Unit 1

ATOMIC STRUCTURE AND PERIODIC PROPERTIES OF THE ELEMENTS

Early Philosophical Ideas about Matter

Ancient Greek philosophers debated the nature of matter—whether it was continuously divisible or composed of indivisible particles. Most philosophers, including Plato and Aristotle, believed matter was continuous. However, Democritus (460–370 BC) proposed that matter could be divided until reaching tiny, indestructible particles called "atomos," meaning "indivisible."

Dalton's Atomic Theory

Though Democritus's ideas were based on philosophical speculation and not widely accepted for nearly 2000 years, John Dalton revived and expanded on these ideas in 1808, creating an atomic theory grounded in scientific evidence. Dalton's theory was based on two fundamental laws:

1. **Law of Conservation of Mass**: Mass is neither created nor destroyed in chemical reactions.
2. **Law of Definite Proportions**: A chemical compound always contains the same elements in the same proportion by mass.

Dalton formulated his atomic theory based on these laws, asserting that all matter is composed of atoms, which are indivisible and indestructible, and that atoms of the same element are identical in mass and properties.

Example Problems

1. **Mass Calculation from Water**:
    - Given that water is 11.2% hydrogen and 88.8% oxygen by mass:
        - For 18.0 g of water:
            - Mass of hydrogen = 0.112 × 18.0 g = 2.02 g
            - Mass of oxygen = 18.0 g - 2.02 g = 15.98 g
        - For 1.00 g of water:
            - Mass of hydrogen = 0.112 × 1.00 g = 0.112 g
            - Mass of oxygen = 1.00 g - 0.112 g = 0.888 g
2. **Law of Multiple Proportions**:
    - Consider the compounds A, B, and C with different nitrogen-oxygen ratios:

        - Compound A: 1.750 g of nitrogen per 1 g of oxygen
        - Compound B: 0.8750 g of nitrogen per 1 g of oxygen
        - Compound C: 0.4375 g of nitrogen per 1 g of oxygen
    - The ratios of nitrogen masses in these compounds (4:2:1) illustrate the law of multiple proportions, which states that when two elements combine in different ways to form different compounds, the ratios of the masses of one element that combine with a fixed mass of the other element are small whole numbers.

Discovery of the Electron

J.J. Thomson's Experiments: In 1897, J.J. Thomson conducted experiments using cathode rays, which led to the discovery of the electron. He used a glass tube with electrodes connected to a high-voltage source. When the current was turned on, a greenish light appeared, caused by cathode rays originating from the cathode. These rays were deflected by electric and magnetic fields, leading Thomson to conclude that they consisted of negatively charged particles (electrons), present in all matter.

Thomson measured the mass-to-charge ratio of an electron as -5.686×10^{-12} kg/C. However, the exact mass or charge of the electron was determined later by Robert A. Millikan through his oil-drop experiment. Millikan measured the charge of an electron as -1.602×10^{-19} C, allowing the calculation of the electron's mass as 9.109×10^{-31} kg.

Discovery of Radioactivity

Radioactivity is the spontaneous emission of particles or radiation from unstable atomic nuclei. Discovered shortly after Dalton's theory, radioactivity was found to involve three types of radiation:

- **Alpha (α) rays**: Positively charged particles, identical to helium nuclei.
- **Beta (β) rays**: Negatively charged electrons.
- **Gamma (γ) rays**: High-energy rays with no charge.

Discovery of the Nucleus and Neutron

Rutherford's Gold Foil Experiment: Ernest Rutherford tested Thomson's "plum-pudding" model by directing α-particles at a thin gold foil. He observed that while most particles passed through, some were deflected, suggesting the existence of a small, dense, positively charged nucleus at the center of the atom.

Discovery of the Neutron: In 1932, James Chadwick discovered the neutron, a neutral particle within the nucleus, through alpha-particle scattering experiments. The neutron's mass is nearly identical to the proton's but carries no electric charge.

Subatomic Particles:

Discovery of the Proton:

In 1919, Ernest Rutherford discovered that hydrogen nuclei, or what we now call protons, are formed when alpha particles strike lighter elements like nitrogen. A proton is a nuclear particle with a positive charge equal in magnitude to that of an electron but with a mass of 1.67262×10^{-27}kg, which is about 1840 times the mass of an electron. Protons in a nucleus give the nucleus its positive charge.

