PREFACE

With its grounding in the "guiding pillars of Access, Equity, Equality, Affordability and Accountability," the New Education Policy (NEP 2020) envisions flexible curricular structures and creative combinations for studies across disciplines. Accordingly, the UGC has revised the CBCS with a new Curriculum and Credit Framework for Undergraduate Programmes (CCFUP) to further empower the flexible choice based credit system with a multidisciplinary approach and multiple/ lateral entry-exit options. It is held that this entire exercise shall leverage the potential of higher education in three-fold ways – learner's personal enlightenment; her/his constructive public engagement; productive social contribution. Cumulatively therefore, all academic endeavours taken up under the NEP 2020 framework are aimed at synergising individual attainments towards the enhancement of our national goals.

In this epochal moment of a paradigmatic transformation in the higher education scenario, the role of an Open University is crucial, not just in terms of improving the Gross Enrolment Ratio (GER) but also in upholding the qualitative parameters. It is time to acknowledge that the implementation of the National Higher Education Qualifications Framework (NHEQF), National Credit Framework (NCrF) and its syncing with the National Skills Qualification Framework (NSQF) are best optimised in the arena of Open and Distance Learning that is truly seamless in its horizons. As one of the largest Open Universities in Eastern India that has been accredited with 'A' grade by NAAC in 2021, has ranked second among Open Universities in the NIRF in 2024, and attained the much required UGC 12B status, Netaji Subhas Open University is committed to both quantity and quality in its mission to spread higher education. It was therefore imperative upon us to embrace NEP 2020, bring in dynamic revisions to our Undergraduate syllabi, and formulate these Self Learning Materials anew. Our new offering is synchronised with the CCFUP in integrating domain specific knowledge with multidisciplinary fields, honing of skills that are relevant to each domain, enhancement of abilities, and of course deep-diving into Indian Knowledge Systems.

Self Learning Materials (SLM's) are the mainstay of Student Support Services (SSS) of an Open University. It is with a futuristic thought that we now offer our learners the choice of print or e-slm's. From our mandate of offering quality higher education in the mother tongue, and from the logistic viewpoint of balancing scholastic needs, we strive to bring out learning materials in Bengali and English. All our faculty members are constantly engaged in this academic exercise that combines subject specific academic research with educational pedagogy.We are privileged in that the expertise of academics across institutions on a national level also comes together to augment our own faculty strength in developing these learning materials. We look forward to proactive feedback from all stakeholders whose participatory zeal in the teaching-learning process based on these study materials will enable us to only get better. On the whole it has been a very challenging task, and I congratulate everyone in the preparation of these SLM's.

I wish the venture all success.

Professor Indrajit Lahiri
Vice-Chancellor

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Netaji Subhas Open University

Four Year Undergraduate Degree Programme

Under National Higher Education Qualifications Framework (NHEQF) & Curriculum and Credit Framework for Undergraduate Programmes

Course Type: Discipline Specific Course (DSC)

Course Title: Inorganic Chemistry – I

Course Code: 6CC-CH-05

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Contents

Unit-1 : Extra nuclear Structure of atom	**7-25**
Unit-2 : Idea about Quantum Numbers	**26-38**
Unit 3 : Rules of Electronic Configuration & Nuclear Charge	**39-64**
Unit-4 : Radioactivity and nuclear chemistry	**65-89**
Unit-5 : Nuclear Reactions	**90-110**
Unit 6 : Applications of radio-isotopes	**111-126**
Unit-7 : Periodic Table	**127-149**
Unit 8 : Chemical periodicity	**150-178**
Unit 9 : Chemistry of S-block elements	**179-219**
Unit 10 : Chemistry of p-block elements	**220-271**
Unit-11 : Redox Reactions and precipitation reactions	**272-293**
Unit 12 : Basis of redox titration and redox indicators	**294-310**
Unit 13 : Acid-Base concept	**311-337**
Unit 14 : Thermodynamic acidity parameters	**338-359**

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Module 1: Atomic Structure

Unit 1 ❐ Extra Nuclear Structure of Atom

Contents

1.0 Objectives

1.1 Introduction

1.2 Introduction of Different Atomic Model

1.3 Bohr's Atomic Model

1.4 Atomic spectrum of hydrogen

1.5 Sommerfeld's modifications of Bohr's atomic model

1.6 Wave Mechanics and de Broglie Equation

1.7 Heisenberg's Uncertainty Principle

1.8 Schrödinger's wave equation (without application and solution detail), & Significance of ψ and ψ^2

1.9 Summary

1.10 Model Questions

1.11 References

1.0 Objectives

- Understanding Atomic Models: To comprehend the historical development and evolution of atomic models, with a focus on the introduction of atomic models.
- Bohr's Model and Hydrogen Spectrum: Analyzing Bohr's model and its application to the atomic spectrum of hydrogen, including the limitations associated with it.
- Sommerfeld's Modifications: Exploring Sommerfeld's modifications to Bohr's model and understanding how these modifications address some of its limitations.
- Wave Mechanics Principles: Grasping the fundamental principles of wave mechanics,

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including de Broglie's equation and Heisenberg's uncertainty principle and their significance in the context of atomic structure.

- Schrödinger's Wave Equation: Understanding Schrödinger's wave equation without delving into its detailed application and solutions, focusing on its theoretical underpinnings.
- Significance of ψ and ψ^2: Investigating the physical significance of the wave function (ψ) and its square (ψ^2) in the context of atomic structure.

1.1 Introduction

In this chapter, we're exploring the world of tiny atoms, like solving a cool puzzle! We look back at how clever scientists like Niels Bohr pictured atoms, thinking electrons move in special orbits around the center called the nucleus. This helped understand atoms, especially simple ones like hydrogen.

But guess what? Science keeps improving, so we check Bohr's model and find where it needs fixing. Arnold Sommerfeld helps out by tweaking things, adding different orbits and considering how electrons spin. It's like getting a new puzzle piece!

Now, it gets exciting with waves and particles. Picture electrons acting like both at once—De Broglie's equation explains it. It's a bit tricky but leads to a whole new way of thinking about atoms—quantum mechanics!

Hold on tight because Heisenberg's uncertainty principle makes things uncertain. We can't measure everything exactly, like an electron's position and speed at the same time.

Our journey peaks with Schrödinger's wave equation, a cool math tool for understanding particles in the quantum world. We won't dive into all the details yet, but we'll talk about magic symbols—wave functions (ψ) and their squares (ψ^2)—predicting where particles might be.

As we explore atoms and quantum stuff, get ready for a strange ride with surprises. We're unlocking the secrets of the tiny universe where waves, particles, and probabilities blend, creating an amazing picture of how things work in the smallest world. Let's unravel the secrets of the quantum world together!

1.2 Introduction of Different Atomic Model

The atomic model is a scientific theory that describes the structure and behavior of atoms, the basic building blocks of matter. Over the centuries, various models have been proposed to explain the nature of atoms, each building upon the knowledge and experimental evidence available at the time. Here's a brief overview of the historical development of the atomic model:

Dalton's Model (1803): John Dalton proposed the first modern atomic theory, suggesting that atoms are indivisible, indestructible particles with unique masses. He also introduced the idea that elements are composed of atoms with specific ratios.

Thomson's Model (1897): J.J. Thomson discovered the electron and proposed the "plum pudding" model, envisioning atoms as a positively charged "pudding" with negatively charged electrons embedded within it.

Rutherford's Model (1911): Ernest Rutherford conducted the famous gold foil experiment, leading to the discovery that atoms have a small, dense nucleus at their center, surrounded by mostly empty space where electrons orbit. This model is often referred to as the "planetary" or "solar system" model.

Bohr's Model (1913): Niels Bohr expanded on Rutherford's model by incorporating the idea that electrons orbit the nucleus in specific energy levels or shells. This model successfully explained the spectral lines of hydrogen.

Quantum Mechanical Model (1926): Developed by Schrödinger, Heisenberg, and others, the quantum mechanical model describes electrons as existing within probability distributions called orbitals. This model is based on the principles of quantum mechanics and provides a more accurate depiction of the behavior of electrons in atoms.

Modern Understanding: Today, the quantum mechanical model is the accepted atomic model. It recognizes that electrons do not follow precise orbits but exist within regions of probability around the nucleus. This model also introduces the concept of electron spin and the Pauli exclusion principle, which restricts the number of electrons in a given orbital.

The atomic model has evolved over time as scientists have gained a deeper understanding of the subatomic world through experimental evidence and theoretical developments.

The current model provides a comprehensive framework for understanding the behavior of atoms and is essential for various fields, including chemistry and physics.

1.3 Bohr's Atomic Model

Bohr's atomic model, proposed by Danish physicist Niels Bohr in 1913, was a significant advancement in the understanding of the structure of atoms. Prior to Bohr's model, the prevailing theory was the Rutherford model, which depicted the atom as a miniature solar system with electrons orbiting the nucleus in a random fashion.

Bohr introduced several key ideas in his model:

Quantized Energy Levels: Bohr suggested that electrons orbit the nucleus in specific, quantized energy levels. These orbits, also known as shells or energy levels, are designated by integer values (n = 1, 2, 3, ...). Electrons in higher energy levels have more energy than those in lower levels.

Angular Momentum Quantization: Bohr proposed that the angular momentum of an electron in its orbit is quantized, meaning it can only have certain discrete values. The formula for angular momentum (L) is given by $L = (nh) / (2\pi)$, where n is the principal quantum number, h is Planck's constant, and π is pi.

Energy Absorption and Emission: Electrons can absorb or emit energy only when transitioning between these quantized energy levels. When an electron absorbs energy, it moves to a higher energy level; when it emits energy, it moves to a lower level. The energy of the emitted or absorbed radiation is quantized and corresponds to the energy difference between the initial and final energy levels.

Stability of Orbits: According to Bohr, electrons in stable orbits do not emit radiation, and therefore, they do not lose energy. This stability occurs when the angular momentum is an integer multiple of $h / (2\pi)$.

Despite its success in explaining certain features of the hydrogen spectrum, Bohr's model had limitations and was later superseded by more sophisticated quantum mechanical models. The Bohr model could not explain the spectra of atoms with more than one electron or the fine details observed in complex atoms. Nevertheless, Bohr's work laid the groundwork for the development of quantum mechanics, which provides a more comprehensive understanding of atomic structure.

Some key points highlighting the success of Bohr's atomic model:

Quantization of Energy Levels:

Bohr introduced the concept of quantized energy levels, where electrons orbit the nucleus in specific, discrete orbits without emitting radiation.

This addressed the classical electromagnetic theory's failure to explain the stability of atoms.

Angular Momentum Quantization:

Bohr quantized the angular momentum of electrons, stating that it is an integral multiple of $h/2\pi$ (Planck's constant divided by 2π).

Stability of Orbits:

Bohr's model explained why electrons do not spiral into the nucleus due to the emission of electromagnetic radiation, as classical physics suggested.

Spectral Lines of Hydrogen:

Bohr's model successfully explained the spectral lines of hydrogen by relating them to the transitions of electrons between quantized energy levels.

Rydberg Formula:

The model derived the Rydberg formula, which accurately predicted the wavelengths of spectral lines for hydrogen.

Bohr Radius:

Introduced the concept of the Bohr radius, which is a measure of the most probable distance of the electron from the nucleus in a hydrogen atom.

Explanation of the Periodic Table:

Bohr's model provided a theoretical basis for understanding the periodic table by linking electron arrangement to atomic number and chemical properties.

Transition States:

Described the transitions of electrons between energy levels, accompanied by the absorption or emission of photons.

Quantum Theory Foundation:

Bohr's model played a crucial role in the development of quantum theory and provided a bridge between classical physics and quantum mechanics.

Limitations and Later Developments:

While successful for hydrogen-like species, Bohr's model had limitations for atoms with more than one electron.

It laid the foundation for more advanced atomic models, such as the Schrödinger model and the development of quantum mechanics.

Bohr's model marked a significant step forward in understanding the atomic structure, and its success was crucial in the evolution of quantum theory.

Some Important Limitations of Bohr's Atomic Model

Bohr's atomic model, proposed by Niels Bohr in 1913, was a significant step in understanding the structure of atoms. However, it had several limitations that were later addressed by more advanced models such as the quantum mechanical model. Here are some of the limitations of Bohr's atomic model:

Limited to Hydrogen-like Atoms: Bohr's model was primarily developed for hydrogen-like atoms, which have only one electron. It was not directly applicable to atoms with more than one electron.

Circular Orbits: Bohr suggested that electrons move in fixed, circular orbits around the nucleus. However, this concept violated the principles of classical electromagnetism because an accelerating charged particle, like an electron in orbit, should emit radiation and lose energy. Consequently, the electron would spiral into the nucleus, leading to the collapse of the atom, which contradicted experimental observations.

Quantization of Angular Momentum: Bohr postulated that the angular momentum of electrons is quantized and is an integral multiple of $h/2\pi$ (Planck's constant divided by 2π). This was an ad hoc assumption and lacked a theoretical basis at the time.

Absence of Explanation for Quantum Numbers: Bohr's model did not provide a clear explanation for the quantum numbers that later became fundamental in understanding the electronic structure of atoms. Quantum numbers were introduced in the more advanced quantum mechanical model.

Failure for Heavier Atoms: The model did not accurately predict the spectral lines of atoms with more than one electron. As the complexity of the atom increased, Bohr's model failed to explain the observed spectra.

Inability to Explain Fine Structure: The model could not account for the fine structure of spectral lines, which became apparent with advancements in experimental techniques. Fine structure refers to the splitting of spectral lines, and Bohr's model lacked the details to explain this phenomenon.

Wave-Particle Duality: Bohr's model did not address the wave-particle duality of electrons, which was later explained by quantum mechanics. The behavior of particles at the atomic level is inherently both wave-like and particle-like, a concept not captured by the Bohr model.

Absence of Electron Spin: Bohr's model did not incorporate the concept of electron spin, which is a fundamental property of electrons and a key factor in the understanding of electron configurations and the Pauli exclusion principle.

In summary, while Bohr's atomic model was a significant advancement in atomic theory, it had limitations, and subsequent developments in quantum mechanics provided a more comprehensive and accurate description of the behavior of electrons in atoms.

1.4 Atomic Spectrum of Hydrogen

The atomic spectrum of hydrogen is a crucial aspect of atomic physics that played a pivotal role in the development of quantum mechanics. It refers to the specific set of wavelengths of light emitted or absorbed by hydrogen atoms as electrons transition between different energy levels.

The hydrogen atom consists of a single proton in its nucleus and an electron that orbits the nucleus. According to classical physics, an electron in orbit around the nucleus should continuously emit electromagnetic radiation, lose energy, and eventually spiral into the nucleus. However, observations of hydrogen and other atoms did not match these predictions.

In the early 20th century, Niels Bohr proposed a model to explain the spectral lines of hydrogen. Bohr's model incorporated quantized orbits for electrons, where electrons could only exist in certain discrete energy levels. The electron could absorb or emit

energy only in discrete amounts, corresponding to the energy difference between these levels.

The key features of the hydrogen spectrum are:

Emission Spectrum:

When an electron in a higher energy level transitions to a lower energy level, it releases energy in the form of light. Each transition corresponds to a specific wavelength or frequency of light.

The spectral lines observed in the hydrogen emission spectrum are named based on the final energy level of the electron. The principal series lines are named Lyman, Balmer, Paschen, Brackett, and Pfund.

Lyman Series:

Transitions ending in the n = 1 energy level.

The lines are in the ultraviolet region.

Balmer Series:

Transitions ending in the n = 2 energy level.

The lines are in the visible region, and they are the most prominent lines in the hydrogen spectrum.

Paschen, Brackett, and Pfund Series:

Correspond to transitions ending in the n = 3, n = 4, and n = 5 energy levels, respectively.

Lines in these series are in the infrared region.

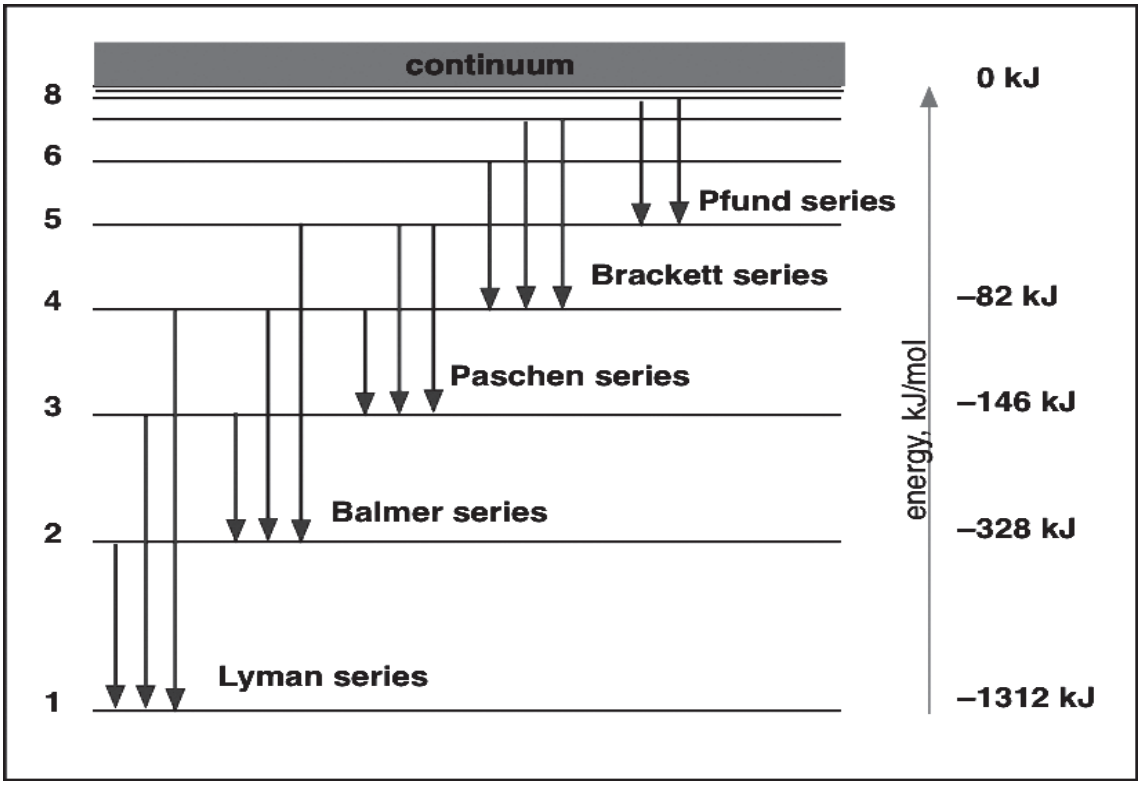
Absorption Spectrum:

When a continuous spectrum of light passes through a cool hydrogen gas, certain wavelengths are absorbed by the gas, creating dark lines in the spectrum.

These lines correspond to the same wavelengths as the emission lines, indicating that electrons are absorbing photons and moving to higher energy levels.

The mathematical expression for the allowed electron orbits and the energy levels of hydrogen is given by the Rydberg formula and later refined by Sommerfeld to account for elliptical orbits and finer details.

The hydrogen spectrum was a significant challenge to classical physics and played a crucial role in the development of quantum mechanics. The quantization of energy levels proposed by Bohr laid the foundation for the more comprehensive and accurate quantum mechanical description of atoms. The wave-particle duality of electrons and the probabilistic nature of their behavior were later elaborated by Schrödinger, Heisenberg, and others, providing a more complete understanding of the atomic world.



Pictorial Diagram of Hydrogen Spectrum Series

1.5 Sommerfeld's Modifications of Bohr's Atomic Model

Sommerfeld's modifications refer to the adjustments and improvements made by the German physicist Arnold Sommerfeld to the Bohr model of the atom, which was proposed by Niels Bohr in 1913. The Bohr model successfully explained some features of the hydrogen atom spectrum but had limitations, particularly in its treatment of more complex atoms.

Sommerfeld introduced several modifications to the Bohr model to account for these limitations:

Elliptical Orbits:

Bohr originally proposed that electrons orbit the nucleus in circular paths. Sommerfeld extended this idea by allowing for elliptical orbits instead of perfect circles. This modification provided a more accurate description of the electron's motion, especially for electrons in higher energy states.

Azimuthal Quantum Number (Angular Momentum Quantum Number):

Sommerfeld introduced an additional quantum number called the azimuthal quantum number (l) to describe the shape of the electron orbits. The azimuthal quantum number can take integer values from 0 to (n-1), where n is the principal quantum number. This modification allowed for a more precise description of the electron's motion in an atom.

Quantization of Angular Momentum:

Sommerfeld proposed that the angular momentum of an electron in an orbit is quantized not only in terms of an integer multiple of $h/2\pi$ (where h is Planck's constant) but also included a factor related to the azimuthal quantum number. This refinement helped to account for the spectral lines of more complex atoms.

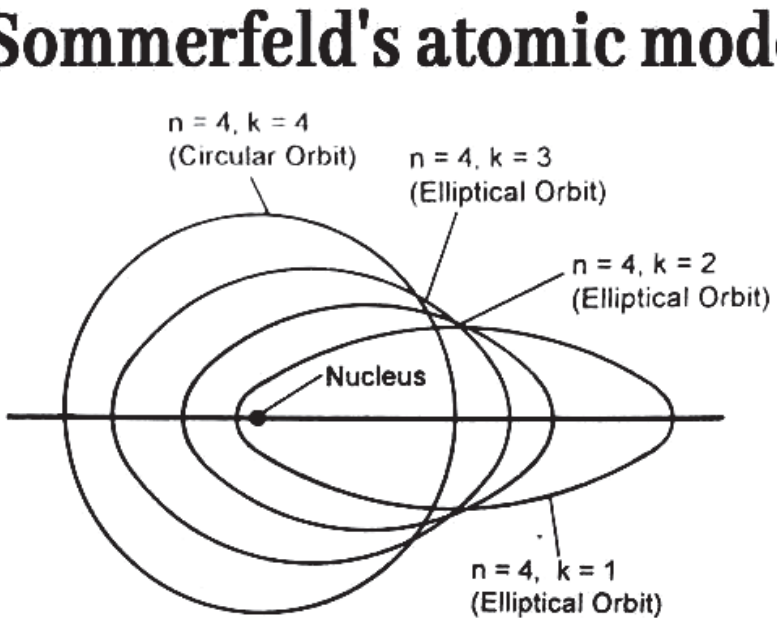
Fine Structure:

Sommerfeld's modifications led to the prediction of additional spectral lines that were not accounted for by the original Bohr model. These extra lines, known as fine structure, were later experimentally observed and provided further evidence for the validity of Sommerfeld's modifications.

Spin-Orbit Interaction:

Sommerfeld introduced the spin-orbit interaction, which accounts for the interaction between the orbital motion of an electron and its intrinsic spin. This interaction helps explain certain fine details in the atomic spectrum.

Sommerfeld's modifications marked an important step in the development of quantum theory and contributed to a more accurate description of the behavior of electrons in atoms. While the Bohr model laid the foundation, Sommerfeld's adjustments paved the way for later developments in quantum mechanics, ultimately leading to the more sophisticated quantum mechanical models used today.



1.6 Wave Mechanics and de Broglie Equation

Wave mechanics, also known as quantum mechanics, is a fundamental theory in physics that describes the behavior of particles at the quantum level. One of the key developments in wave mechanics is associated with Louis de Broglie and his groundbreaking equation, which relates the wavelength of a particle to its momentum.

