CASCH 131
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Contents

Chapter 1

Atomic Theory and the Nature of Modern Chemistry

1.1   1.1 - The Nature of Modern Chemistry

> **Definition 1.1.1: Conservation of Energy and Mass**
>
> Energy and mass are conserved in ordinary chemical reactions. The total mass of the products equals the total mass of the reactants.

> **Theorem 1.1.1** Macroscopic and Nanoscopic Length Scales
> Chemical reactions occur on the scale of nanometers, yet are observed in laboratories on scales of grams and centimeters.

1.2   The Atom in Modern Chemistry

> **Note:-**
> Modern Chemistry Timeline

Modern chemistry is approximately 300 years old, with its roots dating back to the late 18th and early 19th centuries. Several foundational laws and principles emerged during this period, forming the basis of modern chemical science.

1.2.1   Lavoisier: Conservation of Mass and Energy

> **Definition 1.2.1: Law of Conservation of Mass and Energy**
>
> Antoine Lavoisier (1743–1794) formulated the Law of Conservation of Mass, which states that in a chemical reaction, mass is neither created nor destroyed. This principle was later extended to include energy, particularly after the development of modern physics.

> **Note:-**
> Note on Lavoisier's Contribution

Lavoisier's discovery revolutionized chemistry by providing a quantitative approach to chemical reactions. He is often called the "Father of Modern Chemistry."

1.2.2 Proust: Law of Constant Composition

Definition 1.2.2: Law of Constant Composition (Definite Proportions)

Joseph Proust (1754–1826) established the Law of Constant Composition, which states that a given chemical compound always contains its component elements in a fixed ratio by mass, regardless of its source or method of preparation.

Note:-
Proust's Discovery

This law was critical in distinguishing compounds from mixtures and emphasized the fixed, predictable nature of chemical compounds.

1.2.3 Dalton: Law of Multiple Proportions

Definition 1.2.3: Law of Multiple Proportions

John Dalton (1766–1844) introduced the Law of Multiple Proportions, which states that when two elements form more than one compound, the masses of one element that combine with a fixed mass of the other are in ratios of small whole numbers.

Note:-
Example of Dalton's Law

For example, carbon and oxygen form two compounds: carbon monoxide (CO) and carbon dioxide (CO_2). The mass ratio of oxygen in CO_2 to CO is 2:1.

1.2.4 Gay-Lussac: Law of Combining Volumes

Definition 1.2.4: Law of Combining Volumes

Joseph Louis Gay-Lussac (1778–1850) discovered that when gases react together at constant temperature and pressure, the volumes of the reactants and products (if gaseous) are in simple whole number ratios. This is known as the Law of Combining Volumes.

Note:-
Gay-Lussac's Contribution

This law played a crucial role in understanding the stoichiometry of gaseous reactions and helped pave the way for Avogadro's hypothesis.
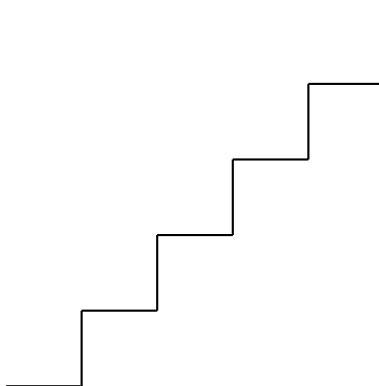
The staircase diagram illustrates the progressive development of chemistry over time, where each step represents a major discovery that builds on the previous one.

1.3   1.2 - Elements: The Building Blocks of Matter

Definition 1.3.1: Mixtures and Compounds

Mixtures can be separated by physical processes (e.g., filtration, distillation). Compounds are substances that can only be separated into simpler substances by chemical reactions.

1.4   1.3 - Indirect Evidence for the Existence of Atoms

Definition 1.4.1: Dalton's Atomic Theory

Atoms are indivisible, retain their identity in chemical reactions, and combine in fixed whole-number ratios to form compounds.

Note:-

Laws of Chemical Combination

The laws of definite proportions and multiple proportions form the basis for determining chemical formulas.

1.5   1.4 - The Physical Structure of Atoms

Definition 1.5.1: Cathode Ray Experiment

Cathode rays are negatively charged particles (electrons) with a charge-to-mass ratio measured by Thomson and charge measured by Millikan.

Theorem 1.5.1 Planetary Model of the Atom

The scattering of alpha particles by gold established the planetary model: a dense nucleus surrounded by electrons.

1.6   1.5 - Mass Spectrometry and Isotopes

Note:-

Relative Atomic Masses

Elements have isotopes with different masses but identical chemical properties.

1.7   1.6 - The Mole: Counting Molecules by Weighing

Definition 1.7.1: Avogadro's Number

$1\,\text{mol} = 6.022 \times 10^{23}$ molecules. Molar mass is used to convert between mass, moles, and the number of molecules.

Chapter 2

19 - Nucleosynthesis of the Elements

2.1   19.1 - Mass-Energy in Nuclei

> **Definition 2.1.1: Nuclear Symbols**
>
> Number of nucleons A
> Number of protons Z
>
> $$^{A}_{Z}\text{X}$$

2.2   19.2 - Nuclear Decay

> **Definition 2.2.1: Nuclear Decay Process**
>
> $^{A}_{Z}\text{X}$ — Alpha Decay → $^{A-4}_{Z-2}\text{Y} + ^{4}_{2}\text{He}$
>
> Beta (Minus) Decay
>
> Gamma Decay
>
> $^{A}_{Z+1}\text{Y} + ^{0}_{-1}\beta$ $\qquad$ $^{A}_{Z}\text{X}^{*} \rightarrow ^{A}_{Z}\text{X} + \gamma$
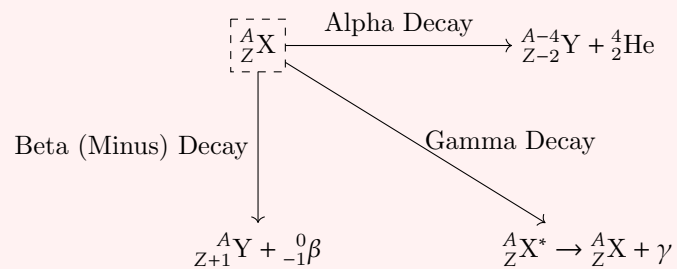
> **Definition 2.2.2: Alpha Decay**
>
> **Alpha decay** is the most common nuclear decay process.
> Alpha decay is most common in nuclei with atomic number greater than 82 (the highest binding energy per nuclei).