Subatomic Particles:

Atoms consist of three primary subatomic particles: protons, neutrons, and electrons. Their properties are summarized in the table below:

Particle	Actual Mass (kg)	Relative Mass (amu)	Actual Charge (C)	Relative Charge
Proton (p)	1.672622×10^{-27}	1.007276	1.602×10^{-19}	+1
Neutron (n)	1.674927×10^{-27}	1.008665	0	0
Electron (e^-)	9.109383×10^{-31}	5.485799×10^{-4}	-1.602×10^{-19}	-1

Atomic Number and Mass Number:

- The **atomic number (Z)** of an element equals the number of protons in the nucleus of its atoms. Each element has a unique atomic number.
- The **mass number (A)** is the total number of protons and neutrons in the nucleus of an atom.

Atomic Mass and Isotopes:

All atoms of an element have the same atomic number but can differ in mass number. These variations are called isotopes. Isotopes are atoms with the same number of protons but different numbers of neutrons. For example, carbon has three naturally occurring isotopes: ^{12}C, ^{13}C, and ^{14}C, with mass numbers 12, 13, and 14 respectively.

Isotopes in Nature:

Most elements in nature are mixtures of isotopes. The average atomic mass of an element is calculated as the weighted average of the masses of its isotopes, taking into account their relative abundances.

Sample Exercises:

1. **Proton and Neutron Count:**
    - **${}_{13}^{27}Al$:** 13 protons, 14 neutrons
    - **${}_{16}^{32}S$:** 16 protons, 16 neutrons
    - **${}_{30}^{64}Zn$:** 30 protons, 34 neutrons
    - **${}_{82}^{207}Pb$:** 82 protons, 125 neutrons
2. **Element Identification:**
    - **Element X:** Contains 24 protons, identified as Chromium (Cr).
    - **Isotopes:** ${}^{50}Cr$, ${}^{52}Cr$, ${}^{53}Cr$, ${}^{54}Cr$ for neutrons 26, 28, 29, and 30 respectively.
3. **Isotope Abundance Calculation for Boron:**
    - ${}^{10}B$: Calculate based on given isotopic masses and observed atomic mass of 10.811 amu.
4. **Lithium Isotope Abundance:**
    - Determine which isotope, ${}^{6}Li$ or ${}^{7}Li$, occurs in greater abundance by comparing their masses to the atomic mass of lithium.

Atomic Spectra

Atomic spectra, also known as line spectra, are produced when atoms emit photons of light (electromagnetic radiation). These spectra are unique to each element and occur when atoms are energized, typically through an electric discharge, such as a spark passing through a gas like hydrogen. The electric current excites the electrons in the atoms, raising them to higher energy levels. When these electrons return to lower energy levels, they release the absorbed energy as light.

If this light is passed through a prism, it produces a series of discrete lines instead of a continuous spectrum like sunlight. These lines represent specific wavelengths of light that correspond to the energy differences between the atomic energy levels. Each element has a unique atomic spectrum, which can be used to identify the element.

The Bohr Model of the Hydrogen Atom

In 1913, Niels Bohr developed a model of the hydrogen atom to explain why the electron does not radiate energy as it orbits the nucleus. He proposed that the energy changes in the atom are quantized, meaning only certain energy levels are allowed.

Key assumptions of Bohr's model include:

1. The electron orbits the nucleus in a circular path.
2. The energy of the electron is proportional to its distance from the nucleus; the further away, the higher the energy.
3. Only certain orbits with specific energies are allowed (quantized orbits).
4. The angular momentum of the electron is an integer multiple of $h/2\pi$ (where h is Planck's constant).
5. The electron does not lose or gain energy while in a given orbit.
6. The electron moves to a higher orbit by absorbing light and emits light when falling to a lower orbit, with the energy difference corresponding to the photon emitted or absorbed.

Bohr showed that the radius of permitted orbits for a hydrogen atom is proportional to the square of an integer called the quantum number (nnn). The energy levels of the electron in the hydrogen atom can be calculated using the equation:

$$E_n = -\frac{RH}{n2}$$

where R_H is the Rydberg constant (2.18×10^{-18} J). The negative sign indicates that the energy of an electron in an atom is lower than that of a free electron, which has zero energy.