Louis de Broglie proposed that if electromagnetic waves, like light, can exhibit both particle and wave-like properties (as demonstrated by the phenomenon of wave-particle duality), then particles, such as electrons, could also exhibit wave-like behavior. This idea challenged the classical view of particles as purely localized entities with definite trajectories.

De Broglie's equation is expressed as:

$\lambda = h/p$

where:

λ is the wavelength of the particle,

h

h is Planck's constant (a fundamental constant in quantum mechanics, denoted by

6.626×10^{-34} J.s

p is the momentum of the particle.

This equation indicates that particles, traditionally thought of as discrete entities with well-defined positions and momenta, also have associated wavelengths. The wavelength is inversely proportional to the momentum of the particle. For macroscopic objects, such as a baseball or a car, the corresponding wavelengths are extremely small and practically undetectable. However, for particles at the atomic and subatomic levels, such as electrons, the wavelengths become significant and observable.

De Broglie's insight was instrumental in providing a theoretical foundation for the wave nature of particles and laid the groundwork for the development of quantum mechanics. The wave-particle duality concept, supported by de Broglie's equation, has been experimentally confirmed in numerous studies, such as the famous double-slit experiment, where particles like electrons display interference patterns characteristic of waves.

In summary, de Broglie's equation is a crucial element of wave mechanics, offering a profound understanding of the dual nature of particles and establishing a bridge between classical and quantum physics. This equation has played a pivotal role in shaping the conceptual framework of quantum mechanics and continues to be a cornerstone in the study of the behavior of matter at the quantum level.

1.7 Heisenberg's Uncertainty Principle

Heisenberg's uncertainty principle is a fundamental concept in quantum mechanics, formulated by the German physicist Werner Heisenberg in 1927. The principle states that there is a limit to the precision with which certain pairs of properties of a particle, such as its position and momentum, can be simultaneously known.

The uncertainty principle is often expressed mathematically as follows:

$\Delta x \, \Delta p \geq h / 4\pi$

where:

Δx is the uncertainty in position,

Δp is the uncertainty in momentum,

$\hbar$ is the reduced Planck constant, approximately equal to 1.054571×10^{-34} J.s.

This principle implies that the more precisely one property is known, the less precisely the other can be known. In other words, there is an inherent limit to the precision with which certain pairs of complementary properties of a particle can be simultaneously determined.

Significance of Heisenberg's Uncertainty Principle

Heisenberg's uncertainty principle has several profound implications and significance in the realm of quantum mechanics and our understanding of the behavior of particles at the microscopic level. Here are some key aspects of its significance:

- **Fundamental Limit on Precision:**

The uncertainty principle sets a fundamental limit on the precision with which certain pairs of complementary properties, such as position and momentum, can be simultaneously known. This is not due to experimental limitations but is inherent in the nature of quantum systems.

- **Challenges Classical Intuition:**

The uncertainty principle challenges classical, deterministic views of physics. In classical mechanics, it is assumed that the properties of a particle, such as its position and momentum, can be precisely determined if one has enough information. The uncertainty principle introduces a level of inherent uncertainty and randomness into the description of particle behavior.

- **Wave-Particle Duality:**

The principle is intimately connected to the wave-particle duality of quantum particles. It implies that particles exhibit both wave-like and particle-like properties, and the more precisely we try to measure one aspect (e.g., position), the more uncertain the complementary aspect (e.g., momentum) becomes.

- **Quantum Measurements Disturb Systems:**

The act of measuring a quantum system disturbs the system itself. This is a departure from classical mechanics, where measurements can be made without significantly affecting

the system being measured. In the quantum world, the act of measurement alters the state of the system.

- **Limits on Technological Applications:**

The uncertainty principle places fundamental limits on certain technological applications. For example, it poses challenges in the development of extremely precise measuring instruments and limits the accuracy with which certain properties of particles can be manipulated in quantum technologies.

- **Philosophical Implications:**

Heisenberg's uncertainty principle has sparked philosophical discussions about the nature of reality, determinism, and the limitations of human knowledge. It underscores the probabilistic nature of quantum mechanics and the idea that, at the quantum level, certain properties do not have well-defined values until they are measured.

- **Foundation of Quantum Mechanics:**

The uncertainty principle is a cornerstone of quantum mechanics. It played a crucial role in the development of this branch of physics and led to the formulation of new principles and mathematical frameworks to describe the behavior of particles at the quantum level.

In summary, Heisenberg's uncertainty principle is a foundational concept in quantum mechanics, challenging classical views, shaping our understanding of the quantum world, and influencing both theoretical and experimental aspects of physics.

1.8 Schrödinger's wave equation (without application and solution detail), & Significance of ψ and ψ2

Schrödinger's wave equation is a fundamental equation in quantum mechanics that describes the behavior of quantum systems, such as electrons in atoms. The equation was formulated by the Austrian physicist Erwin Schrödinger in 1926. The wave equation is a partial differential equation that represents the wave function, denoted by the symbol ψ (psi).

The equation itself is complex and takes different forms depending on the nature of the system under consideration. In general, it describes how the quantum state of a physical system changes over time. The time-dependent Schrödinger equation is given by:

$$i\hbar \frac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{H}\left|\psi(t)\right\rangle$$

Here,

i is the imaginary unit,

$\hbar$ is the reduced Planck constant,

$\partial / \partial t\left|\psi(t)\right\rangle$ is the partial derivative of the wave function with respect to time,

$\hat{H}$ is the Hamiltonian operator representing the total energy of the system, and ψ is the wave function.

The significance of the wave function ψ lies in its connection to the probability distribution of finding a particle in a particular state. The square of the absolute value of the wave function, $|\psi|2$, gives the probability density of finding a particle in a specific position. This is denoted by the symbol $|\psi|2$, and it is related to the likelihood of finding a particle in a particular region of space.

In summary, the wave function ψ in Schrödinger's equation represents the quantum state of a system, and the probability distribution associated with $|\psi|2$ provides information about the likelihood of finding a particle in different positions or states. The square of the wave function's magnitude is crucial in interpreting the probabilistic nature of quantum mechanics.

1.9 Summary

This section explores what's inside an atom, beyond its nucleus. We start by looking at different ideas about how atoms are structured. We pay special attention to Bohr's model and how it explains the colors we see when hydrogen atoms give off light.

Bohr's model was a good start, but it had some problems. So, we talk about changes made by Sommerfeld to improve it.

Then, we get into wave mechanics. De Broglie came up with an equation showing that particles, like electrons, can also act like waves. This is a bit weird, but it helps us understand things better. Heisenberg's uncertainty principle is a big idea here, telling us

there are limits to how precisely we can measure certain properties of particles, like where they are and how fast they're moving.

Next, we briefly mention Schrödinger's equation. It's a math thing, but we don't get into all the details. We do talk about the importance of the wave function (ψ) and its square (ψ^2), which helps us figure out where electrons are likely to be in an atom.

In a nutshell, this section guides us through the history of atomic models, from Bohr to Sommerfeld. We then step into wave mechanics, exploring de Broglie's ideas and the uncertainty principle by Heisenberg. Lastly, we touch on Schrödinger's equation, paving the way for a deeper look into how atoms work in the world of quantum mechanics.

1.10 Model Questions

A. Some Multiple-Choice Questions

a. Who proposed the first atomic model, suggesting that atoms were indivisible and indestructible?

i. Rutherford ii. Dalton

iii. Bohr iv. Thomson

b. In Bohr's model of the atom, electrons orbit the nucleus in fixed paths. What are these paths called?

i. Shells ii. Orbits

iii. Rings iv. Circuits

c. Which spectral series is associated with the transitions of electrons to the n=2 energy level in hydrogen?

i. Lyman series ii. Balmer series

iii. Paschen series iv. Brackett series

d. What was one of the limitations of Bohr's model that Sommerfeld addressed with his modifications?

i. Lack of stability in electron orbits

ii. Only applicable to hydrogen

iii. Failure to explain spectral lines

iv. Neglect of electron spin

e. According to de Broglie's equation, what property is associated with particles such as electrons?

i. Mass ii. Charge

iii. Wavelength iv. Energy

f. Heisenberg's uncertainty principle states that it is impossible to simultaneously know the exact values of which two properties of a particle?

i. Position and velocity ii. Mass and charge

iii. Spin and orbit iv. Energy and momentum

g. Which mathematical equation forms the basis of wave mechanics and describes the behavior of electrons in atoms?

i. Maxwell's equations ii. Planck's equation

iii. Schrödinger's wave equation iv. Heisenberg's matrix equation

h. In the context of Schrödinger's equation, what does the symbol ø represent?

i. Electron spin ii. Atomic radius

iii. Wave function iv. Orbital shape

i. The square of the wave function ($ø^2$) gives the probability density of finding an electron in a specific:

i. Energy state ii. Orbital

iii. Quantum number iv. Subshell

B. Short Type Questions

1. What is the focus of Unit-1: Extra Nuclear Structure of the atom?
2. Why is Bohr's model important, and what does it explain about the atomic spectrum of hydrogen?
3. What are the limitations of Bohr's model, and how did Sommerfeld try to address them?

4. Explain the key concept introduced by de Broglie's equation in wave mechanics.
5. Why is Heisenberg's uncertainty principle significant in understanding the behavior of particles?
6. Briefly describe Schrödinger's wave equation and its role in the study of atomic structure.
7. Without going into details, what is the significance of the wave function (ø) in atomic theory?
8. What modifications did Sommerfeld make to Bohr's model, and why were they necessary?
9. How does de Broglie's equation contribute to our understanding of particles like electrons?
10. In what way does Heisenberg's uncertainty principle impact our ability to measure particle properties accurately?

C. Assay Types Questions

1. Discuss the evolution of atomic models, starting from early ideas to Bohr's model, and the subsequent modifications by Sommerfeld.
2. Explain the significance of the atomic spectrum of hydrogen in the context of Bohr's model and its limitations.
3. Analyze the contributions of de Broglie's wave-particle duality concept to our understanding of the behavior of particles in the atomic structure.
4. Evaluate the impact of Heisenberg's uncertainty principle on the precision of measuring particle properties and its broader implications in quantum mechanics.
5. Elaborate on the modifications made by Sommerfeld to Bohr's atomic model, highlighting the improvements and addressing the limitations.
6. Explore the foundational principles of wave mechanics, including de Broglie's equation and its implications for our understanding of matter.
7. Critically examine the role of Schrödinger's wave equation in the study of atomic structure, without going into specific application details.

8. Discuss the concept of the wave function (ø) and its square (ø^2), and how they contribute to determining the probable locations of electrons in an atom.
9. Compare and contrast Bohr's model with the wave mechanics introduced by de Broglie, Heisenberg, and Schrödinger.
10. Assess the overall significance of Unit-1 in shaping our understanding of the extra-nuclear structure of atoms and its implications for quantum mechanics.

1.11 References

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Unit 2 ❐ Idea about Quantum Numbers

Contents

2.0 Objectives

2.1 Introduction

2.2 Quantum numbers

2.3 Radial and angular wave functions for hydrogen atom (qualitative idea)

2.4 Radial and angular probability distribution curves

2.5 The shapes of s, p, d, and f orbitals

2.6 Summary

2.7 Model Questions

2.8 References

2.0 Objectives

- Establish a fundamental understanding of quantum numbers
- Explore quantum mechanical wave functions
- Introduce the concept of wave functions in quantum mechanics.
- Explain the radial and angular wave functions for a hydrogen atom.
- Discuss the concept of probability density in the context of quantum mechanics.
- Analyze probability distributions in quantum mechanics:
- Present the radial and angular probability distribution curves for a hydrogen atom.
- Examine the shapes of atomic orbitals:
- Introduce the different types of atomic orbitals: s, p, d, and f.
- Provide a qualitative idea of the shapes of these orbitals using visual representations.
- Explore the significance of azimuthal quantum number (l) in determining the shapes of orbitals.
- Illustrate the influence of orbital shapes on electron density.

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2.1 Introduction

Let's talk about tiny things inside atoms – electrons. Imagine these electrons as little dancers in a special place called quantum mechanics. To understand their dance, we use something like a map called quantum numbers. These numbers tell us where the electrons are, how much energy they have, and other important details.

Now, let's zoom in on the hydrogen atom. It gets even more interesting! We use special ideas, like dance moves for electrons, called radial and angular wave functions. It's like guessing where a dancer might be on a dance floor. These wave functions help us guess where electrons might be around the center of the atom.

As we explore this electron dance, we picture curves showing the chances of finding electrons at different spots and directions. These curves reveal cool patterns, helping us understand how electrons act in the hydrogen atom.

Another cool part of our journey is checking out the shapes of electron homes, called orbitals. They have names like s, p, d, and f. Each orbital is like a unique house for electrons with its own shape. These shapes aren't random – they help us see how atoms stick together and make molecules.

So, as we try to understand quantum numbers, wave functions, and orbital shapes, it's like going on a fun adventure. We explore a tiny world where things don't always behave as we expect. This adventure takes us into the heart of quantum mechanics, using models and pictures to figure out how electrons move in the hydrogen atom and, in the big picture, how all the chemistry pieces fit together.

2.2 Quantum Numbers

Quantum numbers are a set of four values that describe the state of an electron in an atom. These numbers arise from the solutions to the Schrödinger equation, which is a fundamental equation in quantum mechanics that describes the behavior of electrons in an atom.

The four quantum numbers are:

Principal Quantum Number (n): This quantum number defines the energy level of an electron in an atom. It can have positive integer values (1, 2, 3, ...), with higher values indicating higher energy levels and larger orbits.

Angular Momentum Quantum Number (l): This quantum number is related to the shape of the electron's orbital. It can have values from 0 to (n – 1) and determines the subshell in which an electron is found. The subshells are labeled s (l = 0), p (l = 1), d (l = 2), f (l = 3), and so on.

Magnetic Quantum Number (m): This quantum number specifies the orientation of the orbital in space. Its values range from –l to +l, including zero. For example, if l = 1 (p subshell), m can be –1, 0, or 1, representing the three possible orientations of the p orbitals along the x, y, and z axes.

Spin Quantum Number (m): This quantum number describes the intrinsic spin of the electron. It can have values of +1/2 or –1/2, representing the two possible spin states of an electron.

Significance of Quantum Numbers

Quantum numbers play a crucial role in describing the quantum state of an atomic or subatomic particle within the framework of quantum mechanics. These numbers provide a set of parameters that characterize various aspects of the particle's behavior and its position within an atom. The four quantum numbers commonly used are the principal quantum number (n), azimuthal quantum number (l), magnetic quantum number ($m_{l)}$, and spin quantum number (m_s). Here's a brief overview of their significance:

Principal Quantum Number (n):

Significance:

- Determines the main energy level or shell of an electron.
- Higher values of n correspond to higher energy levels farther from the nucleus.
- Helps in understanding the size and energy of an electron's orbital.

Azimuthal Quantum Number (l):

Significance:

- Describes the shape of the electron's orbital.
- Values of l range from 0 to (n-1), indicating different sublevels or subshells.
- s (l = 0), p (l = 1), d (l = 2), and f (l = 3) orbitals have distinct shapes.

Magnetic Quantum Number (m_l):

Significance:

- Specifies the orientation of the orbital in space.
- Values range from –l to +l, including zero, indicating the different spatial orientations of orbitals within a subshell.
- Helps in defining the spatial distribution of electrons in an atom.

Spin Quantum Number (m_s):

Significance:

- Describes the intrinsic angular momentum or spin of an electron.
- Can have values of +1/2 or –1/2, indicating the two possible spin orientations.
- Plays a role in the Pauli Exclusion Principle, ensuring that no two electrons in an atom can have the same set of quantum numbers.

The significance of quantum numbers lies in their ability to provide a comprehensive description of the electronic structure of atoms, guiding our understanding of the distribution, arrangement, and behavior of electrons. This understanding is crucial for predicting and explaining the properties of elements, chemical bonding, and the overall behavior of matter at the atomic and subatomic levels.

2.3 Radial and Angular wave Functions for Hydrogen Atom (Qualitative idea)

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2.4 Radial and Angular Probability Distribution Curves

Radial and angular probability distribution curves are terms often used in the context of quantum mechanics and the study of electrons in atoms. These curves provide insights into the probability of finding an electron in a particular region around the atomic nucleus.

Radial Probability Distribution Curve:

The radial probability distribution curve shows the probability of finding an electron at a particular distance from the nucleus of an atom.

In the context of the hydrogen atom, for example, the radial probability distribution is often depicted as a graph of the probability density as a function of the distance from the nucleus.

It helps visualize the likelihood of finding an electron at various radial distances from the nucleus, with peaks indicating regions where the electron is more likely to be found.

Angular Probability Distribution Curve:

The angular probability distribution curve is associated with the angular part of the electron's wave function. It provides information about the probability of finding an electron at a particular angle (è and ö in spherical coordinates) relative to a reference axis.

In the case of hydrogen-like atoms, the angular distribution is often represented by spherical harmonics, which are mathematical functions that describe the shape of the electron cloud in different orbitals.

The angular part of the probability distribution is crucial for understanding the shape and orientation of atomic orbitals.

In summary, while the radial probability distribution curve focuses on the likelihood of finding an electron at different distances from the nucleus, the angular probability distribution curve provides information about the distribution of electron probability in terms of angles around the nucleus. Together, these curves contribute to a comprehensive understanding of the spatial distribution of electrons in an atom, as described by quantum mechanics.

2.5 The Shapes of s, p, d, and f Orbitals

The shapes of s, p, d, and f orbitals refer to the spatial distribution of probability density for finding an electron in an atom. These orbitals are part of the quantum mechanical model used to describe the behavior of electrons in an atom. Here's a qualitative description of the shapes of these orbitals:

s Orbital:

Shape: Spherical

Description: The s orbital is the simplest and has a spherical shape. It is centered around

the nucleus and is symmetrical in all directions. The probability of finding an electron is highest at the nucleus and decreases as you move away from it. An atom can have one or more s orbitals.

p Orbital:

Shape: Dumbbell-shaped (three orientations - p_x, p_y, p_z)

Description: The p orbitals come in sets of three, designated as p_x, p_y, and p_z. Each p orbital has a characteristic dumbbell shape along one of the coordinate axes (x, y, or z). The lobes of the dumbbell represent regions of high electron probability. The three p orbitals are mutually perpendicular, providing a more complex spatial arrangement than the s orbital.

d Orbital:

Shape: Complex and diverse (five orientations - d_{xy}, d_{xz}, d_{yz}, d_{x2-y2}, d_{z2})

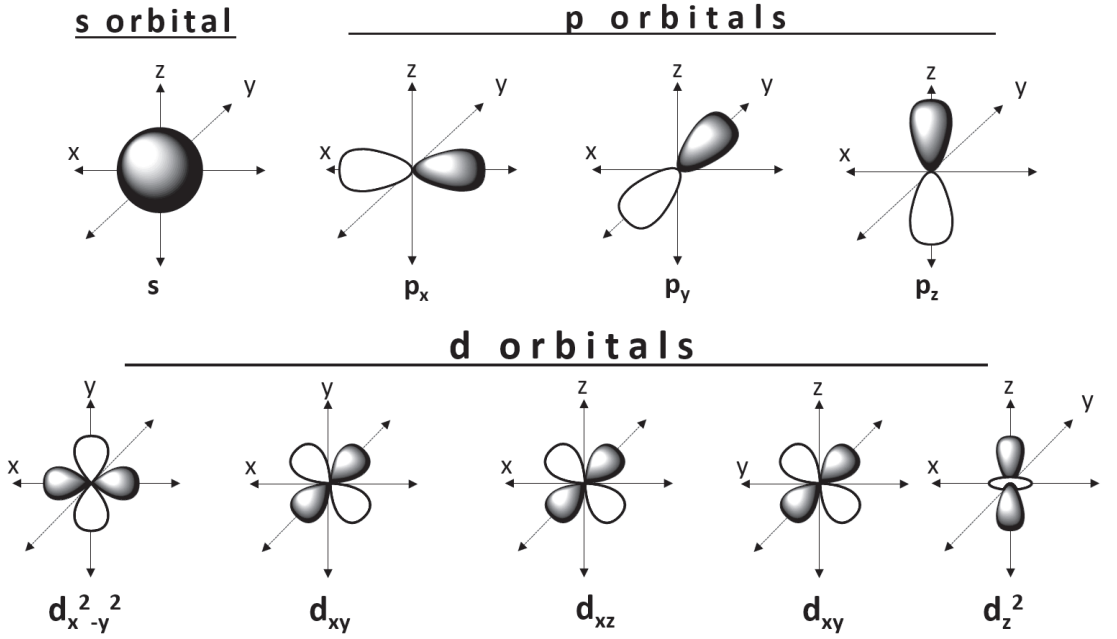
Description: The d orbitals exhibit more complex and varied shapes compared to s and p orbitals. There are five different d orbitals, each with a unique orientation in space. These orbitals are labeled as d_{xy}, d_{xz}, d_{yz}, d_{x2-y2}, and d_{z2}. The shapes involve multiple lobes, nodes, and angular momentum components, making them more intricate than s and p orbitals.

f Orbital:

Shape: Complex and intricate (seven orientations)

Description: The f orbitals are even more complex than d orbitals and have a total of seven different orientations. The specific shapes of these orbitals are quite intricate and involve multiple lobes, nodes, and angular momentum components. Due to their complexity, describing the exact shapes without visual aids can be challenging.

In summary, as one moves from s to p to d to f orbitals, the complexity of the shapes increases, reflecting the increasing angular momentum and quantum numbers associated with these orbitals. Visual representations or diagrams are often used to convey these shapes more accurately.



Shapes of different orbitals

The significance of s, p, d, and f orbitals

The significance of s, p, d, and f orbitals lies in their role in describing the distribution of electrons in an atom. These orbitals help explain the electronic structure of atoms, their chemical properties, and their behavior in chemical reactions. Here are the significances of each type of orbital:

s Orbitals:

- Spherical Symmetry: s orbitals are spherical in shape and exhibit radial symmetry. This symmetry is crucial for understanding the spherical distribution of electron density around the nucleus.
- Core Electrons: The innermost electrons in an atom often occupy s orbitals, contributing to the core electron configuration.

p Orbitals:

- Dumbbell Shape: The distinctive dumbbell shape of p orbitals reflects the directional

nature of electron density. This is essential for explaining molecular geometry and the formation of chemical bonds.

- Pi Bonds: p orbitals play a significant role in the formation of pi bonds in double and triple bonds between atoms.

d Orbitals:

- Complex Geometry: d orbitals have more complex and varied shapes compared to s and p orbitals. Their different orientations contribute to the diverse geometric arrangements observed in transition metal complexes.
- Transition Metal Chemistry: d orbitals are particularly important in transition metal chemistry, where they contribute to the color, magnetic properties, and catalytic activity of transition metal compounds.

f Orbitals:

- Complex Electron Distributions: f orbitals have intricate shapes and multiple orientations. They are important for accommodating a large number of electrons in heavy elements.
- Inner Transition Elements: f orbitals are associated with the inner transition elements (lanthanides and actinides), contributing to their unique electronic and magnetic properties.

In summary, the significance of these orbitals lies in their ability to provide a detailed and nuanced description of the electronic structure of atoms. This information, in turn, is crucial for understanding the periodic trends, chemical bonding, and the behavior of elements in various chemical reactions.