Definition 2.2.3: Binding Energy per Nucleon

$$\Delta E = \Delta m c^2$$

$$\Delta E = M_{Z,A} - (M_{Z-2} + M_{2,\alpha})\, c^2 > 0$$

If $\Delta E > 0 \quad \Rightarrow \quad$ Decay Occurs

If $\Delta E < 0 \quad \Rightarrow \quad$ Stable

Figure 1
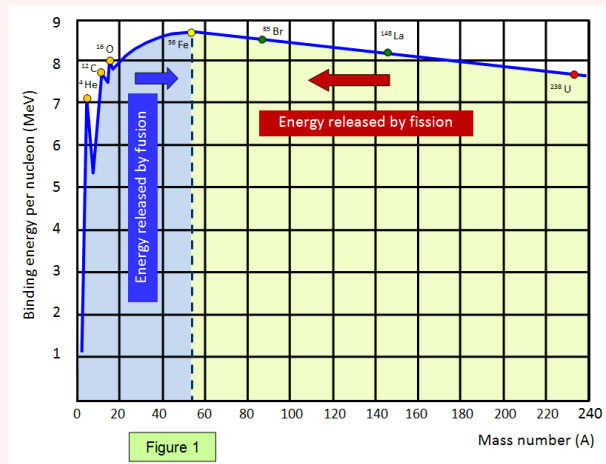
Definition 2.2.4: Beta Decay

Beta decay occurs when a nucleus emits or absorbs a neutron.
Beta decay is very common in nuclei with atomic number less than 82.

Definition 2.2.5: Gamma Decay

Gamma decay occurs when a nucleus emits or absorbs a photon.
Gamma decay is rare, but it can occur in high-energy nuclei.
Photons of electromagnetic radiation that carry away excess energy when nuclei make γ decay.

2.3 19.6 - Nuclear Fusion

Definition 2.3.1: Origin of elements

Fusion of elements involves 2 nuclei of very low A amalgamating to a form a more stable nucleus.
Getting the A value nearer to 56 (the highest Binding Energy per nucleon).

> **Note:-**
>
> Hubbles observaions of red shift in further galaxies and knowledge of fusion leads us to predict the existence of a singularity at the start of the current universe. What came before this is not known, but it is believed to be a singularity of the same type as the one at the end of the universe.
> **The Steady State model** states that the densigty of the expanding universe should remain constant. As the universe expands, the density of matter stays the same as more matter is created.

Definition 2.3.2: Initial Events of Big Bang

$$_0^1\text{n} \rightarrow _1^1\text{H} + e^- + \bar{\nu}_e$$
$$_1^1\text{H} + \nu_e \rightarrow _0^1\text{n} + e^+$$
$$_1^1\text{H} + _0^1\text{n} \rightarrow _1^2\text{H} + \gamma$$
$$e^+ + e^- \rightarrow \gamma + \gamma$$

Then

$$_1^1\text{H} + _0^1\text{n} \rightarrow _1^2\text{H} + \gamma$$
$$_1^2\text{H} + _1^2\text{H} \rightarrow _2^3\text{He} + _0^1\text{n}$$
$$_2^3\text{He} + _0^1\text{n} \rightarrow _2^4\text{He} + \gamma$$
$$_2^3\text{He} + _1^1\text{H} \rightarrow _2^4\text{He}$$
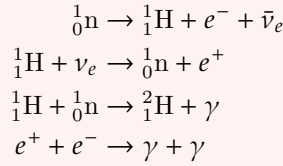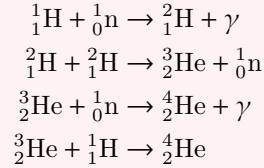
Helium 3 (werid particle due to its quantum behavior) and helium 4 are created $1/10$ of the time

Note:-

The fusion of 1 gram deuterium and helium 3 gives about 350 billion joules of energy. Reason for which we are trying to reproduce fission on earth

Theorem 2.3.1 Clusters

Ripples in the helium and tritium gas clouds form denser regions, which group further due to gravity $\rightarrow$ hydrogen burn $\rightarrow$ HE is formed in a star cycle of reactions (proton-proton cycle) and heavier elements move towards the center. Outer portions do proton-proton burn, inner denser portions of the start do helium burn.$\rightarrow$ Helium 4's combine to make Beryllium $_4^8\text{Be}$. Beryllium and Helium combine to make carbon 12 $_6^{12}\text{C}$. $\rightarrow$ CARBON CYCLE occurs as $_6^{12}\text{C}$ is the catalyst. By adding helium $_2^4\text{He}$ to all the elements in the dense cores, all the elements up to iron $_{26}^{56}\text{Fe}$ formed, and then stopped due to it having the highest binding energy per nucleon.

Theorem 2.3.2 After Iron

A 14 particle collision is needed to make elements after Iron, which is very unlikely.

$$_{26}^{56}\text{Fe} + 13_0^1\text{n} \rightarrow _{26}^{69}\text{Co} + e$$
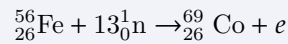
Note:-

Fusion only gets us 26 elements (in stars).

Chapter 3

Chemical Structures

3.1 Drawing Lewis Dot Structures

Lewis dot structures are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. Here's a step-by-step guide on how to draw Lewis dot structures:

### 3.1.1 Steps to Draw a Lewis Dot Structure

1. **Count the Valence Electrons:** Find the total number of valence electrons in the molecule by adding up the valence electrons of all atoms.
    2. **Arrange the Atoms:** Write the atoms in the molecule with the least electronegative atom as the central atom (except for hydrogen, which is always terminal).
    3. **Form Bonds Between Atoms:** Connect the atoms with single bonds. Each bond represents a pair of shared electrons.
    4. **Distribute Remaining Electrons:** Distribute the remaining valence electrons as lone pairs around the atoms to satisfy their octet (or duet for hydrogen).
    5. **Complete Octets:** Make sure that each atom (except hydrogen) has 8 electrons around it by sharing additional pairs of electrons to form double or triple bonds if necessary.
    6. **Check Formal Charges:** If necessary, minimize formal charges to ensure that the most stable structure is drawn.

3.1.2 Example Structures

Water (H_2O)

The water molecule consists of two hydrogen atoms and one oxygen atom. Oxygen has 6 valence electrons, and each hydrogen has 1 valence electron, making a total of 8 valence electrons.
    The Lewis structure is drawn as follows:

$$O$$
$$H \qquad H$$
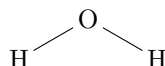
    In this structure, the oxygen atom forms single bonds with each hydrogen atom and has two lone pairs of electrons.

Carbon Dioxide (CO_2)

The carbon dioxide molecule consists of one carbon atom and two oxygen atoms. Carbon has 4 valence electrons, and each oxygen has 6, making a total of 16 valence electrons.
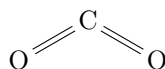   The Lewis structure is drawn as follows:

$$C$$
$$O \qquad\qquad O$$

    In this structure, the carbon atom forms double bonds with each oxygen atom, and each oxygen has two lone pairs of electrons.

3.2   Common Molecular Shapes

3.2.1   2 Electron Pairs - Linear - AX$_2$

In molecules with 2 bonding pairs and no lone pairs, the atoms are arranged in a straight line, resulting in a bond angle of 180°.

$$B \text{——} A$$

3.2.2   3 Electron Pairs - Trigonal Planar - AX$_3$

When there are 3 bonding pairs and no lone pairs, the atoms are positioned around the central atom in a single plane, forming a bond angle of 120°.
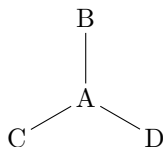
3 Electron Pairs (1 Lone Pair) - Bent - AX$_2$E

If there are 2 bonding pairs and 1 lone pair, the lone pair causes a repulsion that slightly decreases the bond angle to less than 120°.
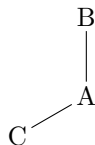
3.2.3   4 Electron Pairs - Tetrahedral - AX$_4$

For 4 bonding pairs and no lone pairs, the atoms are arranged in a tetrahedral shape with bond angles of 109.5°.
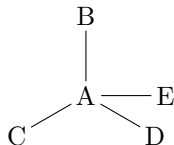
4 Electron Pairs (1 Lone Pair) - Trigonal Pyramidal - AX$_3$E

When there are 3 bonding pairs and 1 lone pair, the structure becomes trigonal pyramidal, and the lone pair repulsion decreases the bond angles to slightly less than 109.5°.