The lowest energy state (n=1) is the ground state, and higher energy states (n > 1) are excited states. The Bohr model can also be used to calculate the energy change when an electron transitions between two energy levels, which corresponds to the emission or absorption of light.

Limitations of the Bohr Model

Although the Bohr Model was a significant advancement, it has limitations:

- It only explains the spectra of hydrogen and hydrogen-like ions (such as He^+ and Li^{2+}).
- It cannot explain the spectra of more complex atoms.
- It does not account for the splitting of spectral lines in a magnetic field (Zeeman effect).
- It assumes electrons have a known radius and orbit, which contradicts Heisenberg's Uncertainty Principle.

Atomic Spectra Series

In hydrogen, the spectral lines are grouped into series, each corresponding to transitions to a lower energy level. Notable series include:

- **Lyman Series**: Transitions to n=1n=1n=1 (ultraviolet region).
- **Balmer Series**: Transitions to n=2n=2n=2 (visible and ultraviolet region).
- **Paschen Series**: Transitions to n=3n=3n=3 (infrared region).
- **Brackett Series**: Transitions to n=4n=4n=4 (infrared region).

Each spectral line corresponds to a specific electron transition, and the greater the drop in energy level, the higher the energy of the emitted photon.

The Wave-Particle Duality of Matter and Energy

In 1924, Louis de Broglie, a French physicist, proposed a revolutionary idea: if energy can exhibit both wave-like and particle-like properties, then perhaps matter can also exhibit wave-like properties. This idea was groundbreaking because it offered a new way to explain the fixed energy levels of electrons in atoms, which were a mystery at the time.

De Broglie combined Einstein's equation for energy and mass equivalence ($E=mc^2$) with Planck's equation for the energy of a photon ($E=hv=\frac{hc}{\lambda}$). By doing so, he derived an equation for the wavelength of any particle with mass m and velocity v:

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

According to this equation, matter, like energy, exhibits both wave-like and particle-like properties. This dual nature is only noticeable at the atomic level; in the macroscopic world, the wave properties of matter are negligible.

The Quantum Mechanical Model of the Atom

The Bohr model, which depicted electrons as orbiting the nucleus like planets around the Sun, had limitations. It could not explain certain atomic properties. To address these shortcomings, scientists developed quantum mechanics, a theory that provides a more accurate description of how electrons are arranged in atoms.

Two key concepts in quantum mechanics are the wave behavior of matter and the uncertainty principle. These ideas are crucial for understanding the electronic structure of atoms.

The Heisenberg Uncertainty Principle

Werner Heisenberg, a German physicist, introduced the uncertainty principle in 1927. This principle states that it is impossible to know both the position and momentum of a particle with great precision at the same time. For a subatomic particle like an electron, if you measure its momentum precisely, its position becomes less certain, and vice versa. Mathematically, this is expressed as:

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

This principle has significant implications for atomic and subatomic particles, where precise measurements are impossible due to the wave-like nature of particles.

Schrödinger's Wave Equation and Quantum Numbers

Erwin Schrödinger proposed a mathematical equation, called the wave function (ψ), to describe the behavior of electrons in an atom. The square of the wave function (ψ^2) gives the probability of finding an electron in a certain region of space. This probability distribution defines the electron's orbital, which is the region around the nucleus where the electron is most likely to be found.

In quantum mechanics, each electron in an atom is described by four quantum numbers:

1. **Principal Quantum Number (n):** Indicates the main energy level of the electron.
2. **Angular Momentum Quantum Number (ℓ):** Describes the shape of the orbital.
3. **Magnetic Quantum Number (m_ℓ):** Specifies the orientation of the orbital in space.
4. **Spin Quantum Number (m_s):** Describes the spin of the electron, which can be either +½ or -½.

These quantum numbers define the unique state of an electron in an atom.

Shapes of Atomic Orbitals

- **s orbitals** are spherical and centered around the nucleus.

- **p orbitals** are dumbbell-shaped and oriented along the x, y, and z axes.
- **d orbitals** have more complex shapes and are found in higher energy levels.