2.6 Summary

We want to understand important things about atoms. Atoms are like tiny building blocks, and we're exploring how they work. Quantum numbers are like secret codes helping us find where electrons are in atoms. These codes tell us where electrons live in atoms, like giving them an address. It's like streets, house numbers, and rooms in a big electron house. Scientists use these codes to understand how atoms behave. Imagine electrons doing dance moves in atoms.

We're looking at how electrons groove in the hydrogen atom, but keeping it simple.

Think of maps showing where electrons like to hang out in atoms. Similar to guessing where a friend might be in a big park. Atoms have different rooms for electrons with unique shapes. Picture these shapes like rooms in a house where electrons have their own spaces. This unit is like a key to unlock atom secrets. We're exploring electron dance moves, where they like to be, and imagining electron rooms in atoms. It's like a fun journey into the tiny world of atoms!

- Quantum numbers uniquely identify and describe the state of an electron in an atom.
- They provide a framework for understanding the electronic structure and behavior of atoms.
- Quantum numbers are essential for constructing electron configurations and predicting chemical properties.
- The Pauli Exclusion Principle, based on quantum numbers, governs the arrangement of electrons in an atom, preventing identical quantum states for electrons in the same atom.
- In quantum mechanics, the radial wave function describes the probability amplitude of finding a particle at a certain distance from the nucleus in an atom. It is a part of the total wave function that depends only on the radial distance from the nucleus. The radial wave function is often represented by the symbol R(r), where 'r' is the radial coordinate.
- The angular wave function is part of the total wave function that depends on the angular coordinates (usually denoted as è and ö) describing the orientation of the particle's position in three-dimensional space. It is responsible for determining the angular distribution of the probability density of finding a particle.

2.7 Model Questions

A. Multiple Choice Type Questions

1. What is the primary role of quantum numbers in describing electrons in an atom?

A. Determining atomic mass

B. Identifying electron spin

C. Describing electron dance moves

D. Defining molecular geometry

2. Which quantum number defines the energy level of an electron and can have positive integer values?

A. Magnetic Quantum Number (m)

B. Angular Momentum Quantum Number (l)

C. Principal Quantum Number (n)

D. Spin Quantum Number (m)

3. What is the significance of the azimuthal quantum number (l) in quantum mechanics?

A. Describes electron spin

B. Determines electron orientation

C. Defines the shape of the electron's orbital

D. Specifies the energy level of an electron

4. What does the radial probability distribution curve illustrate in quantum mechanics?

A. Probability of finding an electron at a particular angle

B. Probability of finding an electron at a specific distance from the nucleus

C. Electron spin orientations

D. Shapes of atomic orbitals

5. Which orbital has a spherical shape and is symmetrical in all directions?

A. p Orbital

B. s Orbital

C. d Orbital

D. f Orbital

6. What is the primary function of p orbitals in molecular geometry?

A. Forming sigma bonds

B. Contributing to pi bonds

C. Providing complex geometry

D. Exhibiting spherical symmetry

7. How many orientations do the d orbitals have, and what is their role in transition metal chemistry?

A. Three orientations; contribution to pi bonds

B. Five orientations; contribution to color and magnetic properties

C. Seven orientations; role in inner transition elements

D. Two orientations; forming sigma bonds

8. What does the Pauli Exclusion Principle, based on quantum numbers, prevent in an atom?

A. Identical quantum states for electrons

B. Formation of chemical bonds

C. Electron dance moves

D. Existence of s orbitals

9. In the context of quantum mechanics, what does the angular wave function determine?

A. Energy levels of electrons

B. Angular distribution of probability density

C. Quantum states of electrons

D. Radial distance from the nucleus

10. What is the primary role of the radial wave function in quantum mechanics?

A. Describing the angular orientation of electrons

B. Determining the energy levels of electrons

C. Defining the spatial distribution of electrons

D. Describing the probability amplitude at a certain distance from the nucleus

B. Short Type Questions

1. What are quantum numbers, and why are they important in quantum mechanics?
2. Explain the principal quantum number (n) and its significance in determining electron energy levels.
3. How does the azimuthal quantum number (l) contribute to the description of atomic orbitals?

4. Define the magnetic quantum number (m) and its role in specifying orbital orientation.
5. What is the spin quantum number (m), and how does it relate to the intrinsic spin of electrons?
6. Describe the radial probability distribution curve and its significance in quantum mechanics.
7. What information does the angular probability distribution curve provide in quantum mechanics?
8. Discuss the shapes of s, p, d, and f orbitals and their importance in understanding electron distribution.
9. How do s, p, d, and f orbitals differ from each other in terms of shape and complexity?
10. Explain the significance of quantum numbers in predicting and explaining the properties of elements and chemical bonding.

C. Assay Type Questions

1. Discuss the fundamental role of quantum numbers in quantum mechanics and their significance in describing the state of electrons in an atom. Provide examples to illustrate your points.
2. Explain the concept of the principal quantum number (n) and its implications for electron energy levels. How does the value of 'n' influence the size and energy of an electron's orbital?
3. Elaborate on the azimuthal quantum number (l) and its relationship to the shapes of atomic orbitals. Provide a detailed discussion on the distinctive shapes of s, p, d, and f orbitals.
4. Define the magnetic quantum number (m) and its role in determining the spatial orientation of orbitals. How does 'm' contribute to our understanding of the distribution of electrons within a subshell?
5. Explore the spin quantum number (m) and its significance in describing the intrinsic spin of electrons. Discuss how the spin quantum number is related to the Pauli Exclusion Principle.
6. Provide a detailed explanation of the radial probability distribution curve in the

context of quantum mechanics. How does this curve contribute to our understanding of the likelihood of finding electrons at different distances from the nucleus?

7. Discuss the angular probability distribution curve and its importance in describing the angular part of an electron's wave function. How does this curve contribute to our understanding of the spatial distribution of electron probability in terms of angles?
8. Examine the shapes of s, p, d, and f orbitals, focusing on their spatial distribution of probability density. How do these shapes reflect the increasing complexity and angular momentum of orbitals as one moves from s to f orbitals?
9. Explain the significance of s, p, d, and f orbitals in the electronic structure of atoms. Discuss how these orbitals contribute to our understanding of chemical properties and behavior in chemical reactions.
10. Incorporate quantum numbers into your discussion on predicting and explaining the properties of elements and chemical bonding. How do quantum numbers provide a framework for constructing electron configurations and guiding our understanding of chemical phenomena at the atomic level?

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Unit 3 ❐ Rules of Electronic Configuration & Nuclear Charge

Contents

3.0 Objectives

3.1 Introduction

3.2 Basic Concept Electronic Configuration of Atoms

3.3 Pauli's Exclusion Principle

3.4 Aufbau Principle and its limitation

3.5 Hund's Rules and Multiplicity

3.6 Exchange energy

3.7 Effective Nuclear Charge

3.8 Shielding and Penetration

3.9 Slater's Rule

3.10 Applications of Slater's Rule

3.11 Summary

3.12 Model Questions

3.13 References

3.0 Objectives

- Understand the concept of electronic configuration in atoms.
- Explore the rules governing the filling of electron orbitals.
- Analyze the relationship between electron configuration and nuclear charge.
- Investigate how nuclear charge influences electronic structure.
- Comprehend Pauli's Exclusion Principle and its significance in electron arrangement.
- Explore the Aufbau Principle and its role in the building of electron configurations.

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- Identify limitations and exceptions to these principles.
- Examine scenarios where Pauli's Exclusion Principle and Aufbau Principle may not fully apply.
- Understand Hund's Rules and their impact on electron distribution.
- Analyze the concept of multiplicity in electron arrangements.
- Explore how these principles contribute to the stability of electron configurations.
- Investigate the concept of exchange energy in the context of electron interactions.
- Understand how exchange energy influences the overall stability of electron configurations.
- Learn how to determine electronic configurations for different atoms.
- Explore the relationship between an atom's position in the periodic table and its electronic configuration.
- Understand the concept of effective nuclear charge.
- Explore how effective nuclear charge affects the behavior of electrons in an atom.
- Investigate the role of shielding in electron-electron repulsion.
- Understand the concept of penetration and its impact on electron distribution.
- Learn about Slater's rule and its application in calculating effective nuclear charge.
- Apply Slater's rule to determine the effective nuclear charge for specific atoms.
- Understand the practical implications of Slater's rule in predicting electron behavior.
- Explore how Slater's rule contributes to a more accurate understanding of atomic properties.

3.1 Introduction

Studying how electrons arrange themselves in atoms and the influence of nuclear charge is crucial for understanding atomic structure. These basic concepts guide us through the intricate movements of electrons, influencing the characteristics of all elements in the periodic table. We will explore the rules that dictate how electrons are arranged and how the nucleus affects them, unravelling the mysteries of the microscopic world of atoms.

An atom's electronic configuration, or how its electrons are organized in orbitals, follows specific rules. These rules, like Pauli's Exclusion Principle and the Aufbau Principle, provide insights into the behavior of atoms. As we delve deeper, Hund's Rules and the idea of multiplicity shed light on how electrons stabilize and arrange themselves within an atom. Additionally, exchange energy, a key player in electron interactions, enhances our understanding of the forces at work in atomic structures.

The exploration extends to the concept of effective nuclear charge, investigating how the nucleus pulls on electrons. Shielding and penetration, guided by Slater's rule, reveal the complexities of electron distribution within an atom. This comprehensive understanding has practical applications in predicting electron behavior and contributes to a more nuanced grasp of atomic properties. Come along as we unravel the captivating world of electrons, orbitals, and the influential forces that shape the fundamental building blocks of matter.

3.2 Basic Concept Electronic Configuration of Atoms

The electronic configuration of an atom describes the distribution of its electrons in different energy levels and sublevels within an atom. Electrons are arranged in shells, which are designated by principal quantum numbers (n). Each shell can contain subshells, which are labelled by letters (s, p, d, f). The subshells, in turn, consist of orbitals, and each orbital can hold a maximum of two electrons.

The rules for filling electron orbitals are based on the Pauli Exclusion Principle, Hund's Rule, and the Aufbau Principle. These principles govern the arrangement of electrons in a way that minimizes their energy.

The Aufbau Principle states that electrons fill the lowest energy orbitals first before moving to higher energy ones. The order of filling is given by the increasing order of the principal quantum number (n) and the azimuthal quantum number (l).

Hund's Rule states that electrons occupy orbitals of the same energy level in a way that maximizes the number of unpaired electrons and minimizes electron repulsion.

The Pauli Exclusion Principle dictates that no two electrons in an atom can have the same set of quantum numbers. This means that each orbital can hold a maximum of two electrons with opposite spins.

The electronic configuration is usually expressed using a notation that includes the energy level, sublevel, and the number of electrons in each sublevel. For example, the electronic configuration of carbon (atomic number 6) is $1s^2\ 2s^2\ 2p^2$, which indicates that there are two electrons in the 1s sublevel and four electrons in the 2s and 2p sublevels combined.

Understanding the electronic configuration of atoms is crucial for predicting their chemical behavior, as it determines how atoms will form bonds with other atoms to achieve a more stable electron configuration, typically filling their outermost energy levels.

- **Energy Levels (Shells):** Electrons are arranged in energy levels or shells, designated by the principal quantum number (n). The first energy level (n = 1) is closest to the nucleus, followed by higher energy levels (n = 2, 3, and so on).
- **Sublevels (Subshells):** Each energy level consists of sublevels, which are labelled by letters: s, p, d, and f. The number of sublevels in an energy level is equal to its principal quantum number (n). For example, the first energy level (n = 1) has only an s sublevel, while the second energy level (n = 2) has s and p sublevels.
- **Orbitals:** Sublevels are further divided into orbitals, which are regions within an energy level where electrons are likely to be found. Each orbital can hold a maximum of two electrons. The s sublevel has one orbital, the p sublevel has three orbitals, the d sublevel has five orbitals, and the f sublevel has seven orbitals.

3.3 Pauli's Exclusion Principle

Pauli's Exclusion Principle is a fundamental concept in quantum mechanics, and it states that no two electrons in an atom can have the same set of quantum numbers. This principle was formulated by the Austrian physicist Wolfgang Pauli in 1925 and is a crucial part of the quantum mechanical description of electrons in atoms.

The four quantum numbers that describe an electron are:

Principal Quantum Number (n): Represents the energy level of the electron's orbital.

Angular Momentum Quantum Number (l): Determines the shape of the orbital.

Magnetic Quantum Number (m): Specifies the orientation of the orbital in space.

Spin Quantum Number (m): Describes the intrinsic spin of the electron.

The Pauli Exclusion Principle focuses on the spin quantum number. The spin quantum number can have two possible values: +1/2 (spin-up) or -1/2 (spin-down). This means that each orbital can accommodate a maximum of two electrons—one with spin-up and the other with spin-down.

Here's a more detailed explanation:

- **Spin States:** Electrons are fermions, a type of particle with half-integer spin, and as such, they obey Fermi-Dirac statistics. This means that no two electrons in an atom can have the same set of quantum numbers, and specifically, no two electrons in the same orbital can have the same spin.
- **Orbital Filling:** When filling the orbitals of an atom according to the Aufbau Principle (filling from lower to higher energy levels), each orbital can hold a maximum of two electrons with opposite spins. This ensures that the two electrons in the same orbital have different quantum states and comply with Pauli's Exclusion Principle.

Example: Consider the electron configuration of oxygen (O), which has the atomic number 8. The electron configuration is $1s^2\ 2s^2\ 2p^4$. The last four electrons are distributed in the 2s and 2p orbitals. In the 2s orbital, the electrons have opposite spins: $2s^2$ ↑↓ . In the 2p orbitals, the electrons follow the same rule, with each orbital accommodating two electrons with opposite spins: 2pt ↑↓ ↑↓ .

Consequence: Pauli's Exclusion Principle ensures that electrons within an atom are distinct from one another, preventing them from occupying the same quantum state. This principle plays a crucial role in determining the electronic structure of atoms and is essential for understanding the stability and behavior of matter.

In summary, Pauli's Exclusion Principle prohibits electrons from having identical quantum numbers, specifically with regard to their spin. This principle has far-reaching implications for the arrangement of electrons in atoms, influencing the overall stability and properties of matter.

3.4 Aufbau Principle and its limitation

The Aufbau principle, also known as the "building-up" principle, is a fundamental concept in quantum mechanics and chemistry. It describes the order in which electrons fill atomic orbitals as they are added to an atom. The principle is based on the idea that electrons occupy the lowest energy orbitals first before moving to higher energy ones.

Detailed explanation of the Aufbau principle:

❒ **Energy Levels and Sublevels:**

Atoms consist of energy levels (shells) and sublevels (orbitals) within these energy levels.

Energy levels are numbered (1, 2, 3, etc.), and each level can contain one or more sublevels.

Sublevels are labeled s, p, d, and f, each with a specific number of orbitals and orientation in space.

❒ **Order of Filling:**

Electrons fill the lowest energy level first (closest to the nucleus) before moving to higher levels. Within a given energy level, sublevels are filled in a specific order: s, p, d, and f.

The s sublevel has the lowest energy, followed by p, d, and f.

❒ **Electron Spin:**

Each orbital can hold a maximum of two electrons with opposite spins (represented as ↑ and ↓). Electrons prefer to occupy empty orbitals before pairing up in the same orbital.

❒ **Pauli Exclusion Principle:**

No two electrons in an atom can have the same set of four quantum numbers. This means that each orbital can accommodate a maximum of two electrons with opposite spins.

❒ **Hund's Rule:**

When filling degenerate (equal energy) orbitals, electrons occupy different orbitals with the same spin before pairing up.

This minimizes the repulsion between electrons in the same orbital.

Limitations of the Aufbau Principle:

Exceptional Cases:

While the Aufbau principle provides a general guideline for electron configuration, there are exceptions in transition metals where the 3d orbital may have a lower energy than the 4s orbital.

Electron-Electron Repulsion:

The principle assumes that electrons are added one at a time, neglecting the fact that electron-electron repulsion can influence the actual order of filling.

Quantum Mechanics and Relativity:

The Aufbau principle is a simplified model that does not consider relativistic effects on electrons moving at high speeds or the detailed intricacies of quantum mechanics.

Ionization and Excitation:

The principle is mainly applicable to neutral atoms in their ground state. Ionization or excitation can alter the electron configuration as electrons may be removed or promoted to higher energy levels.

Magnetic Effects:

Magnetic effects and electron-electron interactions are not fully accounted for in the Aufbau principle.

In summary, while the Aufbau principle is a useful guideline for predicting electron configurations, it has limitations due to the complexities of quantum mechanics and the dynamic nature of electrons in atoms. Advanced models and techniques are needed to account for these limitations and provide a more accurate description of electronic structure.

- Let's consider the electron configurations of a few elements as examples, following the Aufbau principle:

Hydrogen (H):

Hydrogen has one electron. According to the Aufbau principle, it fills the lowest energy level first, which is the 1s orbital.

Electron configuration: $1s^1$

Helium (He):

Helium has two electrons. The second electron also goes into the 1s orbital.

Electron configuration: $1s^2$

Lithium (Li):

Lithium has three electrons. The third electron goes into the next available orbital, which is the 2s orbital.

Electron configuration: $1s^2 2s^1$

Carbon (C):

Carbon has six electrons. The fourth, fifth, and sixth electrons fill the 2p orbitals.

Electron configuration: $1s^2 2s^2 2p^2$

Oxygen (O):

Oxygen has eight electrons. The seventh and eighth electrons fill the 2p orbitals.

Electron configuration: $1s^2 2s^2 2p^4$

Neon (Ne):

Neon has ten electrons. The ninth and tenth electrons fill the 2p orbitals.

Electron configuration: $1s^2 2s^2 2p^6$

Let's look at the electron configurations of some elements with higher atomic numbers, keeping in mind the Aufbau principle:

Sodium (Na):

Sodium has 11 electrons. The eleventh electron goes into the 3s orbital.

Electron configuration: $1s^2 2s^2 2p^6 3s^1$

Phosphorus (P):

Phosphorus has 15 electrons. The fifteenth electron goes into the 3p orbitals.

Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^3$

Chlorine (Cl):

Chlorine has 17 electrons. The seventeenth electron goes into the 3p orbitals.

Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^5$

Potassium (K):

Potassium has 19 electrons. The nineteenth electron goes into the 4s orbital.

Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

Iron (Fe):

Iron has 26 electrons. The twenty-sixth electron goes into the 3d orbitals.

Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Silver (Ag):

Silver has 47 electrons. The forty-seventh electron goes into the 5s orbital.

Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$

Xenon (Xe):

Xenon has 54 electrons. The fifty-fourth electron goes into the 5p orbitals.

Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$

These examples demonstrate how electrons progressively fill orbitals following the Aufbau principle as you move across the periodic table. The pattern of filling is based on the increasing energy levels and sublevels of the orbitals. Keep in mind that these are simplified representations, and actual electronic structures can be more complex due to factors like electron-electron repulsion and quantum mechanical effects.

3.5 Hund's Rules and Multiplicity

Hund's Rules are a set of guidelines that dictate how electrons are distributed in subshells within an atom. The rules were formulated by German physicist Friedrich Hund. The rules are as follows:

Hund's Rule of Maximum Multiplicity:

Hund's Rule is a principle in quantum mechanics that deals with the filling of electrons in atomic orbitals. It states that electrons will occupy degenerate orbitals (orbitals with the same energy level) singly before pairing up. In simpler terms, each orbital in a subshell is occupied by a single electron before any one orbital gets a second electron.

The rule is based on the idea that electrons repel each other due to their negative charge. By occupying different orbitals within the same subshell, electrons can spread out and minimize their repulsion, thereby lowering the overall energy of the atom.

Key Points of Hund's Rule:

1. Degenerate Orbitals: Hund's Rule applies to orbitals with the same energy level, which are known as degenerate orbitals. Examples include the p orbitals in a given shell.

2. Single Occupancy: Electrons fill degenerate orbitals one by one before pairing. This results in the maximum number of unpaired electrons.
3. Maximizing Multiplicity: The rule is often stated in terms of maximizing the total electron spin, or the multiplicity (2S + 1), where S is the total electron spin. By maximizing the number of unpaired electrons, the total electron spin is maximized, leading to a higher multiplicity.

Example:

Consider the electron configuration of nitrogen (N) with atomic number 7: $\mathbf{1}s^2\mathbf{2}s^2\mathbf{2}p^3$

In the 2p subshell, there are three degenerate orbitals. According to Hund's Rule, the electrons will fill these orbitals one by one before pairing up. So, the electron configuration for the 2p subshell of nitrogen is: $\mathbf{2}p^1\uparrow\ \mathbf{2}p^1\uparrow\ \mathbf{2}p^1\uparrow$

Here, the up arrow represents the spin of the electron, and you can see that each orbital is singly occupied before any orbital gets a second electron. This follows Hund's Rule and results in the maximum number of unpaired electrons for nitrogen.

Multiplicity:

Multiplicity, in the context of electron configuration, refers to the number of unpaired electrons in a set of degenerate (having the same energy) orbitals. It is related to the spin quantum number (s), which can have two values: +1/2 or -1/2.

The formula for multiplicity (2S + 1) is used to determine the number of possible electron spin states, where S is the total electron spin. The values for S depend on the number of unpaired electrons.

For example:

- If all electrons in a set of degenerate orbitals are paired (have opposite spins), the multiplicity is 1 (2 * 0 + 1).

Example: The electron configuration for helium is $1s^2$. Since there are no unpaired electrons, the multiplicity is 1.

- If there is one unpaired electron, the multiplicity is 2 (2 * 1 + 1).

Example: The electron configuration for nitrogen is $1s^2\ 2s^2\ 2p^3$. The three unpaired electrons in the p orbitals result in a multiplicity of 2.

- If there are two unpaired electrons, the multiplicity is 3 (2 * 2 + 1).

Example: The electron configuration for oxygen is $1s^2\ 2s^2\ 2p^4$. The two unpaired electrons in the p orbitals result in a multiplicity of 3.

Hund's Rule and Multiplicity work together to explain the arrangement of electrons in atomic orbitals, ensuring stability and minimizing the energy of the atom.

3.6 Exchange energy

Exchange energy is a concept within quantum mechanics that plays a crucial role in understanding the behavior of electrons in atoms and molecules. It is a component of the total energy of a system and arises due to the indistinguishability of electrons. This indistinguishability is a fundamental quantum mechanical principle that states that electrons, being identical fermions, cannot be distinguished from one another.

Here are some key points to consider when discussing exchange energy:

Electron Indistinguishability:

Electrons are indistinguishable particles, meaning that there is no way to uniquely identify one electron from another based on their intrinsic properties like mass or charge.

The Pauli Exclusion Principle further enforces this indistinguishability by stating that no two electrons in an atom can have the same set of quantum numbers.

Pauli Exclusion Principle:

This principle dictates that no two electrons in an atom can have the same set of quantum numbers. As a result, electrons must occupy different quantum states, and this leads to the filling of electron orbitals in atoms.

Fermi-Dirac Statistics:

Electrons follow Fermi-Dirac statistics, which describe the distribution of particles in a system of non-interacting, indistinguishable fermions at thermal equilibrium. These statistics play a key role in understanding the behavior of electrons in a many-electron system.

Exchange Energy Contribution:

Exchange energy arises from the requirement that the total wave function describing a system of electrons must be antisymmetric under the exchange of any two electrons.

This antisymmetry ensures that the wave function remains unchanged when the positions of two electrons are swapped.