4 Electron Pairs (2 Lone Pairs) - Bent AX$_2$E$_2$

With 2 bonding pairs and 2 lone pairs, the shape is bent, with bond angles further reduced to less than 109.5°.

3.2.4 5 Electron Pairs - Trigonal Bipyramidal

For 5 bonding pairs and no lone pairs, the shape is trigonal bipyramidal, with bond angles of 90° (axial) and 120° (equatorial).

$$
\begin{array}{c}
B \\
C \diagdown \ \ \big| \ \diagup F \\
A \\
D \diagup \ \big| \\
E
\end{array}
$$
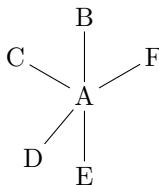
5 Electron Pairs (1 Lone Pair) - Seesaw

With 4 bonding pairs and 1 lone pair, the structure becomes a seesaw, and the bond angles are slightly adjusted due to lone pair repulsion.

$$
\begin{array}{c}
B \\
C \diagdown \ \ \big| \\
A \\
D \diagup \ \big| \\
E
\end{array}
$$
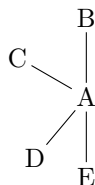
5 Electron Pairs (2 Lone Pairs) - T-Shaped

When there are 3 bonding pairs and 2 lone pairs, the shape is T-shaped, with bond angles around 90°.

$$
\begin{array}{c}
B \\
\big| \\
C \longrightarrow A \\
\big| \\
D
\end{array}
$$
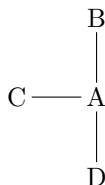
5 Electron Pairs (3 Lone Pairs) - Linear

With 2 bonding pairs and 3 lone pairs, the shape reverts to linear with a bond angle of 180°.

$$ B \longrightarrow A $$

3.2.5 6 Electron Pairs - Octahedral

In a molecule with 6 bonding pairs and no lone pairs, the atoms are arranged in an octahedral shape with bond angles of 90°.

$$
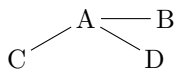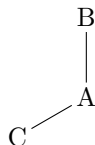\begin{array}{c}
B \\
C \diagdown \ \big| \ \diagup F \\
A \\
D \diagup \ \big| \ \diagdown G \\
E
\end{array}
$$
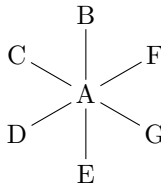
6 Electron Pairs (1 Lone Pair) - Square Pyramidal

For 5 bonding pairs and 1 lone pair, the structure is square pyramidal, with slightly less than 90° bond angles due to lone pair repulsion.

$$
\begin{array}{c}
B \\
C \diagdown \ \big| \ \diagup F \\
A \\
D \diagup \ \big| \\
E
\end{array}
$$

11
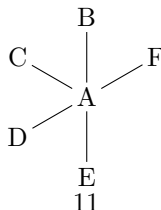
6 Electron Pairs (2 Lone Pairs) - Square Planar

With 4 bonding pairs and 2 lone pairs, the molecule is square planar, maintaining bond angles of 90°.

$$
\begin{array}{c}
\text{B} \\
\text{C} \quad | \\
\quad \diagdown \text{A} \\
\text{D} \quad \diagup \\
\quad | \\
\text{E}
\end{array}
$$
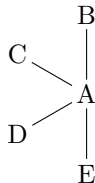
3.2.6 7 Electron Pairs - Pentagonal Bipyramidal

For 7 bonding pairs and no lone pairs, the atoms are arranged in a pentagonal bipyramidal shape with bond angles of 72° (within the pentagon) and 90° (between axial and equatorial positions).
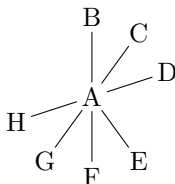
3.3 Dipole Moment

The dipole moment is a measure of the separation of positive and negative charges in a molecule. It is a vector quantity, possessing both magnitude and direction. Molecules with polar bonds may have a net dipole moment if their molecular geometry does not cancel out the individual bond dipoles. The dipole moment influences many physical properties such as solubility, boiling point, and reactivity.

3.3.1 Examples

Carbon Tetrachloride (CCl_4)

Carbon tetrachloride is a symmetric molecule where the four C–Cl bonds are directed towards the corners of a tetrahedron. Although each C–Cl bond is polar due to the difference in electronegativity between carbon and chlorine, the symmetry of the molecule causes the bond dipoles to cancel out, resulting in a net dipole moment of zero.
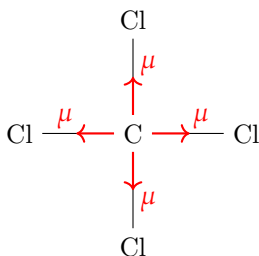
Figure 3.1: Molecular structure of CCl_4 showing bond dipoles cancelling out.

Chloroform ($CHCl_3$)

Chloroform has a similar tetrahedral geometry as carbon tetrachloride but with one hydrogen atom replacing one of the chlorine atoms. This asymmetry results in bond dipoles that do not completely cancel out, giving chloroform a net dipole moment.

12
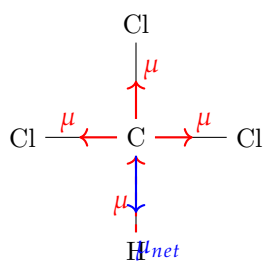
Figure 3.2: Molecular structure of CHCl$_3$ showing bond dipoles and net dipole moment.

Chapter 4

Quantum Mechanics

4.1 Electromagnetic Fields in Light

Electromagnetic (EM) waves are composed of electric and magnetic fields oscillating perpendicularly to each other and to the direction of wave propagation. Light is an example of an EM wave, and it travels at the speed of light in a vacuum.

The electric field (E) and magnetic field (B) are perpendicular to each other, and both are perpendicular to the direction of wave propagation. Below is a simplified representation of an electromagnetic wave:
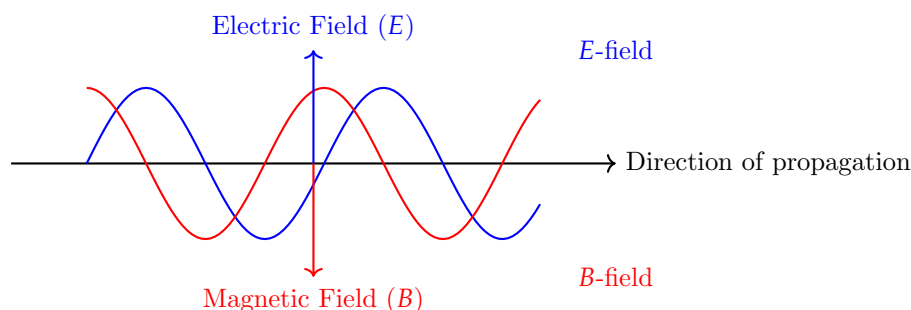
In this diagram, the electric field (E) oscillates in one plane, while the magnetic field (B) oscillates in a perpendicular plane. Both fields are sinusoidal and propagate together in the direction shown.

