which they readily lose to achieve a noble gas configuration, forming $^{1+}$ ions. This process is highly exothermic.
Each emits a characteristic flame color. Because they have low ionization energy, the valence electron is easily excited to a higher energy level, and releases a photon when it returns to the ground state.
Down the group, density increases and melting point decreases.
They react vigorously with water to form metal hydroxides and release hydrogen gas, which often ignites.

$$2\,\mathrm{M(s)} + 2\,\mathrm{H_2O(l)} \longrightarrow 2\,\mathrm{MOH(aq)} + \mathrm{H_2(g)}$$

where $M$ represents an alkali metal.
They also react readily with oxygen, but form different oxygen ions. Lithium (Li) forms lithium oxide ($Li_2O$), which contains oxide ($O^{2-}$). Sodium (Na) forms sodium peroxide ($Na_2O_2$), which contains peroxide (${O_2}^{2-}$). Potassium (K) and heavier alkali metals form superoxides ($MO_2$), which contain superoxide (${O_2}^{-}$).

$$4\,\mathrm{Li(s)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{Li_2O(s)}$$
$$2\,\mathrm{Na(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{Na_2O_2(s)}$$
$$\mathrm{K(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{KO_2(s)}$$

Down the group, atomic radius increases and $I_1$ decreases.
Most naturally occurring alkali metals are found as cations in ionic compounds. Sodium (Na) and potassium (K) are abundant in Earth's crust, seawater, and biological systems.

## Group 2: Alkaline Earth Metals

Alkaline earth metals have properties similar to those of alkali metals but are harder, denser, and have higher melting points and $I_1$. They react with nonmetals, though less vigorously than alkali metals. Those lower in the group have lower $I_1$, are reactive with water at room temperature, and produce a characteristic flame color.
Each has 2 valence electrons. They readily lose both to achieve a noble gas configuration, forming $^{2+}$ ions.
Most naturally occurring alkaline earth metals are found as cations in ionic compounds. Like sodium and potassium, magnesium (Mg) and calcium (Ca) are abundant in Earth's crust, seawater, and biological systems.

## Hydrogen

Hydrogen does not fit into any classical group. It has a single valence electron, like Group 1 metals, and can form $H^+$ cations. However, except under extreme pressure, it does not show metallic properties and has a higher $I_1$ than any metal.

In its elemental form, it is a colorless, diatomic gas, $H_2$.

Because hydrogen has a higher $I_1$ than metals, it forms covalent bonds with nonmetals rather than ionizing to $H^+$. These compounds are often acidic. In such molecules, the nonmetal is more electronegative than hydrogen and attracts the bonding electrons, allowing the hydrogen proton to dissociate as $H^+$.

For example, hydrogen reacts with chlorine (Cl) to form hydrogen chloride (HCl), a gas that acts as an acid when dissolved:

$$\mathrm{H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g)}$$
$$\mathrm{HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)}$$

## Group 16: Chalcogens

Chalcogens have a valence electron configuration of $ns^2np^4$. They require two additional electrons to fill their valence shell and often reach an oxidation number of $-2$.

Down the group, metallic character increases. Oxygen (O), sulfur (S), and selenium (Se) are nonmetals, tellurium (Te) is a metalloid, and polonium (Po) is a radioactive metal. All are solid at room temperature, except oxygen, which is a gas.

### Oxygen

**Allotropes** are different forms of the same element.

Oxygen has two allotropes: molecular oxygen ($O_2$), which makes up 21% of Earth's atmosphere, and ozone ($O_3$), which occurs in the upper atmosphere and absorbs ultraviolet radiation.

Oxygen has a high electron affinity and tends to oxidize other elements. It generally reacts with metals to form oxide ion ($O^{2-}$) and with nonmetals to reach an oxidation number of $-2$. The only element more electronegative is fluorine.

Oxygen can also form peroxide (${O_2}^{2-}$) and superoxide (${O_2}^{-}$) ions. These often decompose to molecular oxygen and oxide.

### Sulfur, Selenium, and Tellurium

Sulfur's most stable form is $S_8$, a solid yellow ring of 8 sulfur atoms, often simplified as S(s).

Sulfur generally reacts with metals to form $S^{2-}$ and with nonmetals to reach an oxidation number of $-2$, but it is less electronegative than oxygen.

Most naturally occurring sulfur is found in metal sulfides.

Selenium is rare but essential in trace amounts in biological systems. It is chemically similar to sulfur, and many of its allotropes resemble $S_8$ rings.

Elemental tellurium forms complex structures.

## Group 17: Halogens

Unless specified otherwise, *halogens* refers to fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). Astatine (At) and tennessine (Ts) are radioactive and unstable, and their properties are mostly unknown.

Halogens are nonmetals and exist as diatomic molecules in their elemental form.

Down the group, melting and boiling points increase. At room temperature, fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid.

Halogens require 1 additional electron to complete their valence shell and are strongly electronegative. They react with metals to form ionic halides and with hydrogen to form hydrogen halides. Hydrogen halides are gases that dissolve in water and act as acids.

Fluorine is the most electronegative and reactive element and strongly oxidizes nearly all substances.

For example, fluorine reacts vigorously with water:

$$2\,H_2O\,(l) + 2\,F_2(g) \longrightarrow 4\,HF\,(aq) + O_2 \qquad \Delta H = -758.9 \text{ kJ}$$

Chlorine is more stable than fluorine and is widely used as a disinfectant. Elemental chlorine is produced from chloride ions ($Cl^-$) by electrolysis. It reacts with water to form both hydrochloric acid (HCl) and hypochlorous acid (HOCl):

$$Cl_2(g) + H_2O\,(l) \longrightarrow HCl\,(aq) + HOCl\,(aq)$$

## Group 18: Noble Gases

The noble gases are nonmetals and exist as monatomic gases at room temperature. Radon (Rn) and oganesson (Og) are highly radioactive, and their properties are mostly unknown.

Noble gases have a complete valence shell, making them exceptionally unreactive. They all have an electron configuration of $ns^2np^6$ except helium, which has $1s^2$. They were initially thought to be incapable of forming stable bonds until krypton (Kr) and xenon (Xe) were synthesized into stable compounds in the 1960s.