Hartree-Fock Approximation:

In practical quantum chemistry, the Hartree-Fock method is often employed to approximate the total energy of a system of electrons. This method incorporates the concept of exchange energy by considering antisymmetrized wave functions.

Role in Electron-Electron Repulsion:

Exchange energy plays a critical role in balancing the effects of electron-electron repulsion within an atom. Without the inclusion of exchange energy, calculations would overestimate the repulsive forces between electrons, leading to inaccurate predictions of electronic structure and bonding.

Significance in Quantum Chemistry:

Understanding exchange energy is essential in the field of quantum chemistry, where accurate predictions of molecular structures, energetics, and reactivity are required. The correct treatment of exchange energy is crucial for obtaining reliable results in electronic structure calculations.

In summary, exchange energy is a fundamental concept in quantum mechanics that arises from the indistinguishability of electrons. Its inclusion in calculations is vital for accurately describing the behavior of electrons in atoms and molecules, contributing to our understanding of electronic structure and chemical bonding.

Calculation of Exchange Energy

The calculation of exchange energy in the context of quantum mechanics and quantum chemistry involves various theoretical approaches. One common method is within the framework of Hartree-Fock theory. Here's a simplified explanation of how exchange energy is calculated using the Hartree-Fock approximation:

Hartree-Fock Approximation:

Hartree-Fock theory is a mean-field approximation used to describe the electronic structure of many-electron systems. It starts with an initial guess for the electron distribution and iteratively refines it to minimize the total energy of the system.

Slater Determinants:

The wave function for a many-electron system is expressed as a Slater determinant, which is an antisymmetrized product of one-electron orbitals. The antisymmetrization ensures that the Pauli Exclusion Principle is satisfied.

Exchange Integral:

The exchange energy arises from the antisymmetrization process and is associated with the exchange of identical fermions. The key mathematical expression involves evaluating the exchange integral, which quantifies the energy change due to the exchange of two electrons. The exchange integral is calculated based on the overlap and interaction of the spatial and spin components of the wave functions.

Slater's Rule:

Slater's rules provide a semi-empirical approach to estimate exchange integrals between atomic orbitals. These rules take into account the effective nuclear charges and the screening effects of other electrons.

Matrix Elements and Hartree-Fock Equations:

The Hartree-Fock equations are solved iteratively to determine the optimal set of one-electron orbitals that minimizes the total energy. The exchange integrals are calculated as matrix elements in these equations, representing the energy contributions due to electron exchange.

Density Matrix:

In the Hartree-Fock self-consistent field (SCF) procedure, the electron density matrix is constructed from the occupied orbitals. The exchange energy is part of the total electronic energy and contributes to the overall stability of the system.

Post-Hartree-Fock Methods:

While Hartree-Fock provides a solid foundation, more accurate methods incorporate electron correlation effects. Post-Hartree-Fock methods, such as configuration interaction (CI) or coupled cluster (CC), go beyond the Hartree-Fock approximation and include additional electron-electron correlation contributions, improving the accuracy of the exchange energy calculation.

Density Functional Theory (DFT):

In density functional theory, exchange energy is typically expressed in terms of the exchange-correlation functional. These functional combines exchange and correlation contributions, and various approximations are employed to model their effects on the electron density.

It's important to note that calculating exchange energy can be computationally demanding, especially for larger systems. Advanced quantum chemistry software packages use numerical methods and efficient algorithms to handle these calculations in a reliable and accurate manner.

Overall, the calculation of exchange energy involves intricate mathematical formulations within the chosen theoretical framework, and researchers often use computational tools to perform these calculations for realistic molecular systems.

3.7 Effective Nuclear Charge

The effective nuclear charge (Zeff) is a concept used in atomic physics to describe the net positive charge experienced by an electron in an atom. It takes into account the shielding effect caused by other electrons in the atom.

In an atom, electrons are attracted to the positively charged nucleus. However, the presence of other electrons between the outer electron and the nucleus reduces the effective attraction felt by that outer electron. This is because the negatively charged electrons partially shield the outer electron from the full force of the positively charged nucleus.

The effective nuclear charge can be calculated using the formula:

$Z\text{eff} = Z - S$

where:

Z is the actual atomic number of the nucleus (the number of protons in the nucleus).

S is the screening constant or shielding constant, representing the effect of electron-electron repulsion.

The shielding constant accounts for the repulsion between electrons in the inner shells and the outer electron. The greater the number of inner electrons, the higher the shielding effect, and thus, the lower the effective nuclear charge experienced by an outer electron.

Understanding the effective nuclear charge is crucial in explaining trends in atomic properties, such as ionization energy and atomic size, within the periodic table. As one moves across a period, the effective nuclear charge generally increases due to the increasing number of protons, leading to changes in atomic properties.

3.8 Shielding and Penetration

Both shielding and penetration effects influence the behavior of electrons in an atom. Shielding, by inner electrons, reduces the effective nuclear charge experienced by outer electrons, while penetration allows certain electrons to get closer to the nucleus, enhancing their screening effect. These concepts are essential for understanding the trends in atomic properties across the periodic table.

Shielding and penetration effects are concepts used in atomic physics to explain the behavior of electrons in an atom.

Shielding Effect:

Definition: Shielding refers to the ability of inner electrons to partially screen or shield outer electrons from the full force of the positive charge in the nucleus.

Mechanism: Electrons are negatively charged particles, and they repel each other. Inner electrons, being closer to the nucleus, exert a repulsive force on outer electrons. This repulsion reduces the net force of attraction between the outer electrons and the nucleus.

Impact on Effective Nuclear Charge: Shielding leads to a decrease in the effective nuclear charge (Zeff) experienced by the outer electrons. The effective nuclear charge is the net positive charge felt by an electron after considering the shielding effect.

Penetration Effect:

Definition: Penetration refers to the ability of electrons to get closer to the nucleus, breaking through the electron cloud of inner shells and coming closer to the nucleus.

Mechanism: Electrons in different orbitals have different degrees of penetration into the space occupied by inner electrons. For example, an electron in an s orbital has better penetration than an electron in a p orbital. Electrons with higher penetration can get closer to the nucleus, experiencing a stronger attraction.

Impact on Effective Nuclear Charge: Electrons with higher penetration contribute

more to shielding, as they can screen other electrons more effectively. Consequently, they have a greater impact on reducing the effective nuclear charge for outer electrons.

3.9 Slater's rule

The Slater's Rules, formulated by the American physicist John C. Slater, are empirical guidelines used to estimate the effective nuclear charge (Zeff) experienced by an electron in a multi-electron atom. These rules take into account the shielding effect of inner electrons on outer electrons, providing a more realistic approximation of the electron-electron interactions within an atom.

As the nuclear charge and the number of electrons in an atom increases, *n, l* also increase. It has been shown earlier that with increase of *n* value the probability of finding of electron at *r* also increases. But it does not mean that there is no electron density close to the nucleus. Electron density gradually decreases to the nucleus together with appearance of nodal plane. Nodal plane is the space where the probability of finding electron is zero and the number of nodal plane is governs by the formula, $n - l - 1$.

Slater proposed that nuclear charge experienced by the electrons closer to the nucleus will be greater compared to the electrons far from the nucleus. This is because of the screening of nuclear charge by the inner electron core. This is called shielding eRect. The screening or shielding emciency decreases with decreasing to penetration properties of the orbitals. Hence, it follows the sequence,

$$s > p > d > f$$

Because of the screening effect, the actual nuclear charge (Z) may be replaced by Z^*_{eff} which is called eFective nuclear charge. It is gven by the equation,

$$Z^*_{eff} = Z - \sigma$$

σ is sum of the shielding contribution.

Estimation of a is governs by the following rules,

(i) The electrons are arranged in sequences of group with increase of *n* and for equal n in order of *l*,

(1*s*,) (2*s*, 2*p*), (3*s*, 3*p*), (3*d*), (4*s*, 4*p*), (4*d*), (4*f*), (5*s*, 5*p*), (5*d*), (5*f*).....

(ii) The contribution of the electrons right to the electron that is under consideration is zero.

(iii) The contribution of each electron from same group 0.35, except 0.3 for 1s.

(iv) If the considered electron is under (*ns, np*) group, all the other electrons present at *n – 1* will contribute 0.85 each and all the other at *n – 2* or further left will contribute 1.00 each.

(v) If the considered electron is under (*nd*) or (*nf*) group, all the other electrons present further left will contribute 1.00 each

Rules are in tabulated form

Electron group	**All group at right side**	***n* group**	**(*n*–1) Groups**	**≤ (n-2) Group**
1*s*	0	0.3	0	0
(*ns, np*)	0	0.35	0.85	1.00
(nd) or (nf).	0	0.35	1.00@	1.00

@ this value will be same for *ns*, *np*.

Electron on consideration	**σ**	**Z*eff = Z = a**
4*s*	(1 × 0.35) + (18 × 0.85) + (10 × 1.00) = 25.65	30 – 25. 65 = 4.35
3*d*	(9 × 0.35) + (18 × 1.00) = 21.15	28 – 21.15 = 6.85
3*s*, 3*p*	(7 × 0.35) + (8 × 0.85) + (2 × 1.00) = 11.25	18 – 11.15 = 6.85
2*s*, 2*p*	(7 × 0.35) + (2 × 0.85) = 4.15	10 – 4.15 = 5.85
1s	0.30	2 – 0. 30 = 1.70

Few Examples:

- Calculate the effective nuclear charge of $4s^1$ electron of Copper?

Effective nuclear charge $Z_{eff} = Z - S$

where Z = atomic number

and S = scmening constant

= 0.35 per electron for electron in nth orbit.

= 0.85 per electron for electrons in (n – 1)th orbit

= 1.00 per electron for electrons in (n – 2)th, (n – 3)th, (n – 4)th orbit

= 0.30 per electron in ls-orbital (when alone)

This electron is screened by 18 electrons in (n – 1), 8-electrons in (n – 2) and 2- electrons in. (n – 3)

Thus, $\sigma = \overbrace{(n-1)s^2p^6}^{8\times0.85} + \overbrace{(n-1)d^{10}}^{1\times10} + \overbrace{(n-2)s^2p^6}^{8\times1} + \overbrace{(n-3)s^2}^{2\times1}$

= 26.8

Thus, Z* = 29 – 26.8 = 2.2

- Calculate the effective nuclear charge for 3delectron of nickel atom.

The expression for the eRective nuclear chase Z*eff is

Z*eff = Z – S

Here, Z is the nuclear atomic number and S is the shielding constant.

For nickel Z = 28 and S = 20.45

Hence, Z*eff Z – S = 28 – 20.45 = 7.55

Hence, the effective nuclear charge for Nickel atom is 7.55.

- Calculate the effective nuclear Charge for 4s electrons of Zn.

The electronic configuration of Zn is $[Ar]3d^{10},4s^2$

Net attractive force on the electron under consideration = Z – S = (Nuclear charge (atomic number) – (screening effect)

Slater's Formula for screening constant

Each electron contributes 0.35 (total electrons minus 1) present in outermost shell.

In penultimate energy level, electrons contribute 0.85.

A contribution of 1.0 is from remaining electrons (present in last but one energy level)

For 4s – electrons: 1 × 0.35 + 10 × 0.85 + 1.0 ×18 = 0.35 + 8.5 + 18.0 = 26.85

Hence, effective nuclear charge for 4s electrons of Zn is = 30 – 26.85 = 3.15

Specific Applications:

Effective Nuclear Charge (Zeff) Calculation:

Slater's rules help estimate the effective nuclear charge experienced by an electron in a multielectron atom. The effective nuclear charge is crucial in understanding the energy levels and electronic configurations of atoms.

Electron Shielding:

Slater's rules are used to determine the degree of electron shielding provided by inner electron shells to outer electrons. This is important in understanding the distribution of electrons in different energy levels.

Electron Configurations:

By taking into account the effective nuclear charge, Slater's rules contribute to the determination of electron configurations in atoms. This includes predicting the order of filling of atomic orbitals.

Chemical Bonding:

Slater's rules can be applied to understand and predict the nature of chemical bonds in molecules. The effective nuclear charge influences the behavior of electrons in bonding and helps in explaining trends in chemical reactivity.

Ionization Energy and Electron Affinity:

The effective nuclear charge affects the ionization energy and electron affinity of atoms. Slater's rules contribute to explaining trends in these properties across the periodic table.

Molecular Structure:

In the context of molecular orbital theory, Slater's rules can be used to estimate the effective nuclear charge experienced by electrons in molecular orbitals. This information is relevant to understanding the stability and properties of molecules.

It's important to note that Slater's rules are empirical and have limitations, particularly in accurately predicting electronic behavior in complex systems. However, they provide a useful framework for gaining insights into atomic and molecular properties based on the concept of effective nuclear charge.

3.10 Applications of Slater's Rule

Slater's rules, formulated by John C. Slater, are used in quantum chemistry to estimate the effective nuclear charge experienced by an electron in a multi-electron atom. The effective nuclear charge is an important factor in determining the energy levels and electron configurations of atoms. Slater's rules provide a simplified method for calculating this effective nuclear charge.

Here are some applications of Slater's rules:

- **Electron Shielding and Effective Nuclear Charge:**

Slater's rules help in estimating the shielding effect of inner electrons on outer electrons. The more effectively inner electrons shield outer electrons from the nuclear charge, the lower the effective nuclear charge experienced by the outer electrons.

- **Electron Configuration:**

The effective nuclear charge influences the arrangement of electrons in an atom. By using Slater's rules, one can estimate the effective nuclear charge for different electrons in an atom, which in turn helps in predicting the electron configuration of the atom.

- **Ionization Energy and Electron Affinity:**

The effective nuclear charge affects the ionization energy (energy required to remove an electron) and electron affinity (energy change when an electron is added) of an atom. Higher effective nuclear charge generally leads to higher ionization energy and lower electron affinity.

- **Chemical Bonding:**

In the context of molecular orbital theory, Slater's rules can be used to estimate the effective nuclear charge felt by electrons in different atoms participating in a chemical bond. This can help in understanding and predicting the strength and nature of chemical bonds.

- **Periodic Trends:**

Slater's rules contribute to explaining periodic trends in the properties of elements. For example, the increase in effective nuclear charge across a period influences trends in atomic size, ionization energy, and electron affinity.

- **Estimation of Screening Constants:**

Slater's rules provide screening constants that are used to estimate the extent to which inner electrons shield outer electrons from the nuclear charge. These screening constants are employed in calculations related to atomic and molecular properties.

- **Prediction of Electron Repulsion:**

Slater's rules account for electron-electron repulsion, which is crucial in understanding the stability and geometry of molecules. This is particularly important in the context of valence bond theory.

It's important to note that Slater's rules are empirical and provide an approximation rather than an exact solution. More sophisticated quantum mechanical methods, such as Hartree-Fock calculations, are used for more accurate descriptions of electron behavior in atoms and molecules.

3.11 Summary

The chapter relate to fundamental concepts in the field of atomic structure and electronic configuration.

- This section likely introduces the arrangement of electrons in atoms, detailing the distribution of electrons in different energy levels and orbitals.
- Pauli's Exclusion Principle states that no two electrons in an atom can have the same set of quantum numbers. This principle is crucial in understanding the behavior of electrons in atomic orbitals.
- The Aufbau Principle outlines the order in which electrons fill atomic orbitals, starting with the lowest energy levels. The limitation may refer to exceptions observed in certain transition metal elements.
- Hund's Rules describe the arrangement of electrons within a subshell, emphasizing that electrons will occupy separate orbitals before pairing up. Multiplicity may relate to the number of unpaired electrons, a key factor in magnetic behavior.
- Exchange energy is likely discussed in the context of electron-electron interactions within a system, contributing to the overall stability of the arrangement.
- Effective nuclear charge refers to the net positive charge experienced by an electron,

which is influenced by shielding and penetration effects. It plays a role in determining electron behavior in an atom.

- Shielding involves inner electrons partially blocking the attractive force between the nucleus and outer electrons. Penetration refers to the ability of electrons to get closer to the nucleus, influencing effective nuclear charge.
- Slater's Rule is a method for calculating the effective nuclear charge experienced by an electron in a multi-electron atom, incorporating the concepts of shielding and penetration.
- This section likely explores practical uses of Slater's Rule, such as predicting atomic properties or understanding the behavior of electrons in complex atomic structures.

In summary, these issues cover essential principles governing the electronic configuration of atoms, addressing concepts like exclusion, orbital filling, electron arrangement rules, and factors influencing electron behavior within an atom.

3.12 Model Questions

A. Multiple Choice Questions

1. What does Pauli's Exclusion Principle state?

a. Electrons in an atom repel each other

b. No two electrons in an atom can have the same set of quantum numbers

c. Electrons occupy orbitals with the same energy simultaneously

d. Electrons always pair up in the same orbital

2. Which principle outlines the order in which electrons fill atomic orbitals?

a. Aufbau Principle

b. Pauli's Exclusion Principle

c. Hund's Rules

d. Exchange Energy

3. What is the main focus of Hund's Rules?

a. Order of orbital filling

b. Electron arrangement within a subshell

c. Penetration effects

d. Effective nuclear charge

4. What does effective nuclear charge take into account?

a. Number of electrons in an atom

b. Electron-electron interactions

c. Attractive force between nucleus and outer electrons

d. Shielding and penetration effects

5. Which principle emphasizes that electrons will occupy separate orbitals before pairing up?

a. Aufbau Principle

b. Pauli's Exclusion Principle

c. Hund's Rules

d. Exchange Energy

6. What is Slater's Rule used for in atomic theory?

a. Predicting atomic properties

b. Calculating electron-electron interactions

c. Determining the order of orbital filling

d. Explaining effective nuclear charge

7. What does shielding involve in the context of atomic structure?

a. Electrons occupying the same orbital

b. Inner electrons blocking the attractive force between nucleus and outer electrons

c. Arrangement of electrons in subshells

d. Exchange energy between electrons

8. Which factor plays a crucial role in determining the stability of electron arrangements within an atom?

a. Effective nuclear charge
b. Penetration effects
c. Shielding
d. Exchange energy

9. In the context of atomic structure, what does "penetration" refer to?

a. The ability of electrons to get closer to the nucleus
b. Electrons occupying the same orbital
c. Electrons pairing up in the same subshell
d. Effective nuclear charge calculation

10. What is the primary focus of the Aufbau Principle?

a. Hund's Rules and Multiplicity
b. Order of orbital filling
c. Effective Nuclear Charge
d. Applications of Slater's Rule

B. Short Type Questions

1. Define Pauli's Exclusion Principle.
2. Explain the Aufbau Principle and provide an example of its application.
3. What are Hund's Rules, and how do they influence the arrangement of electrons in a subshell?
4. Briefly describe the concept of exchange energy in the context of atomic structure.
5. Define effective nuclear charge and its significance in determining electron behavior.
6. What is the main focus of shielding in atomic structure, and how does it affect electron interactions?
7. How does Slater's Rule contribute to understanding the behavior of electrons in multi-electron atoms?

8. Explain the concept of penetration in the context of electron behavior in an atom.
9. What are the limitations of the Aufbau Principle, and when are they observed?
10. Provide an example of an application of Slater's Rule in predicting atomic properties.

C. Assay Type Questions

1. Discuss the significance of Pauli's Exclusion Principle in understanding the electronic structure of atoms. Include examples to illustrate its application.
2. Explain the Aufbau Principle and its role in determining the order in which electrons fill atomic orbitals. Discuss any exceptions to this principle and their implications.
3. Elaborate on Hund's Rules and their impact on the arrangement of electrons within a subshell. Provide examples to illustrate the application of these rules.
4. Describe the concept of exchange energy in the context of electron-electron interactions. How does exchange energy contribute to the stability of electron configurations in atoms?
5. Discuss the concept of effective nuclear charge and its influence on the behavior of electrons in an atom. Include a discussion on how shielding and penetration contribute to effective nuclear charge.
6. Explain the role of shielding in atomic structure. How does shielding affect the effective nuclear charge experienced by outer electrons, and what are its consequences?
7. Provide an in-depth explanation of Slater's Rule. How is it used to calculate effective nuclear charge, and what insights does it offer into the behavior of electrons in multi-electron atoms?
8. Discuss the concept of penetration in the context of electron behavior. How does penetration influence the distribution of electrons in atomic orbitals?
9. Explore the limitations of the Aufbau Principle. When and why do these limitations arise, and how do they impact our understanding of electron configurations in certain elements?
10. Examine an application of Slater's Rule in predicting atomic properties. How does this rule assist in understanding the behavior of electrons in complex atomic structures? Provide specific examples to illustrate its utility.

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Module II: Nuclear Chemistry

Unit 4 ❐ Radioactivity and nuclear chemistry

Contents

4.1 Objectives

4.2 Introduction

4.3 Discovery of Radioactivity

4.4 Atomic Nucleus

4.5 Nuclear Stability

4.6 n/p ratio and different modes of decay

4.7 Group Displacement Law

4.8 Law of Radioactive Decay

4.9 Half-life Period and Mean Life

4.10 Mass Defect

4.11 Nuclear Binding Energy

4.12 Packing Fraction

4.13 Nuclear Forces and Meson Exchange Theory

4.14 Elementary Idea of Nuclear Shell Model and Magic Numbers

4.15 Summary

4.16 Model Questions

4.17 References

4.1 Objectives

- Define the atomic nucleus and its role in an atom.
- Explore the concept of nuclear stability and factors influencing it.

E-Copy

- Investigate the neutron-to-proton (n/p) ratio and its significance in determining nuclear stability.
- Identify and describe different modes of nuclear decay, including alpha decay, beta decay, and gamma decay.
- Examine the consequences of each decay mode on the composition and stability of the nucleus.
- Define mass defect and its importance in nuclear physics.
- Explore the relationship between mass defect and the energy released during nuclear reactions.
- Define packing fraction as a measure of nucleus compactness.
- Explore the concept of nuclear binding energy and its relationship to the stability of the nucleus.
- Explore the Meson Exchange Theory as an explanation for nuclear forces.
- Understand the role of mesons in mediating the strong force between nucleons.
- Provide an elementary idea of the nuclear shell model.
- Explore the concept of energy levels and shells within the atomic nucleus.
- Define magic numbers in the context of nuclear physics.
- Understand the significance of magic numbers in determining the stability and behavior of atomic nuclei.

4.2 Introduction

Radioactivity and nuclear chemistry are really interesting parts of science that help us understand the powerful world of atomic nuclei. These fields explore how substances can change and give off energy in the form of radiation, helping us learn about the basic processes happening inside atoms.

The discovery of radioactivity in the late 19th and early 20th centuries was a big deal in science. It challenged what we knew and led to some important breakthroughs. Radioactivity happens when unstable atomic nuclei release energy to become more stable. This energy release can have a big impact, not just in labs, but also in medical, industrial, and environmental fields.

Understanding radioactivity involves looking at different types of decay, like alpha decay, beta decay, and gamma decay. Each type involves the emission of specific particles or energy, causing one element to turn into another. This process has important applications in various areas of our lives.

Nuclear chemistry, a related field, looks at how atomic nuclei interact and react. It covers everything from making new elements in labs to using radioactive isotopes in medicine for things like imaging and treatment. The combination of radioactivity and chemistry has given us powerful tools and techniques that have changed many scientific fields.

One well-known use of nuclear chemistry is in generating electricity. Nuclear power plants use the energy released during a process called nuclear fission to produce electricity. While this technology has its challenges, like safety and waste management, it has the potential to provide a lot of clean and efficient energy.