4.2 The Wave Equation: $c = f\lambda$

The relationship between the speed of light (c), the frequency (f), and the wavelength (λ) of an electromagnetic wave is given by the equation:

$$c = f\lambda$$

where:

- c is the speed of light in a vacuum, approximately 3×10^8 m/s,

- f is the frequency of the wave (in Hz),

- λ is the wavelength of the wave (in meters).

This equation shows that the speed of light is the product of its frequency and wavelength. As the frequency of a wave increases, its wavelength decreases, and vice versa.

4.3 The Electromagnetic Spectrum

The electromagnetic spectrum encompasses all types of electromagnetic radiation, ranging from low-frequency radio waves to high-frequency gamma rays. Below is a diagram showing the range of the spectrum:

Gamma Ray	X-Ray	Ultraviolet	Visible	Infrared	Microwave	Radio

Increasing Wavelength ←

10^{-12} 10^{-10} 10^{-8} 10^{-7} 10^{-6} 10^{-4} 10^{-2} 10^{0} → Wavelength (
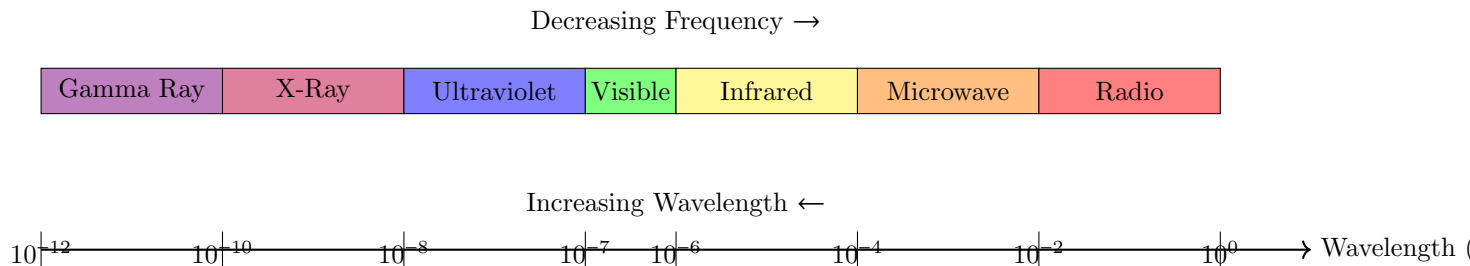
The electromagnetic spectrum ranges from long-wavelength, low-frequency waves like radio waves to short-wavelength, high-frequency waves like gamma rays. Visible light is a small portion of the spectrum, spanning from approximately 400 nm (violet) to 700 nm (red) in wavelength.

4.4   Absorption Spectrum of Elements

The absorption spectrum of an element is a unique pattern of dark lines or bands that appear when white light passes through a gas or vapor composed of the element. These dark lines correspond to specific wavelengths of light that have been absorbed by the element's atoms. Understanding absorption spectra is crucial in fields like astronomy and spectroscopy, as they allow scientists to identify elements in stars and distant galaxies.

4.4.1   How Absorption Spectra Work

When white light (which contains all visible wavelengths) passes through a sample of an element in its gaseous state, the electrons in the atoms of that element absorb specific amounts of energy. This energy corresponds to the difference between specific energy levels or orbits of the electrons.

When electrons absorb this energy, they jump from a lower energy level to a higher energy level, creating an absorption event. Each element has a unique set of energy levels, so the wavelengths absorbed (or "dark lines" in the spectrum) are also unique to each element. These dark lines are referred to as **absorption lines**.

4.4.2   Relationship to Emission Spectrum

The absorption spectrum is closely related to the **emission spectrum** of an element. When an electron drops from a higher energy level to a lower one, it emits light at a wavelength corresponding to the energy difference between these levels. In contrast, the absorption spectrum is formed when electrons move from lower to higher energy levels by absorbing light.

The emission lines and absorption lines occur at the same wavelengths for any given element, but they appear differently in the spectra:

- **Emission Spectrum**: Bright lines on a dark background, representing wavelengths emitted by electrons falling to lower energy levels.

- **Absorption Spectrum**: Dark lines on a bright (continuous) background, representing wavelengths absorbed by electrons jumping to higher energy levels.

4.4.3   Example: Hydrogen Absorption Spectrum

The hydrogen atom, for example, has a simple absorption spectrum. It consists of a series of dark lines in the visible region, corresponding to the specific wavelengths absorbed by electrons as they move to higher energy levels. The Balmer series is a well-known part of hydrogen's absorption spectrum, with lines appearing in the visible light range.

Below is a simplified representation of the absorption spectrum of hydrogen:

— — — — —

The dark lines represent wavelengths absorbed by the hydrogen atoms.

4.4.4 Applications of Absorption Spectra

Absorption spectra are used in a variety of scientific fields to:

- Identify elements present in stars and distant astronomical objects.

- Determine the chemical composition of substances.

- Study the energy levels and quantum mechanics of atoms and molecules.

Since each element has a unique absorption spectrum, this technique allows scientists to detect and analyze the presence of different elements based on the pattern of dark lines that appear in a spectrum.

In this diagram, the gradient from white to black represents the continuous spectrum of light, while the vertical white lines represent absorption lines where specific wavelengths are absorbed by the element.

4.5 Rydberg Equations and Emission Spectra

The planetary model of the atom pictures electrons orbiting the nucleus in the way that planets orbit the sun. Bohr used the planetary model to develop the first reasonable theory of hydrogen, the simplest atom. Atomic and molecular spectra are quantized, with hydrogen spectrum wavelengths given by the formula:

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right),$$

where λ is the wavelength of the emitted EM radiation and R is the Rydberg constant, which has the value

$$R = 1.097 \times 10^7 \text{ m}^{-1}.$$

The constants n_i and n_f are positive integers, and n_i must be greater than n_f.

Bohr correctly proposed that the energy and radii of the orbits of electrons in atoms are quantized, with energy for transitions between orbits given by

$$\Delta E = hf = E_i - E_f, \tag{30.3.22}$$

where ΔE is the change in energy between the initial and final orbits and hf is the energy of an absorbed or emitted photon. It is useful to plot orbital energies on a vertical graph called an energy-level diagram.