Electron Configurations

The arrangement of electrons in an atom's orbitals follows specific rules:

1. **Aufbau Principle:** Electrons fill the lowest energy orbitals first.
2. **Hund's Rule:** Electrons occupy degenerate (equal energy) orbitals singly before pairing up.
3. **Pauli Exclusion Principle:** No two electrons in an atom can have the same set of four quantum numbers.

Understanding these rules helps to predict and explain the chemical properties of elements based on their electron configurations.

The Modern Periodic Table:

The modern periodic table is a systematic arrangement of elements based on their atomic numbers. This arrangement allows scientists to predict the properties of elements and understand their similarities and differences. The concept behind this organization is known as the **periodic law**, which states that the physical and chemical properties of elements repeat in a regular pattern when arranged by increasing atomic number.

Classification of Elements

The periodic table is divided into periods (horizontal rows) and groups (vertical columns). There are 7 periods and 18 groups. Elements in the same group have similar outer-shell electron configurations, leading to similar chemical properties. The period number indicates the principal quantum number (n) of the outermost electron shell.

- **Metalloids** are elements with properties between those of metals and non-metals, such as boron, silicon, and germanium.

Atomic Size (Atomic Radii)

Atomic size is determined by the distance between the nuclei of two adjacent atoms, known as the atomic radius. This size varies in a predictable way across periods and groups due to two main factors: the principal quantum number (n) and the effective nuclear charge (Z_{eff}).

- **Across a Period:** Atomic radius decreases from left to right due to an increase in Z_eff, which pulls electrons closer to the nucleus.
- **Down a Group:** Atomic radius increases as new electron shells are added, increasing the distance between the nucleus and the outermost electrons.

Ionization Energy (IE)

Ionization energy is the energy required to remove an electron from a gaseous atom or ion. It is a key factor in determining an element's chemical reactivity.

- **First Ionization Energy (IE1):** The energy required to remove the first electron.
- **Trends:** Ionization energy generally increases across a period due to increasing Z_eff and decreases down a group as the atomic radius increases, making it easier to remove an electron.

Electron Affinity (EA)

Electron affinity is the energy change when an electron is added to a neutral atom to form a negative ion.

- **First Electron Affinity (EA1):** Typically negative, as energy is released when an electron is added.
- **Trends:** Electron affinity becomes more negative across a period and varies down a group, with elements in groups VIA and VIIA having the most negative values.

Electronegativity

Electronegativity is a measure of an atom's ability to attract and hold onto electrons within a chemical bond.

- **Trends:** Electronegativity increases across a period due to a decreasing atomic radius and increasing Z_eff. It decreases down a group as the atomic radius increases.

Metallic Character

Metallic character refers to the tendency of an element to lose electrons and exhibit metallic properties.

- **Trends:** Metallic character decreases across a period (left to right) as elements are more likely to gain electrons than lose them. It increases down a group as the atomic radius increases, making it easier for atoms to lose electrons.

Advantages of Periodic Classification of Elements

Periodic classification of elements offers several key advantages, making it a powerful tool for understanding and predicting the properties of elements. Here are the main benefits:

1. **Based on Atomic Number**: The periodic table is organized according to the atomic number, a fundamental property of elements, ensuring a logical and consistent arrangement.
2. **Incorporation of Isotopes**: Isotopes of the same element are grouped together in a single place because they have the same atomic number, simplifying their study. For example, chlorine's atomic mass is averaged to 35.5, despite its isotopes having different masses.
3. **Explanation of Periodicity**: The periodic classification explains the repeating patterns in the properties of elements, known as periodicity. This periodicity is directly related to the elements' electronic configurations.
4. **Resolution of Anomalous Pairs**: Elements that seemed out of place when organized by mass number (like argon and potassium) find logical positions when organized by atomic number, resolving previous anomalies.
5. **Separation of Lanthanides and Actinides**: The lanthanides and actinides, which have unique properties, are placed separately at the bottom of the periodic table. This keeps the table's structure clear and focused.
6. **Simplification of Element Properties**: The periodic table provides a simple and systematic way to remember the properties of elements, as it organizes them based on electronic configuration, making it easier to understand and predict their behavior.