However, the same nuclear processes that give us benefits also come with risks, as seen in events like Chernobyl and Fukushima. Understanding radioactivity and nuclear chemistry is crucial to managing these risks and using nuclear technology safely.

In this exploration of radioactivity and nuclear chemistry, we'll look at the history, the basic ideas, and the different ways these fields are used. From unlocking the secrets of the nucleus to using its energy for our needs, learning about radioactivity and nuclear chemistry is like taking an exciting journey into the heart of matter and energy.

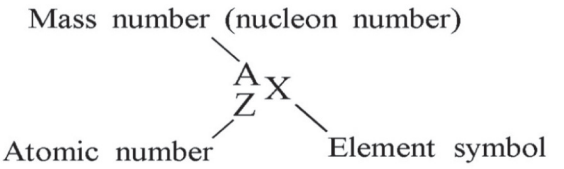
4.3 Discovery of Radioactivity

The phenomenon of radioactivity was discovered by Antoine Henri Becquerel in 1896. He discovered that photographic plates develop bright spots when exposed to uranium minerals [potassium uranyl sulfate : $K_2UO_2(SO_4)_2.2H_2O$], and he concluded that the minerals give off some sort of radiation. Marie Sklodowska Curie (1867-1934), one of the first women in France to attempt doctoral work, pursued the study of uranic rays for her doctoral thesis. Curie discovered two new elements, both of which also emitted uranic rays. Curie named one of her newly discovered elements polonium after her home country of Poland. In 1903, Curie received the Nobel Prize in physics — which she shared with Becquerel and her husband, Pierre Curie — for the discovery of radioactivity. In 1911, Curie was awarded a second Nobel Prize, this time in chemistry,

for her discovery of the two new elements polonium and radium. Element 96 (curium) is named in honor of Marie Curie and her contributions to our understanding of radioactivity.

4.4 Atomic Nucleus

The protons and neutrons in each atom are found in a tiny, central nucleus that measures about 1/100,000 the diameter of the atom itself. The atoms of each element are not necessarily identical; they can differ with respect to the number of neutrons in their nuclei. When an element has two or more species of atoms, each with the same number of protons but a different number of neutrons, the different species are called isotopes. Different isotopes of the same element have the same atomic number, but they have a different mass number, which is the sum of the numbers of protons and neutrons in the nucleus. In the context of nuclear science, protons and neutrons are called nucleons, because they reside in the nucleus. The atom's mass number is often called the nucleon number, and a particular type of nucleus, characterized by a specific atomic number and nucleon number, is called a nuclide. Nuclides are represented in chemical notation by a subscript atomic number (Z) and superscript nucleon number (A) on the left side of the element's symbol (X) :



For example, the most abundant nuclide of uranium has 92 protons and 146 neutrons, so its atomic number is 92, its mass number is 238 (92 + 146), and its symbol is $^{238}_{92}U$. Nuclides can also be described with the name of the element followed by the nucleon number. Therefore, $^{238}_{92}U$. is commonly described as 238 U or uranium-238.

4.5 Nuclear Stability

Two forces act upon the particles within the nucleus to produce the nuclear structure. One, called the electrostatic force (or electromagnetic force), is the force that causes opposite electrical charges to attract each other and like charges to repel each other. The positively charged protons in the nucleus of an atom have an

electrostatic force pushing them apart. The other force within the nucleus, called the strong force, holds nucleons (protons and neutrons) together. If one proton were to encounter another, the electrostatic force pushing them apart would be greater than the strong force pulling them together, and the two protons would fly in separate directions. Therefore, nuclei that contain more than one proton and no neutrons do not exist. Neutrons can be described as the nuclear glue that allows protons to stay together in the nucleus. Because neutrons are uncharged, there are no electrostatic repulsions between them and other particles. At the same time, each neutron in the nucleus of an atom is attracted to other neutrons and to protons by the strong force. Therefore, adding neutrons to a nucleus increases the attractive forces holding the particles of the nucleus together without increasing the amount of repulsion between those particles. As a result, although a nucleus that consists of only two protons is unstable, a helium nucleus that consists of two protons and two neutrons is very stable. The increased stability is reflected in the significant amount of energy released when two protons and two neutrons combine to form a helium nucleus.

$$p + p + n + n \rightarrow {}^{4}_{2}He^{2+}$$

For many of the lighter elements, the possession of an equal number of protons and neutrons leads to stable atoms. For example, carbon-12 atoms, with six protons and six neutrons, and oxygen-16 atoms, with eight protons and eight neutrons, are both very stable. Larger atoms with more protons in their nuclei require a higher ratio of neutrons to protons to balance the increased electrostatic repulsion between protons. Table 2.1. shows the steady increase in the neutron-to-proton ratios of the most abundant isotopes of the elements in group 15 on the periodic table, n/p ratio and different modes of decay.

Neutron-to-Protan Ratio for the Most Abundant Isotopes of the Group 15 Elements

Element	Number of neutrons	Number of protons	Netron-to-proton ration
nitrogen, N	7	7	1 to 1
phosphorus, P	16	15	1.07 to 1
arsenic, As	42	33	1.27 to 1
antimony, Sb	70	51	1.37 to 1
bismuth, Bi	126	83	1.52 to 1

There are 264 stable nuclides found in nature. The graph in Figure 2. 1. shows the neutron-to-proton ratios of these stable nuclides. Collectively, these nuclides fall

within what is known as the **band of stability**. A nuclide containing numbers of protons and neutrons that place it outside this band of stability will be unstable until it undergoes one or more nuclear reactions that take it into the band of stability. We call these unstable atoms **radioactive nuclides,** and the changes they undergo to reach stability are called **radioactive decay.**

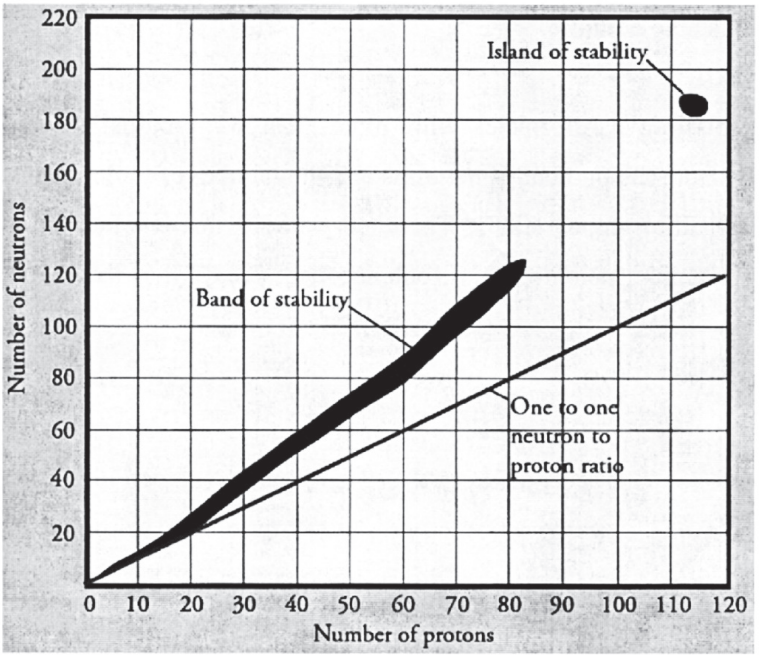


Figure 2.1 The Band of Stability

4.6 n/p Ratio and Different Modes of Decay

Since radioactivity is a nuclear phenomenon, it must be connected with the instability of the nucleus. This can be explained in the basis of relative number of protons and neutrons. The n/p ratio helps us to predict in which way an unstable nucleus will decay.

If for a stable isotope the number of proton in the nucleus is plotted against the number of neutrons in the nucleus, it is seen that the actual n/p plot of stable isotopes breaks from the hypothetical n/p (1:1) plot at around an atomic number '20' and raised rather steeply. This indicates that if the number of protons increases inside the nucleus, the more and more neutrons will be required to stabilise the nucleus. When

an isotope is located above this actual n/p plot, it has too high n/p ratio and when located below the plot, it has too low n/p ratio. In either case the unstable nucleus should decay so as to approach actual n/p plot.

When n/p ratio is too low, i.e, the nucleus is neutron deficient: In this case the nucleus is proton riched, so it decays to reduce its +ve charge. When n/p ratio is very high, the neutron rich nucleus decay in such a way to attain the actual stable n/p ratio.

(i) **Alpha (α) emission :** All nuclei with more than 82 protons are radioactive and decay spontaneously. Both the number of neutrons and the number of protons must be reduced in order to make these radioisotopes stable. The very heavy nuclei often decay by emitting alpha particles. For example, polonium-210 spontaneously decays into lead-206 by emitting an alpha particle

$$^{210}_{84}Po \rightarrow {}^{206}_{82}Pb + {}^{4}_{2}He$$

(ii) **Beta emission (β or β) :** Some radioactive nuclides have a neutron-to-proton ratio that is too high, placing them above the band of stability. To reach a more stable state they undergo **beta emission** (β). In this process, a neutron becomes a proton and an electron. The proton stays in the nucleus, and the electron, which is called a **beta particle** in this context, is ejected from the atom.

$$n \rightarrow p + e^{-}$$

In nuclear equations for beta emission, the electron is written as either β, or β^{-} or $^{0}_{-1}e$. Iodine- 131, which has several medical uses, including the measurement of iodine uptake by the thyroid, is a beta emitter :

$$^{131}_{53}I \rightarrow {}^{131}_{54}Xe + {}^{0}_{-1}e$$

(ii) **Positron emission:** For nuclei with low neutron-to- proton ratios, two common radioactive decay processes occur: positron emission and electron capture. These two processes tend to increase the neutron-to-proton ratio of the neutron-poor atom, bringing the atom closer to, if not within, the band of stability. **Positron emission** is a radioactive decay process that involves the emission of a positron from a nucleus. A **Positron** is a particle with the same mass as an electron but opposite charge; thus, it is represented by the symbol $^{0}_{+1}e$ or

e^+. During positron emission, a proton in the nucleus is converted into a neutron and a positron, and then the positron is emitted.

$$p \rightarrow n + e^+$$

Carbon- 11 undergoes positron emission to form boron-11. Positron emission decreases the number of protons from six to five, and increases the number of neutrons from five to six. The resulting atom, ^{11}B has a neutron-to-proton ratio of 1.2:1, which is within the band of stability.

$$^{40}_{19}K \rightarrow {}^{40}_{18}Ar + {}^{0}_{+1}e$$

(iii) **Electron capture :**

Electron capture is the other common radioactive-decay process that decreases the number of protons in unstable nuclei lying below the band of stability. **Electron capture** occurs when the nucleus of an atom draws in a surrounding electron, usually one from the lowest energy level. This captured electron combines with a proton to form a neutron.

$P + e^- \rightarrow n$

The atomic number of the nucleus decreases by 1 as a consequence of electron capture. The formation of the neutron also results in an X-ray photon being emitted. These two characteristics of electron capture are shown in the electron capture of rubidium-81

$$^{0}_{-1}e + {}^{125}_{53}I \rightarrow {}^{125}_{52}Te + \gamma$$

(iv) Gamma (γ) rays :

Because radioactive decay leads to more stable products, it always releases energy. Some of this energy is released in the form of kinetic energy, adding to the motion of the product particles, but often some of it is given off as the form of radiant energy called gamma rays. **Gamma rays** can be viewed as streams of high energy photons. For example, cesium-137 is a beta emitter that also releases gamma radiation. The energy released in the beta emission leaves the product element, barium-137, in an excited state. When the barium-137 descends to its ground state, it gives off photons in the gamma ray region of the radiant energy spectrum.

$$^{137}_{55}Cs \rightarrow {}^{137}_{56}Ba^* + {}^{0}_{-1}e \rightarrow {}^{137}_{56}Ba + \gamma - photon$$

Radioactive radiations are of three types : Positively charged α-rays, negatively charged β-rays and uncharged γ-rays.

Type of radiation	Nuclear symbol	Nature of the radiation	Mass (amu)	charge	Ionizing power
Alpha	$^{4}_{2}He$	A helium nucleus of 2 Protons and 2 neutrons	4	+2	Very high ionizing power, Low Penetration
Beta	$^{0}_{-1}e$	High kinetic energy electrons	1/1850	–1	Moderate ionizing power, moderate penetration with a smaller mass and charge than the alpha particle
Gamma and X-rays	$^{0}_{0}\gamma$	High frequency electromagnetic radiation	0	0	Low ionizing power, highly penetrating, interact dominantly with the electron shell of the atom
Neutorn	$^{f}n_{0}$	Very high frequency	0	0	The lowest ionizing power of the four, very highly penetrating, interact primarily

4.7 Group Displacement Law

This law was given by Soddy, Russel and Fajans in 1913 to decide the position of element, obtained after radioactive disintegration, in the Peridic Table.

According to this law, 'In an α-emission, the daughter nuclei will occupy a position which is two places left to the position of parent nuclei and in a β-emission, the daughter nuclei will occupy a position one place right to the parent nuclei".

In alpha decay, an element is created with an atomic number less by 2 and a mass number less by four of that of the parent radioisotope, e.g.:

$$^{238}_{92}U \xrightarrow{\alpha} {}^{234}_{90}Th$$

In beta decay, the mass number remains unchanged while the atomic number becomes greater by 1 than that of the parent radioisotope, e, g.:

$$^{234}_{90}Th \xrightarrow{\beta} {}^{234}_{91}Pa \xrightarrow{\beta} {}^{234}_{92}U$$

4.8 Law of Radioactive Decay

When a radioactive material undergoes α, β or γ-decay, the number of nuclei undergoing the decay, per unit time, is proportional to the total number of nuclei in the sample material. So,

If N = total number of nuclei in the sample and ΔN = number of nuclei that undergo decay in time Δt then,

$$\Delta N/\Delta t \propto N$$
$$\text{Or, } \Delta N/\Delta t = \lambda N \ldots (2.1)$$

where λ, = radioactive decay constant or disintegration constant. Now, the change in the number of nuclei in the sample is, $dN = -\Delta N$ in time Δt. Hence, the rate of change of N (in the limit $\Delta t \rightarrow 0$) is,

$$dN/dt = \lambda N$$

$$\text{Or, } dN/N = -\lambda dt$$

Now, integrating both sides of the above equation. we get.

$$\int_{n_0}^{n} f\, dN/N = \lambda \int_{t_0}^{t} dt \ldots (2.2)$$
$$\text{or, In } N - \text{In } N_0 = -\lambda(t - t_0) \ldots (2.3)$$

Where, N_0 is the number of radioactive nuclei in the sample at some arbitrary time t_0 and N is the number of radioactive nuclei at any subsequent time t. Next, we set $t_0 = 0$ and rearrange the above equation (3) to get,

$$\text{In } (N/N0) = -\lambda t$$

$$\text{Or, } N(t) = N_0 e^{-\lambda t} \ldots$$

Equation (2.4) is the Law of Radioactive Decay.

Decay Rate:

In radioactivity calculations, we are more interested in the decay rate R (= $-dN/dt$) than in N itself. This rate gives us the number of unclei decaying per unit time. Even if we don't know the number of nuclei in the sample, by simply measuring the number of emissions of α, β or γ particles in 10 or 20 seconds, we can calculate the

decay rate Let's say that we consider a time interval dt and get a decay count ΔN (= $-dN$). The Decay rate is now defined as,

$$R = -dN/dt$$

Differenting equation (4) on both sides, we get,

$$R = \lambda N_0 e^{-\lambda t}$$

$$\text{Or, } R = R_0 e^{-\lambda t} \ldots (5)$$

Where, R_0 is the radioactive decay rate at time $t = 0$, and R is the rate at any subsequent time t. Equation (5) is the alternative form of the Law of Radioactive Decay. Now we can rewrite equation (1) as follows.

$$R = \lambda N \ldots (6)$$

where R and the numbers of radioactive nuclei that have not yet undergone decay must be evaluated at the same instant.

4.9 Half-life Period and Mean Life

The total decay rate of a sample is also Known as the *activity* of the sample. The S.I. unit for measurement of *activity* is *'becquerel'* and is defined as,

$$1 \text{ becquerel} = 1Bq = 1 \text{ decay per second}$$

An older unit, the curie, is still in common use :

$$1 \text{ curie} = 1\ Ci = 3.7 \times 10^{10}\ Bq \text{ (decays per second)}$$

There are two ways to measure the time for which a radionuclide can last.

Half-life $T_{1/2}$ – the time at which both R and N are reduced to half of their initial value

Mean life τ– the time at which both R and N have been reduced to, e^{-1} of their initial values.

Calculating Half-life Period

Let's find the relation between and the disintegration constant λ, For this, let's imput the following values in equation (5),

$$R = (1/2)\ R_0 \text{ and } t = T_{1/2}$$

So, we get $T_{1/2} = (\text{In } 2)/\lambda$

Or, $T_{1/2} = 0.693/\lambda$ .... (7)

Calculating Mean-life Period

Next, let's find the relation between the mean life τ and the disintegration constant λ, For this, let's consider equation (5),

- The number of nuclei which decay in the time interval : 't' to '$t + \Delta t$' is : $R(t)\ \Delta t = (\lambda N_0 e^{-\lambda t}\ \Delta t)$.
- Each of them lived for time 't'.
- Hence, the total life of all this nuclei is $t\lambda N_0 e^{-\lambda t}\ \Delta t$.

Hence, to obtain the mean life. we integrate this expession over all the times from 0 to ∞ and divide by the total number of nuclei at t = 0 (which is N_0)

$$\tau = \left(\lambda N_0 \int_{\infty}^{0} te^{-\lambda t} dt \right) / N_0$$

$$= \lambda \int_{\infty}^{0} te^{-\lambda t} dt .$$

On solving this integral, we get

$$\tau = 1/\ \lambda$$

Therefore, we can summarise the observations as follows :

$$T_{\frac{1}{2}} = (\text{In}2)/\ \lambda = \tau\ \text{In}\ 2\ \ldots\ (8)$$

4.10 Mass Defect

Nuclear binding energy accounts for a noticeable difference between the actual mass of an atom's nucleus and its expected mass based on the sum of the masses of its non-bound components.

Recall that energy (E) and mass (m) are related by the equation :

$$E = me^2$$

Here, c is the speed of light. In the case of nuclei, the binding energy is so great that it accounts for a significant amount of mass.

The actual mass is always less than the sum of the individual masses of the constituent protons and neutrons because energy is removed when the nucleus is formed. This energy has mass, which is removed from the total mass of the original particles. This mass, known as the mass defect, is missing in the resulting nucleus and represents the energy released when the nucleus is formed.

Mass defect (M_d) can be calculated as the difference between observed atomic mass (m_0) and that expected from the combined masses of its protons (m_p, each proton having a mass of 1.00728 amu) and neutrons (m_n, 1.00867 amu):

$$M_d = (m_n + m_p) - m_o$$

4.11 Nuclear Binding Energy

Once mass defect is known, nuclear binding energy can be calculated by converting that mass to energy by using $E = mc^2$. Mass must be in units of kg.

Once this energy, which is a quantity of joules for one nucleus, is known, it can be scaled into per-nucleon and per-mole quantities. To convert to joules/mole, simply multiple by Avogadro's number. To convert to joules per nucleon, simply divide by the number of nucleons. Nuclear binding energy can also apply to situations when the nucleus splits into fragments composed of more than one nucleon; in these cases, the binding energies for the fragments, as compared to the whole, may be either positive or negative, depending on where the parent nucleus and the daughter fragments fall on the nuclear binding energy curve. If new binding energy is available when light nuclei fuse, or when heavy nuclei split, either of these processes result in the release of the binding energy. This energy—available as nuclear energy— can be used to produce nuclear power or build nuclear weapons. When a large nucleus splits into pieces, excess energy is emitted as photons, or gamma rays, and as kinetic energy, as a number of different particles are ejected.

Nuclear binding energy is also used to determine whether fission or fusion will be a favourable process. For elements, lighter than iron-56, fusion will release energy because the nuclear binding energy increases with increasing mass. Elements heavier than iron-56 will generally release energy upon fission, as the lighter elements produced contain greater nuclear binding energy. As such, there is a peak at iron-56 on the nuclear binding energy curve.

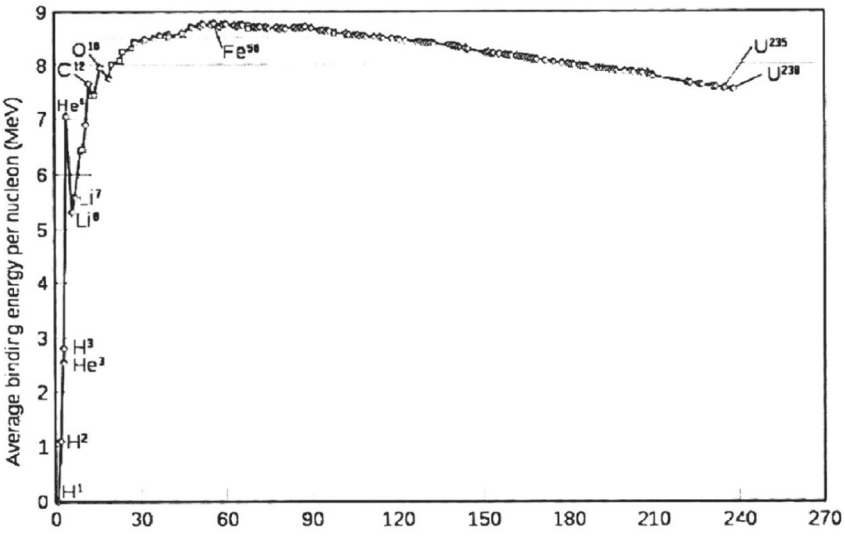


Figure.2.2 Nuclear binding energy curve. This graph shows the nuclear binding energy (in MeV) per nucleon as a function of the number of nucleons in the nucleus. Notice that iron-56 has the most binding energy per nucleon, making it the most stable nucleus.

The rationale for this peak in binding energy is the interplay between the coulombic repulsion of the protons in the nucleus, because like charges repel each other, and the strong nuclear force, or strong force. The strong force is what holds protons and neutrons together at short distances. As the size of the nucleus increases, the strong nuclear force is only felt between nucleons that are close together, while the coulombic repulsion continues to be felt throughout the nucleus; this leads to instability and hence the radioactivity and fissile nature of the heavier elements.

Ex : Let us calculate the mass defect (M_d) of **Helium** ($_2He^4$) atom

He^4 consists 2 protons and 2 neutrons in its nucleus.

Mass of proton (m_p) = 1.0078amu, Mass of neutron (m_n) = 1.0087amu

Total mass of 2 protons = 2 × 1.0078 = 2.0156 amu

Total mass of 2 neutrons = 2 × 1.0087 = 2.0174 amu

Total mass of 2 protons and 2 neutrons of Helium ($_2He^4$) atom is (2.0156 + 2.0174) amu =4.0330 amu

The magnitude of mass defect is a measure of the stability of the nucleus. Thus the mass defect of Helium nucleus to be 0.0304 amu has been converted to energy; the energy is utilized to bind two protons and two neutrons together and is called Binding Energy (B.E).

B.E of nucleus = $m_d \times 931.5$ Mev.

4.12 Packing Fraction

Aston defined Packing Fraction as

Packing Fraction =

$$\frac{\text{Isotopic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

Packing Fraction can have positive, negative or zero value.

i. Zero value of packing fraction is found in mono isotopic elements where the isotopic mass is equal to the mass number.

ii. Negative value of packing fraction indicates that there is mass defect, hence binding energy. Such nuclei are stable.

iii. Positive values of Packing fraction are unstable undergoing fission and fusion process, eg. $^{1}_{1}H$ (+ ve packing fraction) undergoes fusion.