Bohr proposed that the allowed orbits are circular and must have quantized orbital angular momentum given by

$$L = m_e v_n r_n = n \frac{h}{2\pi} \quad (n = 1, 2, 3, \ldots),$$

where L is the angular momentum, r_n is the radius of the nth orbit, and h is Planck's constant. For all one-electron (hydrogen-like) atoms, the radius of an orbit is given by

$$r_n = \frac{n^2}{Z} a_B \quad \text{(allowed orbits } n = 1, 2, 3, \ldots\text{)},$$

Z is the atomic number of an element (the number of electrons it has when neutral) and a_B is defined to be the Bohr radius, which is

$$a_B = \frac{h^2}{4\pi^2 m_e k e^2} = 0.529 \times 10^{-10} \text{ m}.$$

Furthermore, the energies of hydrogen-like atoms are given by

$$E_n = -\frac{Z^2}{n^2} E_0 \quad (n = 1, 2, 3, \ldots),$$

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where E_0 is the ground-state energy and is given by

$$E_0 = \frac{2\pi^2 m_e k^2 e^4}{h^2} = 13.6 \text{ eV}.$$

Thus, for hydrogen,

$$E_n = -\frac{13.6 \text{ eV}}{n^2} \quad (n = 1, 2, 3, \ldots).$$

The Bohr Theory gives accurate values for the energy levels in hydrogen-like atoms, but it has been improved upon in several respects.

4.5.1 Applications of Rydberg Equation

The Rydberg equation is not only crucial for predicting the emission spectrum of hydrogen but also for understanding other one-electron systems like He^+, Li^{2+}, and so forth. By studying the emission spectra of various elements, scientists can gain insights into the structure of atoms and the quantized nature of their energy levels. The emission spectra are also used in astrophysics to identify the elements present in distant stars and galaxies by comparing observed spectral lines with known values.

4.6 Max Planck's 1900 Theory and the Relationship $E = h\nu$

In the early 1900s, Max Planck introduced a revolutionary concept that laid the foundation for quantum mechanics. To address the problem of blackbody radiation, Planck proposed that electromagnetic energy could only be emitted or absorbed in discrete units, or "quanta." This concept was a significant departure from classical physics and led to the development of the famous relationship:

$$E = h\nu,$$

where:

- E is the energy of a quantum (or photon) of electromagnetic radiation.

- h is Planck's constant, with a value of approximately 6.626×10^{-34} Js.

- ν (or f) is the frequency of the electromagnetic radiation.

4.6.1 The Blackbody Radiation Problem

Classical physics predicted that a blackbody (an idealized physical body that absorbs all incident electromagnetic radiation) would emit radiation with an intensity that increases infinitely as the wavelength decreases (known as the "ultraviolet catastrophe"). However, experimental observations showed that the intensity reaches a peak and then drops off at shorter wavelengths. This discrepancy between theory and experiment led to the need for a new understanding of how radiation is emitted.

4.6.2 Planck's Solution: Quantization of Energy

Planck hypothesized that the energy emitted by a blackbody could only take on discrete values, rather than being continuous. He proposed that the energy of each quantum of radiation is proportional to its frequency, leading to the equation:

$$E = h\nu.$$

This assumption meant that electromagnetic radiation is quantized and that the energy levels are spaced in multiples of $h\nu$. In essence, energy could only be emitted or absorbed in "packets" or quanta, not as a continuous wave.

4.6.3   Implications of Planck's Theory

Planck's theory successfully explained the blackbody radiation spectrum, and the constant h, later known as Planck's constant, became a fundamental constant in quantum mechanics. This idea of quantization was groundbreaking because it introduced the concept that energy is not infinitely divisible, contradicting the classical wave theory of light.

The relationship $E = h\nu$ implies that higher frequency (shorter wavelength) radiation has more energy per photon. This paved the way for the development of quantum theory and influenced subsequent discoveries, including:

- **Photoelectric Effect**: Albert Einstein used Planck's concept to explain the photoelectric effect in 1905, showing that light can eject electrons from a material if the frequency is above a certain threshold. This provided further evidence of the particle-like behavior of light.

- **Wave-Particle Duality**: Planck's work suggested that light exhibits both wave-like and particle-like properties, an idea that became central to quantum mechanics.

- **Quantum Energy Levels**: The concept of quantized energy levels led to the understanding of atomic structure and the development of quantum mechanical models, where electrons occupy discrete energy states around the nucleus.

4.6.4   Applications and Further Developments

Planck's relationship, $E = h\nu$, has vast implications in various fields of physics and chemistry. It underpins the understanding of atomic spectra, molecular vibrations, and electronic transitions. It also plays a crucial role in technologies such as lasers, semiconductors, and quantum computing.

Overall, Planck's introduction of the quantization of energy marked the beginning of a new era in physics, laying the groundwork for the development of quantum mechanics and fundamentally changing our understanding of the physical world.

4.6.5   Quantized Emission Spectra

Hydrogen Energy Levels
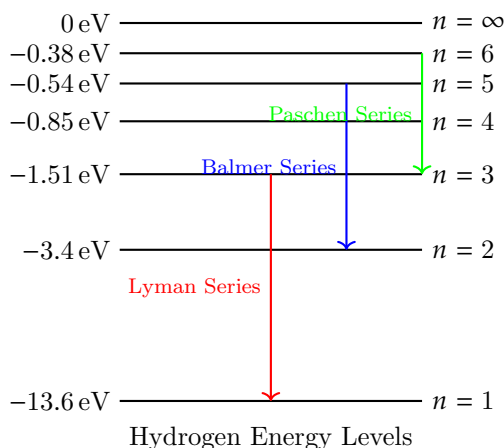
4.7   The Photoelectric Effect

The photoelectric effect is a phenomenon in which electrons are ejected from the surface of a material (usually a metal) when it is exposed to light of sufficient frequency. The experimental observations of the photoelectric effect could not be explained by classical wave theory and led to the development of quantum theory. Albert Einstein provided the explanation for this effect in 1905 by extending Max Planck's concept of quantization of energy.

4.7.1 Einstein's Explanation

According to Einstein, light consists of packets of energy called "photons," each with an energy E given by:

$$E = hf,$$

where:

- h is Planck's constant (6.626×10^{-34} Js).

- f is the frequency of the incident light.

When a photon hits the surface of a material, its energy is transferred to an electron. If the photon's energy is greater than a certain minimum energy needed to free the electron (known as the **work function** Φ of the material), the electron is ejected from the surface.

4.7.2 The Photoelectric Equation

The maximum kinetic energy E_{max} of the ejected electron is given by the equation:

$$E_{\text{max}} = hf - \Phi,$$

where:

- E_{max} is the maximum kinetic energy of the ejected electron.

- hf is the energy of the incident photon.

- Φ is the work function of the material, which is the minimum energy required to free an electron from the surface.

This equation implies that the kinetic energy of the ejected electron depends linearly on the frequency of the incident light, and there is a threshold frequency $f_{\text{threshold}}$ below which no electrons are ejected, regardless of the intensity of the light.

4.7.3 Stopping Voltage and Kinetic Energy

The kinetic energy of the ejected electrons can be measured experimentally using a stopping voltage V_s. The stopping voltage is the voltage required to stop the ejected electrons from reaching the detector. The relationship between the stopping voltage and the kinetic energy is given by:

$$E_{\text{max}} = eV_s,$$

where:

- e is the charge of the electron (1.602×10^{-19} C).

- V_s is the stopping voltage.

By measuring the stopping voltage for different frequencies of light, one can determine the work function Φ of the material and verify the linear relationship between E_{max} and the frequency f of the incident light.

4.7.4 Significance of the Photoelectric Effect

The photoelectric effect provided strong evidence for the quantization of light and supported the particle-like behavior of photons. This was a crucial step in the development of quantum mechanics. The effect also showed that the energy of ejected electrons is independent of the light's intensity (which only affects the number of emitted electrons) and is instead solely dependent on the frequency of the incident light.

Applications of the photoelectric effect are found in various technologies, including photodetectors, solar cells, and photoelectron spectroscopy.

4.7.5 Graph of Voltage vs. Kinetic Energy

The photoelectric equation $E_{\max} = hf - \Phi$ shows that the maximum kinetic energy of ejected electrons is linearly dependent on the frequency of the incident light. Experimentally, this relationship can be studied by plotting the stopping voltage V_s (which is directly proportional to $E_{\max}$) against the frequency f of the incident light.
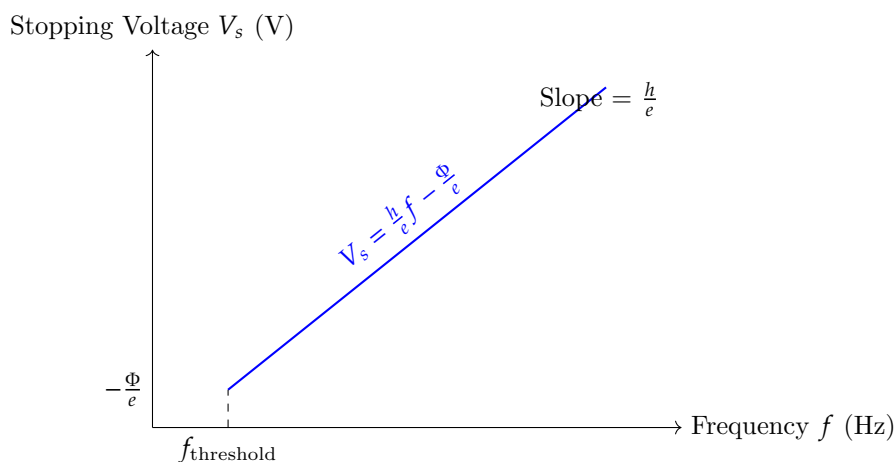
Graph of Stopping Voltage V_s vs. Frequency f

4.7.6 Explanation of the Graph

The graph above represents the relationship between the stopping voltage V_s and the frequency of the incident light f. The linear equation governing this relationship is:

$$V_s = \frac{h}{e}f - \frac{\Phi}{e},$$

where:

- h is Planck's constant.

- e is the charge of an electron.

- Φ is the work function of the material.

  In this graph:

- The **slope** of the line is $\frac{h}{e}$. Since h is Planck's constant and e is a known constant (the electron charge), the slope provides a way to determine Planck's constant experimentally.

- The **y-intercept** is $-\frac{\Phi}{e}$, which corresponds to the work function of the material divided by the electron charge. This intercept is negative, as it represents the minimum energy needed to eject an electron.

- The point at which the line intersects the f-axis is the **threshold frequency** $f_{\text{threshold}}$. For frequencies below this value, no electrons are emitted because the photon's energy is insufficient to overcome the work function Φ.

  The linear nature of this graph is a direct consequence of the photoelectric effect and provides evidence for the quantization of energy in photons. By measuring the slope of this line, one can experimentally determine the value of Planck's constant h.

4.8 Quantized Momentum of an Electron and Standing Waves in Orbits

In the Bohr model of the atom, electrons are assumed to occupy discrete orbits around the nucleus. One of the key ideas is that the angular momentum of an electron in these orbits is quantized. Specifically, the angular
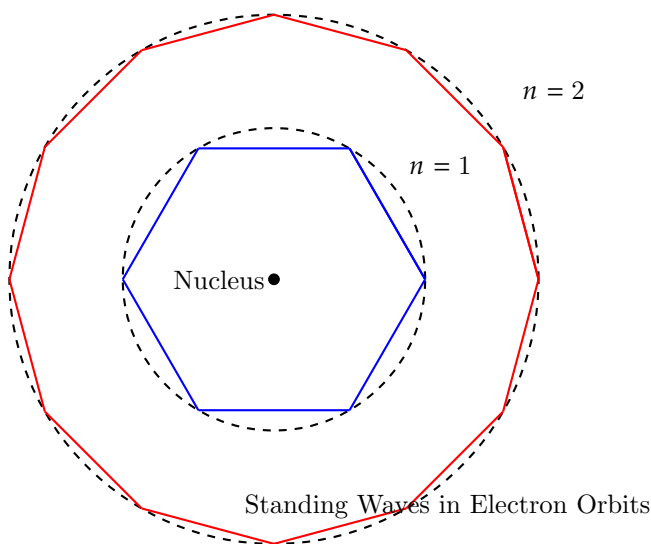
momentum L is given by:
$$L = n\hbar,$$

where:

- n is a positive integer (the principal quantum number).

- $\hbar$ is the reduced Planck's constant ($\hbar = \frac{h}{2\pi}$).

This quantization arises because the electron behaves as a standing wave in its orbit. For a stable orbit, the circumference of the orbit must be an integer multiple of the electron's wavelength λ:

$$2\pi r = n\lambda,$$

where r is the radius of the orbit.

Standing Waves in Electron Orbits

4.8.1 Standing Waves and Quantized Orbits

For each allowed orbit, the electron's de Broglie wavelength λ fits perfectly into the circumference of the orbit, creating a standing wave. This condition ensures that only specific, quantized orbits are possible, corresponding to different values of n. The quantization of angular momentum restricts electrons to these stable orbits, preventing them from spiraling into the nucleus.

In the diagram:

- The dashed circles represent possible orbits.

- The blue and red standing waves correspond to $n = 1$ and $n = 2$, respectively, showing how the electron's wave fits into each orbit.

4.8.2 Quantized Momentum of an Electron

In the Bohr model of the atom, the momentum of an electron is quantized due to its wave-like nature. The electron behaves as a standing wave around the nucleus, and only certain orbits are allowed where the circumference of the orbit is an integer multiple of the electron's wavelength:

$$2\pi r = n\lambda,$$

where r is the radius of the orbit, n is a positive integer (the principal quantum number), and λ is the de Broglie wavelength of the electron.

Since the de Broglie wavelength is related to momentum p by:

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

the quantization condition becomes:

$$p = \frac{n\hbar}{r},$$

where $\hbar = \frac{h}{2\pi}$. This shows that the electron's momentum is quantized, allowing only specific values for each orbit.

4.9 Heisenberg Uncertainty Principle

The Heisenberg Uncertainty Principle is a fundamental concept in quantum mechanics, stating that it is impossible to simultaneously know the exact position and momentum of a particle. This principle arises due to the wave-like nature of particles at the quantum level. When attempting to measure one property (e.g., position), the wavefunction describing the particle's behavior is disturbed, leading to an increased uncertainty in the complementary property (e.g., momentum). This effect is a direct consequence of the properties of wavefunctions and Fourier transforms.