^{235}U (+ve packing fraction) undergoes fission.

The stability of an atom appears to depend on the relative number of protons and neutrons present in the nucleus. Elements having mass number in the range of (40 – 120) have a high binding energy per nucleon and hence greater stability. On the other hand, heavy elements have very low binding energy per nucleon and have unstable nuclei.

The value of n/p ratio determines the nuclear stability. The nucleii of light isotopes have approximately an equal number of protons and neutrons. But for heavier nuclei, the number of neutrons is greater than the number of protons.

The figure given below shows the variation of the number of neutrons with the number of protons in the stable non-radioactive nuclei.

The stable nucleii lie within the shaded area which is called the region or zone of stability. A nucleus that lies outside the zone of stability will therefore be unstable. Nucleii that lie above the zone of stability will therefore be unstable. Nucleii that lie

above the zone of stability have an excess of neutrons, while those lying below have excess of protons.

Nucleii are particularly stable and abundant when they have either Z or n equal to 2, 8, 20, 28, 50, 82 or 126. These are called magic numbers. A nucleus that possesses a higher n/p ratio would try to bring about reduction in number of neutrons and increase in number of protons. Similarly a nucleus that possesses a low n/p ratio would achieve stability by an increase of neutrons or decrease of protons. All such processes involving conversion of an unstable to a more stable nucleus result in radioactive emissions.

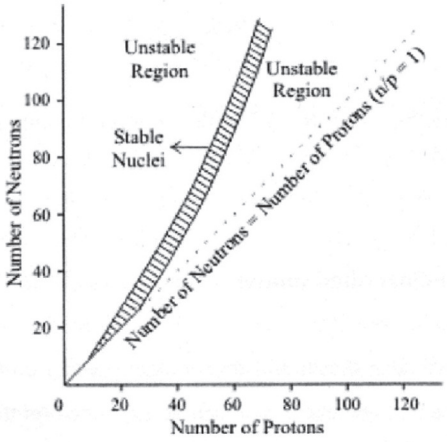


Figure 2.3. The variation of the number of neutron with the number of protons in the stable non radioactive nucleii

4.13 Nuclear Forces and Meson Exchange Theory

Protons have positive charge. In any nucleus containing two or more protons there will be electrostatic repulsion between the like charges. In stable nucleus, attractive forces are greater than repulsive forces and in unstable nucleus, attractive forces are less than repulsive forces. In 1935 Japanese scientist H.Yukawa explained the mechanism of interaction of the elementary particles (Neutrons & Protons) in a nucleus. In order to explain his theory he considered a particle known as pions/ mesons (π°) and that came to be known as **Meson theory.** He postulated the existence of a nuclear particle π meson or pion which acts as a glue binding the protons and neutrons together in the nucleus.

A pion has two sub particles such as π^{-} , π^{+} and π° (neutral).

He explained, a neutron in a nucleus emits out a π^- particle and becomes a proton. Whereas a proton emits a π + and becomes a neutron, this exchange of particles continues repeatedly.

A Visualization of reaction-

neutron $+\pi^- \rightarrow$ • proton.

proton + $\pi^+ \rightarrow$ • neutron

the binding force between like particles, *i.e.* exchange of n — n and p — p involves neutral π mesons.

$p = p + \pi^0$

$n = n + \pi^0$

Due to this exchange of particles there is a strong interactive force existing inside the nucleus.

4.14 Elementary Idea of Nuclear Shell Model and Magic Numbers

In the previous chapter, we have seen that liquid drop model gives a quites clear picture on the nuclear stability and later on we will see that nuclear fission can be explained on the basis of the same. However, there are some other properties of nucleus which can't be explained on th basis of this model. It has been observed by nuclear physicists that nuclei with number of protons or neutrons equal to 2,4,8, 20, 50, 82 and 126, the B.E./A values are higher as compared to their neighbours, giving rise to discontinuities to the binding energy curves. This indicates stability of these nuclei as compared to their neighbouring nuclei of the B.E. curve, For example $^{140}Ce_{58}$ which has 82 neutrons has higher (almost 4 MeV) B.E. compared to its neighbours. The numbers 2,4,8,20,50,82 and 126 are known as magic numbers as they were not understood for quite a long time with existing models such as LDM.

Explanation of Magic numbers—Shell model of a nucleus

Whatever it may be, let me tell you that there is a resemblance between occurrence of magic numbers and higher ionization potential of the noble gases (element with specific atomic number, Z), which is basically a consequence of atomic shell structure. For these atoms the electron shells are completely filled. Therefore, naturally question arise whether nucleus too has a shell structure and if it is so, can it explain the magic numbers? It was not an easy job to shell model of a nucleus similar to atomic shell model as there is no obvious central attractive force in a nucleus. like Coulomb force

in an atom. Secondly, the density of nucluear matter is extremly high ($\sim 10^{17} kgm^{-3}$) and hence free movement of nucleon in a nucleus like electrons in atom is difficult to imagine. However, Barlett Guggenheimer et al. proposed an independent particle model (shell model) for the nucleus in 1933 and could able to explain lower magic numbers (2,4,8) Later on, Maria G. Mayer in 1948 and independently Haxel et al. proposed shell structure of the nucleus and closed shell in nuclei having a corresponding to magic numbers. Their models were able to explain all magic numbers with a consideration of strong spin-orbit forces of nucleons and their coupling. Before discussing the shell structure of the nucleus given by Mayer, let us first discuss the concept of atomic shells and spin-orbit coupling. Atomic shell are basically some energy levels where electrons are allowed to stay following some quantum mechanical conditions. As electrons move in quantized orbits, it has orbital angular momentum associated with it. Apart from orbital angular momentum also spin angular momentum, arises due to its spin motion, which with much simplicity can be understood as a motion about its own axis. Not only electrons. but every elementary particle with such rotational condition has two types of angular momentum, *i.e.* spin angular momentum and orbital angular momentum. The first one is denoted by symbol s and the second one by symbol 1. The particles like electron, proton, neutron etc. have value of s as +1/2 or -1/2. There are several values of 1, corresponding to various orbitals where the particle is moving. In case of electron. the atomic orbitals are denoted by, s, p, d, f, g, h, i, etc. and corresponding 1 values are 0,1,2,3,4,5, 6 respectively. Now the 1 and s values of an electron (similarly, neucleons) can vectorially couple giving rise to a resultant angular momentum, j, where j = 1 s, i.e. 1 1/2. For example. if we consider spectroscopic term s, then, 1 = 0, s = 1/2 and j = 1/2. Now the next step is to consider the potential configuration within which the nucleons move inside the nucleus. The first assumption mode in nuclear shell model is single particle concept with an idea that the spin, parity and moments are determined by the unpaired nucleon alone and hence essentially reducing many nucleon problems to a single particle problem. It is also assumed that each nucleon experiences a central attractive force due to the average effect of the remaining nucleons (core) in the nucleus. This is something similar to the atom where nucleus acts as a central attractive force of the electons in the orbits. In this central field each nucleon is considered to move in a shell having specific energy and angular momentum. Another assumption of shell model is a weak inter nucleon interaction. The model of Mayer considers that the 1 and s values of a nucleon couples giving a distinct j value of a

nucleon. Nucleon having different j values couple by a j-j coupling mode, which eventually explain the origin of magic numbers.

In order to describe shell model a detail quantum mechanical calculation is required by considering some standard potential. Various potential configutations have been chosen by various authors. M.Mayer and Haxel et al. independently showed that harmonic oscillator potential or square well potential can be used to obtain reasonable results. The forms of these potentials are :

(A) $V = -V_0 + 1/2\ M\omega^2r^2$ ..... (m1.42) (linear harmonic oscillator). Where V_0 and ω are constants.

(B) $V = -V_0$ for $r < R$ ..... (m1.43) $= 0$ for $r > R$.

Of late, more realistic potential configuration have been chosen by other Nuclear Physicists.

A detailed mathematical formulation is required to find the energy of the nlecleon in various shells. However, in this lecture we will just show the nucleons distribution in a closed shell and the associated magic numbers.

Shells are defined by principal quantum numbers n whose value runs from 0 to integer numbers. The sequence of nuclear spins with increasing n values as per standard spectroscopic notation is shown in table 2.2.

TABLE 2.2. Filling up of nuclear shells with nucleons corresponding to magic numbers.

Spectroscopic term	n	I	J	Number of states (2J+1)	Number of Nucleons in a shell	Magic number
$^1s_{\frac{1}{2}}$	0	0	$\frac{1}{2}$	2	2	2
$^1p_{\frac{3}{2}}$	1	1	$\frac{3}{2}$	4	6	8
$^1p_{\frac{3}{2}}$	1	1	$\frac{1}{2}$	2		
$^1d_{\frac{5}{2}}$	2	2	$\frac{5}{2}$	6		
$^1d_{\frac{3}{2}}$	2	2	$\frac{3}{2}$	4	12	20

Spectroscopic term	n	I	J	Number of states (2J+1)	Number of Nucleons in a shell	Magic number
$^{1}s_{\frac{1}{2}}$	2	0	$\frac{1}{2}$	2		
$^{1}f_{\frac{7}{2}}$	3	3	$\frac{7}{2}$	8		
$^{1}f_{\frac{5}{2}}$	3	3	$\frac{5}{2}$	6	20	40
$^{2}p_{\frac{3}{2}}$	3	1	$\frac{3}{2}$	4		
$^{2}p_{\frac{1}{2}}$	3	1	$\frac{1}{2}$	2		
$^{1}g_{\frac{9}{2}}$	4	4	$\frac{9}{2}$	10	10	50
$^{1}g_{\frac{7}{2}}$	4	4	$\frac{7}{2}$	8	32	50
$^{2}d_{\frac{5}{2}}$	4	2	2	6		
$^{2}d_{\frac{3}{2}}$	4	2	$\frac{3}{2}$	4		
$^{3}s_{\frac{1}{2}}$	4	0	$\frac{1}{2}$	2		
$^{1}h_{\frac{11}{2}}$	5	5	$\frac{11}{2}$	12		82
$^{1}h_{\frac{9}{2}}$	5	5	$\frac{9}{2}$	10	44	
$^{1}f_{\frac{7}{2}}$	5	3	$\frac{7}{2}$	8		
$^{2}f_{\frac{5}{2}}$	5	3	$\frac{5}{2}$	6		

Spectroscopic term	n	I	J	Number of States (2J+1)	Number of Nucleons in a shell	Magic number
$^3p_{\frac{3}{2}}$	5	1	$\frac{3}{2}$	4		
$^3p_{\frac{1}{2}}$	5	1	$\frac{1}{2}$	2		
$^1i_{\frac{13}{2}}$	6	6	$\frac{13}{2}$	14		126

Now it is clear from the above table that in order to understand nuclear property like magic numbers concept of shell model is must. This model has great implication to understand nuclear structure and hence nuclear spectroscopic studies.

4.15 Summary

The atomic nucleus is the central core of an atom, consisting of protons and neutrons bound together by the strong nuclear force. Understanding nuclear stability involves examining the neutron-to-proton (n/p) ratio. Generally, stable nuclei have a balanced n/p ratio, and deviations from this ratio can lead to radioactive decay.

Different modes of decay include alpha decay (emission of an alpha particle), beta decay (conversion of a neutron to a proton or vice versa), and gamma decay (release of gamma rays). These processes are governed by the desire to achieve a more stable n/p ratio.

Mass defect is the difference between the mass of an atomic nucleus and the sum of the masses of its individual protons and neutrons. This phenomenon is related to Einstein's mass-energy equivalence principle (E=mc^2), and the mass defect contributes to the nuclear binding energy.

The packing fraction represents the binding energy per nucleon in a nucleus. It is the ratio of the mass defect to the total mass of the nucleus. A higher packing fraction indicates a more stable and tightly bound nucleus.

Nuclear binding energy is the energy required to disassemble a nucleus into its individual protons and neutrons. This energy is released during the formation of a nucleus and is responsible for holding the nucleus together.

Nuclear forces, responsible for binding protons and neutrons, are explained by the meson exchange theory. This theory posits the exchange of mesons (particles carrying the strong force) between nucleons.

The nuclear shell model provides an elementary idea of the organization of nucleons within the nucleus. It suggests that protons and neutrons occupy discrete energy levels or shells, similar to electrons in atomic orbitals. Magic numbers are specific values for protons or neutrons that result in greater stability due to completely filled shells.

In summary, the atomic nucleus is a complex system governed by principles of nuclear stability, decay modes, mass defect, packing fraction, nuclear binding energy, and the intricate interplay of nuclear forces explained by meson exchange theory and the nuclear shell model with its magic numbers. These concepts collectively contribute to our understanding of the structure and behavior of atomic nuclei.

4.16 Model Questions

A. Multiple Choice Type Questions

1. Who is credited with the discovery of radioactivity?

A) Marie Curie
B) Albert Einstein
C) Ernest Rutherford
D) Niels Bohr

2. Which subatomic particles are primarily found in the atomic nucleus?

A) Electrons
B) Protons and electrons
C) Neutrons and electrons
D) Protons and neutrons

3. What is a key factor in determining the stability of a nucleus?

A) Atomic number
B) Neutron-to-proton (n/p) ratio
C) Electron configuration
D) Radioactive decay rate

4. In which type of radioactive decay does a neutron transform into a proton?

A) Alpha decay

B) Beta decay

C) Gamma decay

D) Positron emission

5. According to the Group Displacement Law, what happens to the radioactive daughters in a decay series?

A) They move to the left in the periodic table

B) They move to the right in the periodic table

C) They stay in the same group in the periodic table

D) They are not affected by displacement

6. Which law describes the exponential decrease in the number of radioactive nuclei over time?

A) Newton's Law of Motion

B) Boyle's Law

C) Law of Radioactive Decay

D) Ohm's Law

7. The time required for half of a radioactive substance to decay is known as:

A) Decay constant

B) Mean life

C) Half-life period

D) Radioactive period

8. What does the mass defect in a nucleus represent?

A) Excess mass of protons

B) Excess mass of neutrons

C) Excess mass of electrons

D) The difference between actual and calculated mass of the nucleus

9. Nuclear binding energy is released during the:

A) Formation of a nucleus

B) Radioactive decay

C) Electron capture

D) Alpha decay

10. The packing fraction of a nucleus is a measure of its:

A) Size

B) Density

C) Binding energy

D) Half-life

B. Short Type questions

1. Who, along with her husband, discovered the elements polonium and radium, contributing significantly to the understanding of radioactivity?
2. What is the role of the neutron-to-proton (n/p) ratio in determining the stability of a nucleus?
3. Briefly explain the process of alpha decay.
4. What does the Group Displacement Law state in the context of radioactive decay series?
5. Define the term "half-life period" in the context of radioactive decay.
6. What does the term "mass defect" represent in the context of nuclear physics?
7. Explain the concept of nuclear binding energy and its significance.
8. Define the packing fraction of a nucleus and its importance in nuclear physics.
9. According to the meson exchange theory, what role do mesons play in nuclear forces?
10. Briefly describe the fundamental idea behind the nuclear shell model and the concept of magic numbers.

C. Assay Type Questions

1. Discuss the key contributions of Marie Curie and her husband in the discovery of radioactivity, and its impact on the field of nuclear physics.

2. Explore the factors influencing nuclear stability, emphasizing the role of the neutron-to-proton (n/p) ratio.
3. Compare and contrast the different modes of radioactive decay (alpha, beta, and gamma), highlighting their characteristics and significance.
4. Explain the Group Displacement Law in the context of radioactive decay series, providing examples to illustrate its application.
5. Elaborate on the concept of half-life period in radioactive decay, discussing its mathematical representation and practical implications.
6. Define and discuss the concept of mass defect, and explain how it relates to the stability and energy release in nuclear reactions.
7. Explore the concept of nuclear binding energy, detailing its calculation and significance in the stability and behavior of atomic nuclei.
8. Discuss the packing fraction of a nucleus, its calculation, and how it reflects the overall stability and structure of a nucleus.
9. Provide an in-depth explanation of the meson exchange theory, describing the role of mesons in nuclear forces and their implications for nuclear interactions.
10. Analyze the nuclear shell model, outlining its fundamental principles and discussing the concept of magic numbers in relation to nuclear stability.

4.17 References

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Unit 5 ❐ Nuclear Reactions

Contents

5.1 Objectives

5.2 Introduction

5.3 Radioactive Series

5.4 Nuclear Fission

5.5 Nuclear Fusion

5.6 Spallation Reaction

5.7 Natural Radioactivity

5.8 Artificial Radioactivity

5.9 Super Heavy Elementsand Their IUPAC Nomenclature

5.10 Moderator

5.11 Slow and Fast Neutrons

5.12 Summary

5.13 Model Questions

5.14 References

5.1 Objectives

- Radioactive Series Understanding: Comprehend the various radioactive series, such as the uranium and thorium decay chains, and the key isotopes involved in each series.
- Fission Reaction Mechanisms: Investigate the principles and mechanisms behind nuclear fission reactions, including the identification of fissile materials and the release of energy during the process.
- Fusion Reaction Exploration: Explore the concepts and conditions involved in nuclear fusion reactions, including the forces required to overcome the Coulomb barrier and the potential for controlled fusion as an energy source.

E-Copy

- Spallation Reaction Analysis: Examine spallation reactions, understanding the breakup of heavy nuclei into smaller fragments and the implications for applications such as neutron production.
- Artificial Radioactivity Investigation: Investigate the creation of artificial radioactive isotopes through various methods, such as neutron bombardment, and analyze their applications in medicine, industry, and research.
- Super Heavy Elements Study: Explore the properties and synthesis methods of super heavy elements, with a focus on elements beyond the periodic table's stability limits.
- IUPAC Nomenclature Mastery: Understand and apply the International Union of Pure and Applied Chemistry (IUPAC) nomenclature rules for super heavy elements, ensuring accurate and standardized naming conventions.
- Moderator Characteristics: Analyze the role of moderators in nuclear reactions, including their impact on neutron energy and their importance in maintaining controlled nuclear fission reactions.
- Slow Neutron Applications: Examine the characteristics and applications of slow neutrons, particularly in areas such as neutron capture therapy and material analysis.
- Fast Neutron Considerations: Investigate the properties and applications of fast neutrons, including their role in fast breeder reactors and their use in neutron radiography for material inspection.

5.2 Introduction

Let's take a dive into the world of tiny particles—atoms—and explore some fascinating things they can do! This chapter is like an adventure where we learn about the radioactive series, fission, fusion, spallation reactions, artificial radioactivity, super heavy elements, their fancy names (IUPAC nomenclature), and also the helpers in this atomic world—moderators, slow, and fast neutrons.

Firstly, there's something called a radioactive series. It's like a tale about atoms changing over time. We'll get to know about uranium and thorium, and how they transform bit by bit.

Next, we'll talk about fission. Imagine atoms splitting apart and releasing a lot of energy! This is what powers some of our electricity. We'll see how this splitting happens and why it's important.

Now, fusion is like atoms giving each other a big hug and making even more energy. It's similar to what happens in the sun. We'll learn about the challenges and cool possibilities of making energy this way.

Spallation reactions sound fancy, but it's just about big atoms breaking into smaller pieces. This helps us make something called neutrons, which are like the worker bees in the atomic world.

Ever heard of artificial radioactivity? It's when scientists make special atoms in labs. These atoms can help in medicine, industries, and other cool stuff that makes life better.

Then, there's a group of super heavy elements. These are like the rock stars of the atomic world. We'll see how scientists create and name them, pushing the limits of what we thought possible.

We'll also talk about moderators, which are like traffic directors for atoms. They help keep things under control in nuclear reactions.

And finally, meet slow and fast neutrons. They are like the messengers in the atomic world. Slow ones are good for certain jobs like helping in medicine, while fast ones are more like the speedsters, aiding in advanced technologies.

So, buckle up! We're about to journey into the amazing world of atoms and discover how these tiny particles can do some really big things.

5.3 Radioactive Series

The radioactive series is like a fascinating story about how atoms, like uranium and thorium, change bit by bit over time. It shows us how these atoms go through a series of changes called radioactive decays, and this process helps create new elements and release energy. It's like a dynamic journey into the world of tiny particles, uncovering the secrets of atomic transformations.

The sequential decay of a given nuclei results in the production of a nuclei or element. This series of elements thus from is known as a radioactive decay series. There are 3 radioactive series depending on the original progenitor.

Disintegration Series	Parent Element	Last element	Stable Total No.1. of α-an β-particles emitted
1. Thorium Series or 4n series	$_{90}Th^{232}$	$_{82}Pb^{208}$	6α and 4 β
2. Neptunium Series or (4n + 1) series	$_{93}Np^{237}$	$_{83}Bi^{209}$	7α and 4 β
3. Uranium Series or (4n+2) series	$_{92}U^{238}$	$_{82}Pb^{206}$	8α and 6 β
4. Actinium Series or (4n+3) series	$_{92}U^{235}$	$_{82}Pb^{207}$	7α and 4 β

The important features of the radioactive series :

(1) In every one of these three series radioactivity finally ceases with a stable lead Isotope.

(2) Only Inert gas formed in these series are Radon (Rn) Z = 86

(3) In all the d series wherever there is a change in mass number, it alters by 4 only.

(4) Depending upon the masses of the element, the series are named as

Uranium (4n + 2)

Thorium (4n)

Actinium (4n + 3)

(5) There is another artificially produced radioactive series called as Neptunium or (4n +1) series.

5.4 Nuclear Fission

Nuclear fission is an amazing process where the nucleus of an atom splits into two or more smaller nuclei, accompanied by the release of a significant amount of energy. This reaction is particularly notable for its role in power generation and nuclear weapons.

During nuclear fission, a heavy nucleus, often of an isotope like uranium-235 or plutonium-239, absorbs a neutron, becoming unstable. The nucleus then splits into two or more lighter nuclei, along with several neutrons and a substantial release of energy. This energy is harnessed in nuclear power plants to produce electricity.

The chain reaction aspect of nuclear fission is crucial. The neutrons released during the

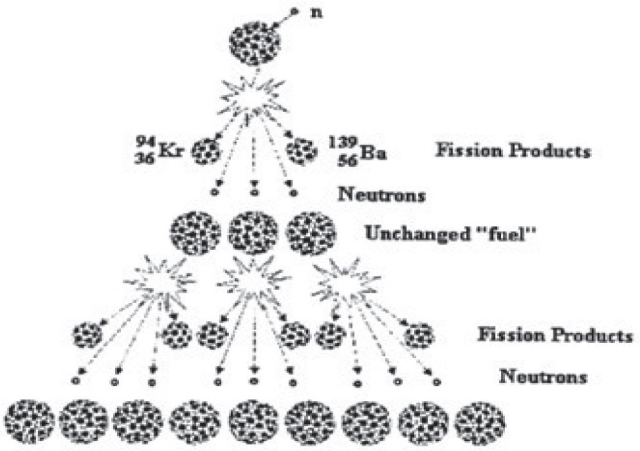
process can go on to initiate further fission reactions in nearby nuclei, creating a self-sustaining chain reaction. Control rods are used in reactors to regulate this chain reaction and prevent it from becoming uncontrollable.

Nuclear fission has played a significant role in shaping both energy production and global geopolitics. Understanding and managing this process are essential for harnessing its benefits while ensuring safety and preventing unintended consequences.