The principle is mathematically represented by the inequality:

$$\boxed{\Delta x \cdot \Delta p \geqslant \frac{\hbar}{4\pi}}$$

where: - Δx is the uncertainty in position, - Δp is the uncertainty in momentum, - $\hbar$ is Planck's constant. In other words, the product of the uncertainties in position and momentum can never be smaller than $\frac{\hbar}{4\pi}$. A similar relationship exists between the uncertainties in energy and time, given by:

$$\boxed{\Delta E \cdot \Delta t \geqslant \frac{\hbar}{4\pi}}$$

where: - ΔE is the uncertainty in energy, - Δt is the uncertainty in time.

This relationship arises because a particle's energy and the time over which it is measured are also complementary variables, meaning that a precise measurement of one leads to increased uncertainty in the other.

The Heisenberg Uncertainty Principle emphasizes the inherent limitations in our ability to measure certain pairs of physical properties simultaneously, reflecting the fundamental nature of quantum systems.

4.10 Schrödinger's Equation and Atomic Orbitals

Schrödinger's equation describes the behavior of quantum particles, particularly electrons in an atom. The time-independent form of the equation is:

$$\hat{H}\psi = E\psi \tag{4.1}$$

where $\hat{H}$ is the Hamiltonian operator, ψ is the wavefunction, and E is the energy of the system. In the context of atoms, solving this equation for electrons leads to quantized energy levels and wavefunctions, known as orbitals.

To reflect the symmetry of the atom, the wavefunction is expressed in spherical coordinates (r, θ, ϕ) rather than Cartesian coordinates (x, y, z). This simplifies the equation due to the spherical symmetry of the Coulomb potential around the nucleus, making it easier to solve for orbitals:

$$\psi_{n,l,m_l}(r, \theta, \phi) = R(r)_{n,l}Y(\theta, \phi)_l \tag{4.2}$$

Here, $R(r)$ describes the radial part, and $Y(\theta, \phi)$ represents the angular part of the wavefunction. The quantum numbers n, l, and m_l arise from these solutions, defining the energy levels and shapes of atomic orbitals.

The quantum numbers have the following values and meanings:

- The principal quantum number n determines the electron's energy level and the shell in which the electron resides. It takes positive integer values: $n = 1, 2, 3, \ldots$. The value of n also correlates with the period (row) of the periodic table in which the element is found, and as n increases, the electron's average distance from the nucleus and energy both increase.

- The azimuthal quantum number l determines the shape of the orbital and the subshell, corresponding to the labels s, p, d, and f:

- $l = 0$: s-orbital (spherical)
- $l = 1$: p-orbital (dumbbell-shaped)
- $l = 2$: d-orbital (more complex shapes)
- $l = 3$: f-orbital (even more complex shapes)

The possible values of l range from 0 to $n - 1$ for a given energy level, defining which subshells are present within a shell.

- The magnetic quantum number m_l defines the orientation of the orbital in space and takes integer values from $-l$ to l: $m_l = -l, -(l-1), \ldots, 0, \ldots, (l-1), l$. It specifies the number of orbitals within a subshell, such as the three orientations of the p-orbitals or the five orientations of the d-orbitals.

These quantum numbers collectively describe the unique characteristics of atomic orbitals, such as energy level, shape, orientation, and how they correspond to the organization of elements in the periodic table.

- Total Nodes $= n - 1$

- Total Angular Nodes $= l$

- Total Radial Nodes $= n - l - 1$

4.11   Energy Diagram for Atomic Orbitals
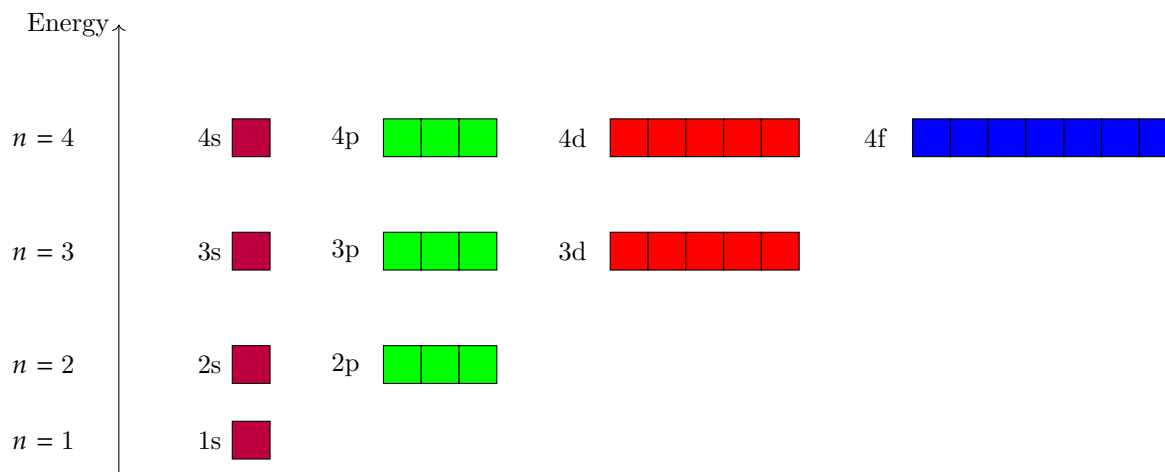
Explanation

The diagram represents the energy levels of atomic orbitals, arranged by the principal quantum number (n) and their corresponding subshells.

- **Energy Axis:** The y-axis represents the increasing energy of the orbitals. As the energy increases, the orbitals are arranged vertically.

- **Principal Quantum Number (n):** Each horizontal row corresponds to a different value of n, the principal quantum number, representing different electron shells. For example:

  - $n = 1$: 1s orbital (lowest energy)
  - $n = 2$: 2s and 2p orbitals
  - $n = 3$: 3s, 3p, and 3d orbitals
  - $n = 4$: 4s, 4p, 4d, and 4f orbitals (highest energy shown)

The value of n corresponds to the shell and relates to the energy level and the row (period) in the periodic table.

- **Subshells and Orbitals:**

  - **s-orbitals** ($l = 0$) are spherical and represented by purple squares. They exist for each value of n (1s, 2s, 3s, 4s).

  - **p-orbitals** ($l = 1$) are dumbbell-shaped and represented by green squares. They appear starting from $n = 2$ (2p, 3p, 4p) and have three possible orientations, corresponding to three green squares for each p-subshell.

  - **d-orbitals** ($l = 2$) are more complex in shape and represented by red squares. They appear starting from $n = 3$ (3d, 4d) and have five possible orientations, represented by five red squares for each d-subshell.

  - **f-orbitals** ($l = 3$) are highly complex in shape and represented by blue squares. They appear starting from $n = 4$ (4f) and have seven possible orientations, represented by seven blue squares for each f-subshell.

The horizontal arrangement of colored squares shows the degeneracy (number of orbitals) for each subshell, while the vertical arrangement corresponds to increasing energy.