The heavy nucleus of radioactive atoms like uranium, plutonium or thorium is bombarded with low energy neutrons which split the nucleus into smaller nuclci. This process is called nuclear fission. For example when uranium-235 atoms are bombarded with neutrons then the heavy uranium nucleus splits to produce Barium-139 and krypton-94 with the emission of three neutrons. A lot of energy is also produced in this reaction because mass is converted into energy.

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{139}_{56}Ba + ^{94}_{36}Kr + 3\,^{1}_{0}n$$

In a typical nuclear fission reaction, more than one neutron is released by each dividing nucleus. When these neutrons collide with and induce fission in other neighboring nuclei, a self-sustaining series of nuclear fission reaction known as a **nuclear chain reaction** can result (figure 2.4). For example. the fission of ^{235}U releases two to three neutrons per fission event. If absorb by other ^{235}U nuclei, those neutrons induce additional fission events, and the rate of the fission reaction increases geometrically. Each series of events is called a generation. Experimentally. it is found that some minimum mass of a fissile isotope is required to sustain a nuclear chain reaction; if the mass is too low, too many neutrons are able to escape without being captured and inducing a fission reaction. The minimum mass capable of supporting sustained fission is called the **critical mass**. This amount depends on the purity of the material and the shape of the mass, which corresponds to the amount of surface area available form which neutrons can eseape, and on the identity of the isotope, if the mass of the fissile isotope is greater than the critical mass. Then under the right conditions. the resulting supercritical mass can release energy explosively. The enormous energy released from nuclear chain reactions is responsible for the massive destruction caused by the detonation of nuclear weapons such as fission bombs, but it also forms the basis of the nuclear power industry.



Schematic diagram of a nuclear chain reaction

The process is initiated by the collision of a single neutron with a ^{235}U nucleus, which undergoes fission. Because each neutron released can cause the fission of another ^{235}U nucleus, the rate of a fission reaction accelerates geometrically.

5.5 Nuclear Fusion

The meaning of fusion is to join or to combine. Therefore, the process in which two nuclei of light elements are combined to form a heavy nucleus is nuclear fusion. In the process of nuclear fusion also tremendous amount of energy is released.

$$2\,{}^{2}_{1}H \rightarrow {}^{3}_{2}He + {}^{1}_{0}n + \text{Energy}$$

$${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n + \text{Energy}$$

The nuclei of atoms are positively charged and thus they repel each other. So in order to combine or fuse these two nuclei to form one heavy nucleus, a lot of heat energy and high pressure is requied. This shows that nuclear fusion is carried out by heating lighter atoms to an extremely high temperature at high pressure. Some mass is also lost in this process which gives tremendous amount of energy.

For example, when deuterium atoms are heated to an extremely high temperature under high pressure than two deuterium nuclei combine to form helium which has a heavy nucleus, a neutron is emitted and a lot of energy is liberated. Temperatures required for fusion reactions exist in stars where fusion reactions are the principle components of energy release. In the Sun, approsimately 90 percent of solar energy is a result of proton–proton interactions in several steps to form helium of mass number 4. These steps all involve binuclear collisions since multi nuclei collisions are very improbable events. Initially, two protons interact to form a deuterium nucleus (deuterium is an isotope of hydrogen with one proton and one neutron; the nucleus is a deuteron) that collides with another proton to form at He, tritrium nucleus. This

nucleus collides with a neutron or another ^{3}He nucleus (with the emission of two protons) to form ^{4}He. The net reaction can be repesented as four protons fusing to form a ^{4}He nucleus releasing 26.7 MeV.

Nuclear fusion reaction is opposite of nuclear fission reaction. The energy produced in nuclear fusion reaction has not been controlled yet and is much more than nuclear fission reaction.

5.6 Spallation Reaction

Spallation reaction is a process where a heavy nucleus is bombarded with high-energy particles, typically neutrons or protons, leading to the fragmentation of the nucleus into smaller pieces. Unlike nuclear fission, which involves the spontaneous splitting of a nucleus, spallation is induced by external projectiles.

In a spallation reaction, a high-energy projectile collides with a target nucleus, causing it to break apart into various fragments, including neutrons, protons, and other smaller nuclei. This process is commonly utilized to produce neutrons for scientific research, as well as for certain industrial applications.

One significant application of spallation reactions is in the generation of neutrons for neutron scattering experiments. Neutrons produced through spallation are valuable for studying the structure and properties of materials on a microscopic scale. Spallation neutron sources are facilities designed to exploit this process, where high-energy particles, often accelerated protons, collide with heavy metal targets, inducing spallation reactions and producing a neutron beam.

Hence,

When an element of intermediate range of mass number and atomic number are bombarded with high energy α-particles, protons, deuterons; they do not undergo nuclear fission into two fragments of close mass; instead of this, these nuclei are split into a variety of nucleus of lower mass and atomic number. Such nuclear reactions are called nuclear spallation reaction.

$$^{75}_{33}As + {}^{2}_{1}H \rightarrow {}^{56}_{25}Mn + 9{}^{1}_{1}H + 12{}^{1}_{0}n$$

Overall, spallation reactions provide a controlled and efficient way to generate neutrons, contributing to advancements in various scientific fields, including materials science, chemistry, and nuclear physics.

5.7 Natural Radioactivity

Natural radioactivity refers to the spontaneous emission of radiation by certain elements or isotopes present in nature. These radioactive elements undergo decay processes, releasing particles and energy in the form of alpha particles, beta particles, and gamma rays.

The three main types of natural radioactive decay are alpha decay, beta decay, and gamma decay. In alpha decay, an unstable nucleus emits an alpha particle, which consists of two protons and two neutrons. Beta decay involves the transformation of a neutron into a proton or vice versa, accompanied by the emission of a beta particle. Gamma decay releases gamma rays, which are electromagnetic radiation of high energy.

Common naturally radioactive elements include uranium, thorium, and radium. These elements are found in rocks, soil, and certain minerals. The decay of these radioactive substances plays a crucial role in the Earth's heat production, contributing to geological processes like plate tectonics.

Natural radioactivity has various applications, such as in dating archaeological artifacts using carbon-14, medical imaging and treatment, and nuclear energy production. While natural radioactivity is a part of our environment, exposure to high levels of radiation can pose health risks, making it important to monitor and regulate exposure in certain contexts, such as occupational settings and medical procedures.

5.8 Artificial Radioactivity

A nuclear process in which a stable element is converted into another element which is radioactive in nature is called artificial or induced radioactivity.

Not all nuclear reactions are spontaneous. These reactions occur when stable isotopes are bombarded with particles such as neutrons. This method of inducting a nuclear reaction to proceed is termed artificial radioactivity. These meant new nuclear reactions, which wouldn't have been viewed spontaneously, could now be observed. Since about 1940, a set of new elements with atomic numbers over 92 (the atomic number of the heaviest naturally occurring element, Uranium) have been artificially made. They are called the transuranium elements. It was first discovered by Curie in 1934. Their experiments is bombardment of aluminium with α particle.

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He}\,(\text{Alpha particle}) \rightarrow {}^{30}_{15}\mathrm{P}^{*} + {}^{1}_{0}\mathrm{n}\,(\text{neutron}) + \mathrm{Q}\,(\text{energy})$$

$$^{30}_{15}\mathrm{P}^{*} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{1}\mathrm{e}\,(\text{Positron})$$

Artificial radioactivity refers to the creation of radioactive isotopes through human-made processes, typically involving the bombardment of stable nuclei with particles. Here are some examples of artificial radioactivity:

Carbon-14 Production:

Process: Nitrogen-14 can be bombarded with neutrons to produce carbon-14.

Application: Carbon-14 is used in radiocarbon dating to estimate the age of organic materials.

Technetium-99m Production:

Process: Molybdenum-98 can be irradiated with neutrons to produce technetium-99m.

Application: Technetium-99m is widely used in medical imaging (single-photon emission computed tomography or SPECT).

Cobalt-60 Production:

Process: Cobalt-59 can be bombarded with neutrons to produce cobalt-60.

Application: Cobalt-60 is used in radiation therapy for cancer treatment.

Iodine-131 Production:

Process: Iodine-130 can be irradiated with neutrons to produce iodine-131.

Application: Iodine-131 is used in medicine for thyroid cancer treatment and diagnostic imaging.

Plutonium-239 Production:

Process: Uranium-238 can absorb neutrons and undergo a series of reactions to produce plutonium-239.

Application: Plutonium-239 is used as a fissile material in nuclear weapons and reactors.

Neptunium-237 Production:

Process: Uranium-238 can absorb neutrons and undergo beta decay to produce neptunium-237.

Application: Neptunium-237 can be used in the production of plutonium-238 for space missions.

These examples highlight the controlled creation of radioactive isotopes for various purposes, including medical diagnostics and treatment, scientific research, and energy production.

5.9 Super Heavy Elementsand Their IUPAC Nomenclature

It is a generally accepted convention that the discoverer of an element has the honour of naming it. The inspiration often comes from origin, mythical characters, place, physical or chemical properties, and more recently to commemorate the names of eminent scientist. Of course, the suggestion has to be ractified by the International Union of Pure And Applied Chemistry (IUPAC).

Newly discovered or undiscovered superheavy elements are often referred to in the scientific literature but until they have received permanent names and symbols from IUPAC, temporary designators are required. In 1978, IUPAC Commission on the Nomenclature of Inorganic Chemistry decided that it is necessary to have a systematic naming for the elements with atomic number greater than 100 (Z >100). even for those which had not been discovered. The Commission decided that these elements would be best named systematically and that names should accord with the following rules :

1. The name is derived directly from the atomic number of the element using the following Latin numerical roots :

Number	Root
0	nil
1	un
2	bi
3	tri
4	quad
5	pent
6	hex
7	sept
8	oct
9	enn

2. The roots are put together in the order of the digits which make up the atomic number and terminated by 'ium' to spell out the name. The final 'n' of 'enn' is elided when it occurs before 'nil', and the final 'i' of 'bi' and of 'tri' when it occurs before 'ium'.
3. The symbol of the element is composed of the initial letters of the numerical roots which make up the name.
4. The root 'un' is pronounced with a long 'u', to rhyme with 'moon'. In the element names each root is to be pronounced separately.

Here are a few examples of the names generated for elements with atomic numbers 101 to 900

Atomic Number	Name	Symbol
101	Unnilunium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uuu
112	Ununbium	Uub
113	Ununtrium	Unt

114	Ununquadium	Uuq
115	Ununpentium	Unp
116	Ununhexium	Unh
117	Ununseptium	Uus
118	Ununoctium	Uuo
119	Ununennium	Uue
120	Unbinilium	Ubn
121	Unbiunium	Ubn
130	Untrinilium	Utn
140	Unquadnilium	Uqn
150	Unpentinilium	Upn
160	Unhexnilium	Uhn
170	Unseptnilium	Usn
180	Unoctnilium	Uon
190	Unennilium	Uen
200	Binilnilium	Bnn
201	Binilunium	Bnu
202	Binilbium	Bnb

300	Trinilnilium	Tnn
400	Quadnilnilium	Qnn
500	Pentnilnilium	Pnn
900	Ennilnilium	Enn

So far, essentially all the transuranium elements have been discovered at four Berkeley National Laboratory in the United States (elements 93 – 101, 106, and joint credit for 103 – 105), the Joint Institute for Nuclear Research in Russia (elements 102 and 114 –118, and joint credit for 103 – 105), the GSI Helmholtz Centre for Heavy Ion Research in Germany (elements 107 – 112), and RIKEN in Japan (element 113)

- 93. neptunium, Np, named after the planet Neptune, as it follows uranium and Neptune follows Uranus in the planetary sequence (1940).
- 94. plutonium, Pu, named after the dwarf planet Pluto. following the same naming rule as it follows neptunium and Pluto follows Neptune in the pre -2006 Planetary sequence (1940).
- 95. americium, Am, named because it is an analog to europium, and so was named after the continent where it was first produced (1944).
- 96. curium, Cm, named after Pierre and Marie Curie, famous scientists who separated out the first radioactive elements (1944), as its lighter analog gadolinium was named after Johan Gadolin.
- 97. berkelium, Bk, named after the city of Berkeley, where the University of California, Berkeley is located (1949).
- 98. californium, Cf, named after the state of California, where the university is located (1950).
- 99. einsteinium. Es, named after the theoretical physicist Albert Einstein (1952).
- 100. fermium, Fm, named after Enrico Fermi, the physicist who produced the first controlled chain reaction (1952).
- 101. mendelevium, Md, named after the Russian chemist Dmitri Mendeleev, credited for being the primary creator of the periodic table of the chemical elements (1955).

- 102. nobelium. No, named after Alfred Nobel (1958).
- 103. lawrencium, Lr, named after Ernest O. Lawrence, a physicist best known for development of the cyclotron, and the person.
- 104. rutherfordium. Rf, named after Ernest Rutherford, who was responsible for the concept of the atomic nucleus (1968).
- 105. dubnium, Db, an element that is named after the city of Dubna.
- 106. seaborgium, Sg, named after Glenn T. Seaborg. This name caused controversy because Seaborg was still alive, but eventually became accepted by international chemists (1974). ;
- 107. bohrium, Bh, named after the Danish physicist Niels Bohr, important in the elucidation of the structure of the atom (1981)
- 108. hassium. Hs, named after the Latin form of the name of Hessen, the German *Bundesland* where this work was performed (1984).
- 109. meitnerium, Mt, named after Lise Meitner, an Austrian physicist who was one of the earliest scientists to study nuclear fission (1982).
- 110. darmstadtium. Ds, named after Darmstadt.
- 111. roentgenium. Rg, named after Wilhelm Conrad Rontgen, discoverer of X-rays (1994).
- 112. copernicium. Cn, named after astronomer Nicolaus Copernicus (1996).
- 113. nihonium. Nh, named after Japan (Nihon in Japanese) where the element was discovered. (2004).
- 114. flerovium, Fl, named after Soviet physicist Georgy Flvorov, founder of the JINR (2004).
- 115. moscovium, Mc, named after Moscow Oblast. Russia, where the element was discovered;
- 116. livermorium, Lv, named after the Lawrence Livermore National Laboratory, a collaborator with JINR in the discovery, (2004).
- 117. tennessine, Ts, named after the state of Tennessee, where the berkelium target needed for the synthesis of the element was manufactured;
- 118. oganesson. Og, named after Yuri Oganessian, who led the JINR team in its discovery of elements 114 to 118.

5.10 Moderator

In nuclear chemistry, a moderator is a substance used to slow down neutrons in a nuclear reactor. The process of slowing down neutrons is crucial for maintaining a sustained chain reaction in a nuclear reactor. Neutrons are initially released in fission reactions with high energies, and for efficient fission to occur, it is necessary to reduce their speed.

A moderator accomplishes this by colliding with fast neutrons and transferring some of their kinetic energy to the moderator material. The most commonly used moderators are materials with light nuclei, such as water (in the form of light or heavy water), graphite, and beryllium. These materials are effective at slowing down neutrons due to their lower mass and higher probability of interaction with the neutrons.

The slowed-down or thermal neutrons are more likely to be captured by fissile isotopes (like uranium-235 or plutonium-239), leading to additional fission reactions. This process helps maintain a controlled and sustainable chain reaction in a nuclear reactor, allowing for the continuous release of energy.

In summary, a moderator in nuclear chemistry plays a crucial role in slowing down fast neutrons produced during fission reactions, facilitating a sustained and controlled chain reaction in a nuclear reactor.

Coolant:

The purpose of collant is to remove the heat liberated during fission and to utilize the same for steam generation. The coolant supply to a nuclear reactor must be continued even if the chain reaction has ceased and reactor shut down. This is to ensure the removal of decay heat and to avoid the melting of reactor core. Water and heavy water are the most common liquid coolants in thermal reactors. Liquid sodium is used as coolant in fast reactors. Helium and CO2 are used as gaseous coolants in Gas-cooled reactors.

5.11 Slow and Fast Neutrons

Nuclear fission can occur when a nucleus is rendered sufficiently unstable by the capture of a passing neutron. The probability for a fission reaction to take place depends much on how energetic these neutrons are. The knowledge of their energies spectrum is vital for an understanding of how nuclear reactors work. One classifies these neutrons in groups according to their energy ranges, the most important being the **'fast'** and **'slow'** neutrons.

Slow neutrons

After a series of collisions with different nuclei, the energy of neutrons produced by fission reactions drops to the order of a few electron volts or a few fractions of an electron volt. Neutrons with energies in this range are collectively referred to as 'slow', and neutrons whose energies match those of the surrounding atoms are known as 'thermal'.

It is these slow neutrons that allow for nuclear reactors to run with fuel based on natural uranium or uranium lightly-enriched in fissile isotope 235. Without them, the most common pressurised (PWR) and boiling water (BWR) reactors would not operate. As a result, the neutrons emitted by nuclear fission have to be slowed down by collisions within a medium called a **moderator.** Reactors operating with natural uranium fuel, which contains only 0.7% of fissile uranium 235, require efficient moderators which absorb very few of the neutrons : such moderators are heavy water and pure graphite.

Fast neutrons

Before they are slowed down by a large number of nuclear collisions, neutrons produced by fission reactions are known as 'fast'. They usually have energies between 0.1 and 2 or 3 MeV.

The fact that they possess a substantial amount of kinetic energy allows fast neutrons to fission more easily nuclei once they get captured. They can therefore split not only nuclei reputed fissile by slow neutrons, but also minor actinides, the heavy nuclei which build up inside nuclear fuel as radioactive waste. Fast neutrons are needed to eliminate these waste products.

The use of fast neutrons in so-called 'fast reactors' allows for the production of more fissile nuclei than are destroyed, as the absorption of at least one neutron per fission by an uranium 238 nucleus transforms this uranium 238 into a fissile plutonium 239 nucleus. This process is known as breeding, leading to an almost inexhaustible supply of nuclear fuel.

One drawback of fast neutrons in reactors is that the probabilities of their capture by nuclei are comparatively small. Travelling in matter, neutrons see nuclei as targets. The apparent cross-section of these targets is much smaller for fast neutrons than it is for slower neutrons. As a result, an intense neutron flux and a fuel rich in fissile elements are both needed to compensate for this lower probability.

5.12 Summary

Nuclear reactions play a vital role in comprehending and tapping into the energy released from atomic processes. Fission, fusion, and spallation reactions are fundamental processes occurring at the nuclear level. Fission entails the splitting of a heavy nucleus into smaller fragments, releasing a substantial amount of energy. Fusion, on the other hand, involves the merging of light nuclei to form a heavier nucleus, releasing even more energy, akin to what occurs in stars. Spallation reactions encompass bombarding a target nucleus with high-energy particles, resulting in the release of diverse nuclear fragments.

Artificial radioactivity pertains to the creation of radioactive isotopes through human-made processes, often involving bombarding stable isotopes with particles. This technique finds applications in medicine, industry, and research.

Super heavy elements are those with atomic numbers significantly higher than those naturally occurring. The International Union of Pure and Applied Chemistry (IUPAC) establishes nomenclature rules for these elements, providing systematic names based on their atomic numbers and other characteristics.

The behavior of neutrons is pivotal in nuclear reactions. Moderators, such as water or graphite, decelerate fast neutrons to enhance the likelihood of their capture by nuclei, fostering sustained nuclear reactions in reactors. Slow neutrons are more effective in inducing fission. Conversely, fast neutrons, possessing higher energy, are crucial in specific applications like nuclear weapons or certain research reactors.

Comprehending these processes and the behavior of neutrons is essential for various scientific, industrial, and energy-related applications, contributing to advancements in nuclear science and technology.

5.13 Model Questions

A. Multiple Type Questions

1. Which process involves the splitting of a heavy nucleus into smaller fragments, releasing a significant amount of energy?

   A. Fission B. Fusion
   C. Spallation D. Radioactivity

2. What is the term for the combination of light nuclei to form a heavier nucleus, releasing energy?

A. Fission B. Fusion
C. Spallation D. Isomerization

3. In spallation reactions, what occurs when a target nucleus is bombarded with high-energy particles?

A. Fusion

B. Fission

C. Release of nuclear fragments

D. Radioactive decay

4. What is the process called when radioactive isotopes are created through human-made processes?

A. Fission

B. Fusion

C. Spallation

D. Artificial radioactivity

5. Which organization establishes nomenclature rules for super heavy elements?

A. UNESCO B. IAEA
C. IUPAC D. WHO

6. Super heavy elements are characterized by:

A. Low atomic numbers

B. Naturally occurring isotopes

C. Atomic numbers significantly higher than those found in nature

D. Stable nuclear configurations

7. Which of the following is a common moderator used to slow down neutrons in nuclear reactions?

A. Helium B. Graphite
C. Lead D. Uranium

8. What types of neutrons are more effective in inducing fission reactions?

A. Slow neutrons

B. Fast neutrons

C. Thermal neutrons

D. Moderated neutrons

9. Fast neutrons, possessing higher energy, are essential in which applications?

A. Nuclear reactors

B. Medical imaging

C. Fusion reactions

D. Radioactive decay

10. Which nuclear process involves the merging of light nuclei to release a large amount of energy, similar to the processes occurring in stars?

A. Fission

B. Spallation

C. Fusion

D. Artificial radioactivity

Answer: A. Fission; Answer: B. Fusion; Answer: C. Release of nuclear fragments; Answer: D. Artificial radioactivity; Answer: C. IUPAC; Answer: C. Atomic numbers significantly higher than those found in nature; Answer: B. Graphite; Answer: A. Slow neutrons; Answer: A. Nuclear reactors; Answer: C. Fusion

B. Short Type Questions

1. What is the process in which a heavy nucleus splits into smaller fragments, releasing energy?
2. Give one application of artificial radioactivity in medicine.
3. Define spallation in the context of nuclear reactions.
4. What does IUPAC stand for, and what role does it play in the context of super heavy elements?
5. Name one common moderator used to slow down neutrons in nuclear reactors.

6. Briefly explain the significance of slow neutrons in inducing fission reactions.
7. What is the term for the combination of light nuclei to form a heavier nucleus, releasing energy?
8. Provide an example of a super heavy element and its atomic number.
9. In the context of nuclear reactions, what is the role of fast neutrons?
10. How does the behavior of neutrons contribute to sustaining nuclear reactions in reactors?

C. Assay Type Questions

1. Discuss the principles and applications of fission reactions, emphasizing their significance in both energy production and nuclear weapons.
2. Explain the process of artificial radioactivity, including the methods used to create radioactive isotopes and their applications in various fields such as medicine, industry, and research.
3. Compare and contrast the fundamental processes of fission and fusion reactions, highlighting their respective advantages, challenges, and real-world applications.
4. Explore the concept of spallation reactions, detailing how they occur and providing examples of their applications in scientific research and technology.
5. Investigate the role and importance of moderators in nuclear reactions. Discuss how different moderators, such as water and graphite, impact the behavior of neutrons in reactors.
6. Elaborate on the nomenclature rules established by the IUPAC for super heavy elements. Provide examples and discuss the significance of naming these elements systematically.
7. Discuss the challenges and advancements in the synthesis and study of super heavy elements. Highlight the methods used to produce and characterize these elements in the laboratory.
8. Examine the characteristics and behaviors of slow neutrons in nuclear reactions. Explain why slow neutrons are more effective in certain reactions and their role in sustaining nuclear fission.