4.11.1 Visualization of Electron Probability Density Functions and Orbitals

1s Orbital

1s Orbital

2s Orbital

2s Orbital

2p Orbital

2p Orbital
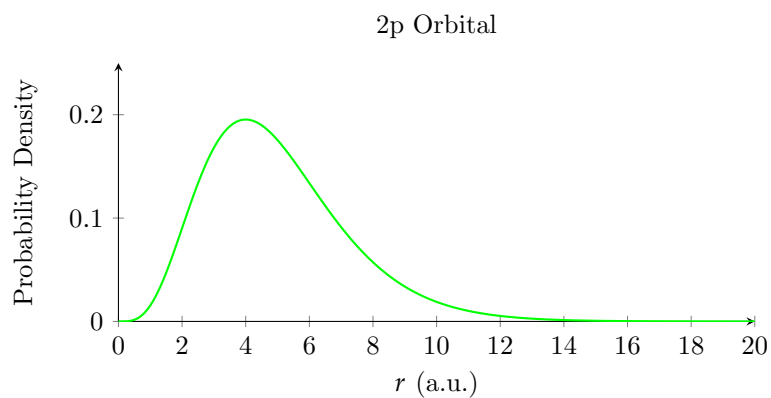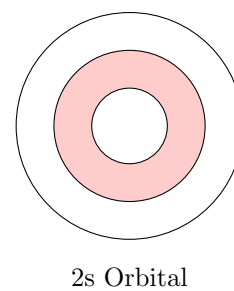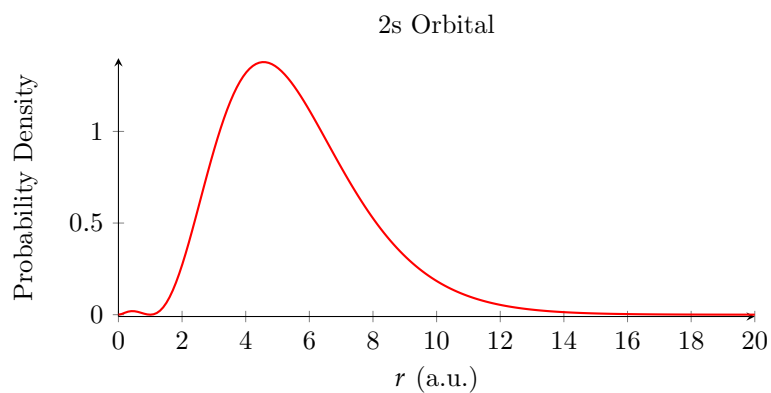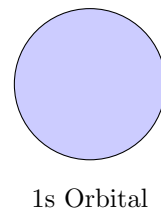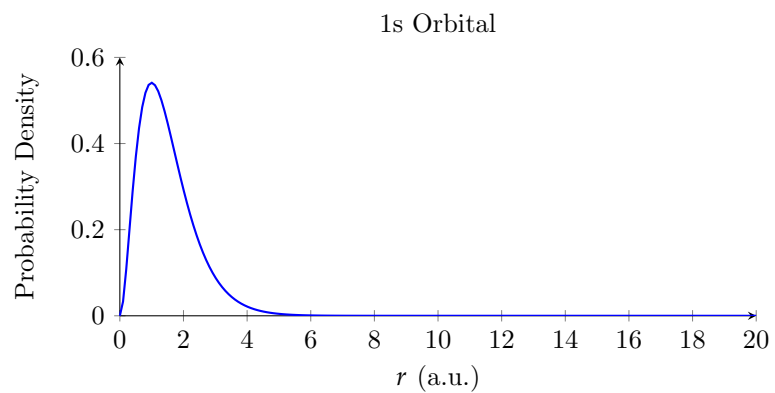
Thermodynamic Formulas and Definitions

Real Gas Equation

$$\left(P + \frac{a}{v^2}\right)(V - bn) = nRT$$

Where:

- P = Pressure of the gas

- V = Volume of the gas

- n = Amount of substance

- R = Universal gas constant

- T = Temperature

- a, b = Van der Waals constants specific to each gas

- v = Molar volume of the gas (V/n)

Partial Pressure

$$P_i = X_i P_{tot}$$

Where:

- P_i = Partial pressure of component i

- X_i = Mole fraction of component i

- P_{tot} = Total pressure of the mixture

Energy Conversions

$$L \cdot \text{atm} = 101.325 \text{ J}$$
$$L \cdot \text{bar} = 100 \text{ J}$$

Definitions:

- L = Liters

- J = Joules

- atm = Atmosphere pressure unit

- bar = Barometric pressure unit

Calorimetry and Enthalpy

$$q_{cal} = c_{cal} \cdot \Delta T$$
$$q_{sys} = n \cdot \Delta H$$
$$\Delta H = \Delta U + P\Delta V$$

Where:

- q_{cal} = Heat absorbed or released in a calorimeter

- c_{cal} = Specific heat capacity of the calorimeter

- ΔT = Change in temperature

- q_{sys} = Heat absorbed or released by the system

- n = Amount of substance (moles)

- ΔH = Change in enthalpy

- ΔU = Change in internal energy

- P = Pressure

- ΔV = Change in volume

Work Done by Gas

$$\Delta U = q + w$$
$$w = -P_{\text{ex}}\Delta V$$
$$w = -nRT \ln \frac{V_f}{V_i}$$

Where:

- ΔU = Change in internal energy

- q = Heat exchange

- w = Work done by or on the system

- P_{ex} = External pressure

- V_f = Final volume

- V_i = Initial volume

Kinetic Energy of a Molecule

$$E(k) = \frac{3}{2}RT = \frac{1}{2}M(kg)v^2$$

Where:

- $E(k)$ = Kinetic energy per molecule

- M = Mass of the molecule

- v = Velocity of the molecule

Graham's Law of Effusion

$$\frac{\text{Rate}(A)}{\text{Rate}(B)} = \frac{\text{time}(B)}{\text{time}(A)} = \sqrt{\frac{M(B)}{M(A)}}$$

Where:

- $\text{Rate}(A)$ and $\text{Rate}(B)$ = Rates of effusion for gases A and B

- $\text{time}(A)$ and $\text{time}(B)$ = Times taken for gases A and B to effuse

- $M(A)$ and $M(B)$ = Molar masses of gases A and B

Changes in Internal Energy and Enthalpy

$$\Delta U = c_v \Delta T$$

$$\Delta H = c_p \Delta T$$

Where:

- ΔU = Change in internal energy

- ΔH = Change in enthalpy

- c_v = Heat capacity at constant volume

- c_p = Heat capacity at constant pressure

- ΔT = Change in temperature

Relationship Between Heat Capacities

$$c_p = c_v + R$$

Where:

- R = Universal gas constant

Heat Transfer

$$q = mc_s \Delta T$$

Where:

- q = Heat transferred

- m = Mass of the substance

- c_s = Specific heat capacity of the substance

Standard Enthalpy of Reaction

$$\Delta H^\circ_{rxn} = \Delta H^\circ_{prod} - \Delta H^\circ_{react}$$

Where:

- ΔH°_{rxn} = Standard enthalpy change of the reaction

- ΔH°_{prod} = Sum of standard enthalpies of products

- ΔH°_{react} = Sum of standard enthalpies of reactants

Temperature Dependence of Enthalpy

$$\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \Delta c_{p,rxn} \Delta T$$

Where:

- $\Delta c_{p,rxn}$ = Change in heat capacity for the reaction