9. Evaluate the applications and potential risks associated with fast neutrons in various fields, including their use in research reactors and potential contributions to nuclear weapons development.
10. Analyze the broader implications of understanding nuclear reactions and the behavior of neutrons in scientific, industrial, and energy-related applications. Discuss how this knowledge contributes to advancements in nuclear science and technology.

5.14 References

1. "Nuclear Chemistry" by G. Friedlander, J. W. Kennedy, E. S. Macias, and J. M. Miller
2. "Introduction to Nuclear Chemistry" by A. Goswami
3. "Nuclear Chemistry" by S. K. Sharma
4. Authored by S. K. Sharma, this book delves into the principles and applications of nuclear chemistry, providing a thorough understanding of the subject.
5. "Radiochemistry and Nuclear Chemistry" by Gregory R. Choppin, Jan-Olov Liljenzin, and Jan Rydberg

Unit 6 ❐ Applications of Radio-Isotopes

Contents

6.1 Objectives

6.2 Introduction

6.3 Determination of Structure using Radio-Isotopes

6.4 Application of Radio-Isotopes in Establishment of Reaction Mechanisms

6.5 Radio-Carbon Dating

6.6 Hazards of Radiation and Safety Measures

6.7 Uses of Radio Active Nuclides

6.8 Summary

6.9 Model Questions

6.10 References

6.1 Objectives

- Explore how radioisotope labeling techniques can provide insights into reaction pathways, protein folding, and other molecular transformations.
- Assess the advantages and limitations of radioisotope-based imaging in visualizing internal structures, including its significance in medical diagnostics and materials science.
- Understand the principles of radioactive decay and the concept of half-life.
- Explore the application of carbon-14 dating in determining the age of organic materials.
- Investigate the limitations and factors influencing the accuracy of radio-carbon dating.
- Identify and assess the different types of radiation and their associated hazards.
- Understand the biological effects of radiation exposure on living organisms.
- Explore the principles of radiation protection and dose limits.
- Investigate safety measures and protocols for working with radioactive materials.
- Develop an awareness of regulatory frameworks and international standards related to radiation safety.

E-Copy

6.2 Introduction

This exploration underscores the pivotal role of radioisotopes in advancing scientific understanding. The integration of cutting-edge computational tools with traditional spectroscopic methods enhances precision in elucidating molecular structures. Isotope labeling techniques contribute to deciphering reaction mechanisms, aiding in the identification of intermediates and understanding complex chemical processes. Radiocarbon dating, with its interdisciplinary nature, establishes chronological timelines, impacting archaeology and geology. Ethical considerations highlight the responsible use of radioisotopes, addressing environmental impact and potential misuse. The discussion on technological advancements emphasizes continuous innovation, enhancing precision and sensitivity. Overall, this narrative emphasizes the transformative power of radioisotopes in scientific inquiry, balancing curiosity with responsible research practices.

6.3 Determination of Structure using Radio-Isotopes

The determination of structure using radioisotopes is a technique employed in various scientific disciplines, including chemistry, biology, and medicine. Radioisotopes are unstable forms of chemical elements that emit radiation, allowing researchers to trace and study the behavior of molecules and compounds in different systems. This method is particularly valuable in elucidating the structure of complex substances and understanding fundamental processes at the molecular level.

When two or more atoms of same element are present is molecule, the question of their structural equivalence or otherwise arises which can be elegantly settled by the isotopic labeling technique. This can be illustrated with reference of two substances (1) phosphorus pentachloride and (2) the thiosulphate ion.

Phosphorus pentachloride

To know whether all the five chlorine atoms in PCl_5 occupy structurally equivalent position or not, the substance is synthesized using PCl_3 and Cl_2 labeled with its radio isotope ^{36}Cl.

$PCl_3 + {}^*Cl_2 \rightarrow P{}^*Cl_5$

Subsequently, the product hydrolyzed when the following reaction takes place.

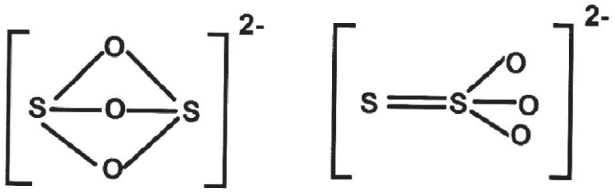
$P{}^*C1_5 + H_2O \rightarrow POCl_3 + 2H{}^*Cl$

experimentally it was found that all the radioactivity remained with HCl and

none with $POCl_3$. It is obvious that two *Cl* atoms in PCl_5 occupy positions different from the rest of three *Cl* atoms. This agree with the trigonal bipyramidal structure for PCl_5, with three *Cl* atoms in the equitorial plane and two along the vertices. Further, the equatorial *P-Cl* bond distance is known to be shorter than the apical *P-Cl* distance.

Thiosulphate ion

Two structures of thiosulphate ion can be envisaged.



(a) (b)

The problem is to know which of the structures (a) or (b) is correct.

This has been solved by synthesizing sodium thiosulphate by boiling a solution of sodium sulphite with sulphur labelled with S-35.

$$Na_2SO_3 + {}^*S \rightarrow Na_2{}^*S_2O_3$$

The product is decomposed subsequently by adding to it a solution of silver nitrate in the presence of nitric acid. An examination of the final products, silver sulphide and sodium sulphate, showed the activity is exclusively on the former.

$$Na_2{}^*S_2O_3 + 2AgNO_3 + HNO_3 \rightarrow Ag_2{}^*S + Na_2SO_4 + \text{products}$$

This points to a non-equivalent structure (b) for the two sulphur atoms in the thiosulphate ion.

6.4 Application of Radio-Isotopes in Establishment of Reaction Mechanisms

The application of radioisotopes in the establishment of reaction mechanisms represents a powerful and vital tool in the realm of chemistry. By incorporating radioactive elements into specific compounds, we can trace the pathways and kinetics of chemical reactions with unparalleled precision. This technique provides invaluable insights into the intricacies of molecular transformations, shedding light on intermediate species, reaction rates,

and the overall mechanisms governing chemical processes. Through radioisotope labeling, researchers can unravel the mysteries of complex reactions, enhancing our understanding of fundamental chemical principles and facilitating advancements in diverse fields such as medicine, industry, and environmental science.

(a) **Solubility of sparingly soluble salt:** The solubility of lead sulphate can be determined as follows. A lead salt containing known amount of radioactive lead is taken and is dissolved in water. Sulphuric acid is then added to the aqueous solution to precipitate lead as lead sulphate.

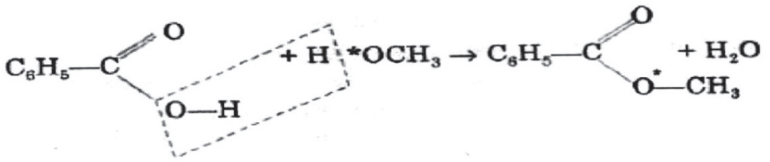
$$Pb^{*}(NO_3)_2 + H_2SO_4 \rightarrow Pb^{*}SO_4 + 2\,HNO_3$$

The precipitate is filtered. The radioactivity of filtrate is measured. From this the amount of lead still remaining solution is calculated.

(b) Tracer technique can be used to study the mechanisms or rates of chemical reactions. For example, consider the esterification of benzoic acid

$$C_6H_5COOH + HO - CH_3 \rightarrow C_6H_5COOCH_3 + H_2O$$

In order to decide whether oxygen of ester comes from alcohol or from acid we use radioactive alcohol containing 18 isotope. The ester formed is found to contain O^{18} isotope but no radioactivity is detected in H_2O. This indicates that reaction follows the II path and not the I. This implies that during esterification oxygen comes from the alcohol and reaction involves replacement of OH part of acid with OCH_3 part of alcohol.



6.5 Radio-Carbon Dating

It is a method of determining the ages of the archeological objects (wood, dead plants and animals). This technique was developed by Willard Libby. It helps in determining the date at which a particular plant or animal died. Libby was awarded Nobel Prize for his technique.

The principle of this technique lies in the fact that due to bombardment of cosmic rays, nitrogen atoms present in the upper atmosphere are converted into radioactive carbon, ^{14}C according to the reaction :

$$^{14}_{7}N + ^{1}n_{0} \rightarrow ^{14}_{6}C + ^{1}_{1}H$$

Carbon-14 is radioactive and has half-life period of 5770 years. It is oxidised in the air to give radioactive carbon dioxide. Thus, the atmospheric carbon dioxide

contains a small proportion of ^{14}C carbon dioxide

($^{14}CO_2$) which is ascimilated by plants and animals. Living plants and animals have a definite and constant proportion of ^{12}C and ^{14}C. When plant or animal dies, no fresh L: C nuclei as $^{14}CO_2$ are received by the plant or animal. The C present in these, decays according to the reaction

$$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}e; t_{\frac{1}{2}} = 5770 \text{ years.}$$

The amount of ^{14}C in a sample can be accurately determined by counting the number of 13-particles emitted per minute by one gram of the sample. By knowing ^{14}C content and half-life period, the age of the sample can be determined.

It may be noted that older the sample is, smaller is count rate. Ages of samples up to 50,000 years old can be determined accurately by this method.

6.6 Hazards of Radiation and Safety Measures

The use of radioisotopes in scientific research and various industries brings with it the potential hazards associated with ionizing radiation. Understanding these hazards is paramount to ensuring the safety of individuals working with radioactive materials. This explores in detail the hazards posed by radiation and the essential safety measures to mitigate these risks. Ionizing radiation comes in various forms, including alpha, beta, and gamma radiation. Each type has distinct properties that influence its penetration ability and potential biological impact. This section provides an in-depth examination of the characteristics of different radiation types, laying the foundation for understanding their associated hazards.

Radiation exposure can have detrimental effects on living tissues. The mechanisms of ionizing radiation's interaction with cells and the resulting biological consequences

include DNA damage, cell mutation, and the potential for long-term health effects such as cancer.

Most people who grew up during the Cold War developed a strong fear of radiation. From fallout shelters to air raid drills, they faced constant reminders of nuclear war and its dangers.

While people feared the powerful blasts associated with nuclear weapons, the prospect of radiation was even more terrifying. Invisible and insidious, radiation could have devastating effects on humans. Those who were spared painful deaths would face highly increased chances of cancers and other problems. So when a tsunami crippled Japan's Fukushima nuclear power plant this spring, leading to the largest accidental release of radiation since the 1986 Chernobyl disaster, it came as no surprise that many people began to panic. For example, some Pacific coast residents began buying iodine pills to protect themselves from the effects of any radiation that would blow across the ocean.

What they didn't realize is that, on an average day, most of us are exposed to far more radiation than they could ever expect to receive from an accident halfway across the world. In addition, many of us are exposed to additional radiation through the nature of our jobs.

Simply put, radiation is energy that travels through the air. While there are many types of radiation, they are fall into one of two classes: ionizing or non-ionizing. The primary difference between the two is that ionizing radiation is able to change the atoms to which it is exposed by removing electrons. That's an important distinction, because human cells are made up of atoms, so they can be affected by ionizing radiation.

Although non-ionizing radiation can cause atoms to move or vibrate, it cannot remove electrons. Non-ionizing radiation is all around us — in forms as diverse as radio waves and visible light — and we use many of those forms in our daily life. When you put a sandwich in a microwave oven, non-ionizing radiation causes the atoms in the sandwich to vibrate and warm up. While the temperature and texture of the sandwich changes, its atoms remain the same, so it's safe to eat. Similarly, when you place a call with a cell phone, non-ionizing radio waves travel from the phone to the nearest tower to connect you with other towers and, eventually, the person you're calling.

When people talk about the hazards of radiation, they're generally referring to ionizing radiation. It's called that because when it removes electrons from atoms, it

creates charged particles that are known as ions. If ions are used in a controlled manner, they can serve very useful purposes, whether that's generating electricity or wiping out cancer cells in the body. But when the body is exposed in other ways, those useful ions can become quite damaging. There are three basic types of ionizing radiation: alpha particles, beta particles, and a group that includes gamma rays and x-rays. Each operates at different frequencies and has different effects. For example, when used with special film, x-rays can be sent through an object such as person's arm or a welded pipe. Areas in the object that are denser will absorb the x-rays, so fewer of them will reach the film, which creates a lighter image. The resulting dark areas can pinpoint problems such as fractures, whether that's in a pipe or a human bone.

How does radiation affect people?

While all forms of ionizing radiation can have significant health effects, the potential impact depends upon the type of radiation and the amount to which a person is exposed. The different types of radiation affect different kinds of tissue in the body, primarily because of the amount of energy involved and the 'nature of each type of radiation. As an example, if a person is exposed to equal amounts of alpha and gamma radiation, the alpha particles will concentrate their energy in a much smaller area, and the gamma rays will spread out. ' Ionizing radiation can affect any type of living tissue in humans. The severity of the damage from radiation depends upon both the amount of radiation being received and the amount of time involved. What are known as stochastic health effects are those that result from long-term exposure to low levels of ionizing radiation. The most common of these is the various forms of cancer. A healthy body is able to regulate the growth of new cells and repair those that have been damaged. But when radiation causes damage that affects those regulation and repair processes, cells can grow at an uncontrolled rate. That uncontrolled growth is what we call cancer.

Another type of stochastic effect involves changes to DNA, which is the set of instructions that tells our cells how to form and behave. Changing DNA creates what are known as mutations. Some mutations affect only the individual who has been exposed to radiation, while others can be passed on through the womb to children.

Non-stochastic health effects are usually the result of exposure to significantly higher levels of radiation, often for a very short time. The effects include burns and what's known as radiation "poisoning," which can be fatal. High doses of radiation

can destroy bone marrow, shut down the nervous and/or digestive system, and lead to the loss of limbs.

Radiation in the workplace

You're already aware that ionizing radiation in the form of x-ray machines is used in healthcare facilities and manufacturing settings. In healthcare, radiation is also used in a wide variety of diagnostic devices, such as CT scanners, and concentrated for the treatment of tumors and cancers.

In industrial settings, radiation can be used in testing devices, for sterilization of products, for determining the level of moisture in soils, in weapons production, and yes, in nuclear power plants. None of those uses is inherently dangerous, as long as all of the required safety devices and processes are in place and used properly. Those who work with radiation need to understand the safety procedures, the consequences of failing to follow them, and actions to take in the event of an incident.

Fortunately, the radiation levels encountered in the workplace tend to be very small. In fact, the levels that are high enough to cause non-stochastic health effects don't occur in workplaces. Even workers in towns close to the Fukushima plant received daily doses that were smaller than what most people receive with a dental x-ray. That's why radiation safety focuses on protecting workers from long-term exposure to lower doses.

Being safe around radiation

As with so many other facets of workplace safety, training plays a critical role in working around radiation. Effective safety training focuses on the three ways workers can limit their exposure to radiation: maintaining a safe distance from the source, limiting the time around the source, and using shielding to limit the exposure. Workers should also know what to do when something goes wrong.

Depending upon the work conditions and the type of radioactive material, other safety measures may also be needed. One example is the use of dosimeters that measure radiation on a cumulative basis and sound an alarm when specific thresholds are reached. If workers are around radioactive dust, respirators may be used to keep the dust from being inhaled. Gloves or other kinds of personal protective equipment may also be needed.

Like fire, radiation can be both a valuable tool and a serious danger. As with fire, there's no need to be afraid of radiation, but it's good to develop a healthy respect for its power and to follow practices that minimize the potential danger.

6.7 Uses of Radio Active Nuclides

Nuclide	Nuclear Change	Application
argon–41	beta emission	Measure flow of gases from smokestacks
barium–131	electron capture	Detect bone tumors
carbon–11	positron emission	PET brain scan
carbon–14	beta emission	Archaeological dating
cesium–133	beta emission	Radiation therapy
cobalt–60	beta emission	Cancer therapy
copper–64	beta emission, positron emission, electron capture	Lung and liver disease diagnosis
chromium–51	electron capture	Determine blood volume and red blood cell lifetime; diagnose gas trointestinal disorders
fluorine–18	beta emission, positorn emission, electron capture	Bone scanning; study of cerebral sugar metabolism
gallium–67	electron capture	Diagnosis of lymphoma and Hodgkin disease; whole body scan for tumors

Nuclide	Nuclear Change	Application
gold–198	beta emission	Assess kidney activity
hydrogen–3	beta emission	Biochemical tracer; measurement of the water content of the body
indium–111	gamma emission	Label blood platelets
iodine–125	electron capture	Determination of blood hormone levels
iodine–131	beta emission	Measure thyroid uptake of iodine
iron–59	beat emission	Assessment of blood iron metabolism and diagnosis of anemia
krypton–79	positron emission and electron capture	Assess cardiovascular function
nitrogen–13	positron emission	Brain, heart, and liver imaging
oxyge–15	positron emission	Lung function test
phosphorus–32	beta emission	Leukemia therapy, detection of eye tumors, radiation therapy, and detection breast carcinoma
polonium-210	alpha emission	Radiation therapy
potassium–40	beta emission	Geological dating
radium–226	alpha emission	Radiation therapy
selenium-75	beta emission and electron capture	Measure size and shape of pancreas
sodium-24	beta emission	Blood studies and detection of blood clots
technetium-99	gamma emission	Bone scans and detection of blood clots
xenon-133	beta emission	Lung capacity measurement

6.8 Summary

The chapter covers the multifaceted application of radioisotopes in various scientific endeavors, emphasizing their role in determining structures, establishing reaction mechanisms, and facilitating radiocarbon dating. The use of radioisotopes in structural analysis enables scientists to probe and understand the composition of materials.

Furthermore, these isotopes play a crucial role in elucidating reaction mechanisms, shedding light on the intricacies of chemical processes.

In the realm of archaeology and geology, radioisotopes, particularly carbon-14, are employed for radiocarbon dating, allowing scientists to estimate the age of organic materials. However, amidst the valuable applications of radioisotopes, the summary also addresses the hazards associated with radiation exposure. Recognizing the potential risks, it underscores the importance of implementing safety measures to protect researchers, technicians, and the general public from harmful effects.

Overall, the summary provides a comprehensive overview of the versatile applications of radioisotopes in scientific research, while also highlighting the imperative need for caution and safety measures in handling these radioactive materials.

6.9 Model Questions

1. Which technique utilizes radio isotopes for determining the three-dimensional arrangement of atoms in a molecule?

a) NMR spectroscopy

b) Mass spectrometry

c) X-ray crystallography

d) Infrared spectroscopy

2. Radio isotopes are often employed to establish reaction mechanisms. Which radio isotope is commonly used to track the movement of atoms in chemical reactions?

a) Carbon-14

b) Hydrogen-3 (Tritium)

c) Iodine-131

d) Strontium-90

3. What is the primary isotope used in radio-carbon dating to determine the age of archaeological artifacts?

a) Uranium-238 b) Carbon-12

c) Carbon-14 d) Potassium-40

4. Which type of radiation is most harmful to living tissues and is associated with an increased risk of cancer?

a) Alpha radiation
b) Beta radiation
c) Gamma radiation
d) Neutron radiation

5. What is the primary purpose of using lead shielding in radiation experiments or facilities?

a) To absorb and block alpha particles
b) To reduce exposure to beta radiation
c) To attenuate gamma rays
d) To prevent neutron radiation

6. In X-ray crystallography, what property of crystals is utilized to determine the arrangement of atoms in a molecule?

a) Refraction
b) Diffraction
c) Absorption
d) Fluorescence

7. Which term describes a reaction step where a molecule loses a small fragment, often as a result of the use of radio isotopes in mechanistic studies?

a) Decarboxylation
b) Isomerization
c) Hydrolysis
d) Oxidation

8. What is the half-life of Carbon-14, the isotope commonly used in radio-carbon dating?

a) 5730 years
b) 4.5 billion years
c) 86 years
d) 12.3 hours

9. Which of the following materials is commonly used as personal protective equipment for those working with radioactive materials?

a) Aluminum

b) Lead

c) Copper

d) Plastic

10. What is the recommended distance for a radiation worker to maintain from a radiation source to minimize exposure?

a) As close as possible

b) 1 meter

c) 5 meters

d) 10 meters

Answers: c) X-ray crystallography; b) Hydrogen-3 (Tritium); c) Carbon-14 c) Gamma radiation; c) To attenuate gamma rays; b) Diffraction; a) Decarboxylation; a) 5730 years; b) Lead; b) 1 meter

B. Short Type Questions

1. Briefly explain how X-ray crystallography is used to determine the three-dimensional arrangement of atoms in a molecule.
2. What role does tritium (hydrogen-3) play in the study of reaction mechanisms, and how is it incorporated into molecules?
3. Describe the principle behind radio-carbon dating and why Carbon-14 is suitable for this dating method.
4. What is the biological effect of ionizing radiation on living tissues, and why is gamma radiation particularly concerning?
5. Explain the purpose of a radiation shielding material such as lead and how it is effective in protecting individuals from radiation exposure.
6. In what way does NMR spectroscopy provide information about the structure of molecules, and what type of nuclei are commonly studied using NMR?

7. How can radio isotopes be used to trace the movement of atoms during a chemical reaction, and what specific information does this provide about reaction mechanisms?
8. Discuss a limitation of radio-carbon dating and provide an example of a scenario where this dating method may not be accurate.
9. Briefly outline the main principles of the ALARA (As Low As Reasonably Achievable) concept in radiation protection.
10. What are the key features of a radiation monitoring device, and how does it contribute to the safety of individuals working with radioactive materials?

Answers:

1. X-ray crystallography involves directing X-rays through a crystal to produce a diffraction pattern, from which the atomic structure can be deduced.
2. Tritium can be used as a radioactive tracer, and its incorporation into molecules helps track the movement of atoms in reactions.
3. Radio-carbon dating relies on the decay of Carbon-14 to Carbon-12 to estimate the age of organic materials, as living organisms constantly absorb Carbon-14 from the atmosphere.
4. Ionizing radiation can damage DNA and increase the risk of cancer. Gamma radiation is concerning due to its ability to penetrate tissues deeply.
5. Lead shielding attenuates gamma rays by absorbing and blocking them, protecting individuals from radiation exposure.
6. NMR spectroscopy detects the magnetic properties of atomic nuclei, commonly studying hydrogen nuclei (protons) and carbon-13.
7. Radio isotopes can be used to label specific atoms in a molecule, allowing the tracking of their movement during a reaction, providing insights into reaction mechanisms.
8. Radio-carbon dating is limited by the assumption of constant atmospheric Carbon-14 levels and may not be accurate for materials older than about 50,000 years.
9. ALARA aims to minimize radiation exposure by keeping it “As Low As Reasonably Achievable” through the use of shielding, distance, and exposure time.

10. Radiation monitoring devices, such as dosimeters, measure and record radiation exposure, contributing to the assessment of an individual's radiation dose and ensuring safety.

6.9 Model Questions

1. Design an experiment using a radio isotope to determine the structure of a complex organic molecule. Outline the steps involved in the process.
2. Devise a radioisotope-based experiment to investigate the intermediate steps in a chemical reaction. Explain how the chosen radioisotope will help in elucidating the reaction mechanism.
3. Develop a protocol for conducting a radio-carbon dating analysis on a recently excavated sample. Include the necessary steps and precautions to ensure accurate dating results.
4. Perform a risk assessment for a laboratory working with gamma-emitting isotopes. Outline the potential hazards, preventive measures, and emergency procedures.
5. Create a safety manual for a laboratory handling radioisotopes. Include guidelines for personal protective equipment, waste disposal, and emergency response.
6. Propose a method using radioisotopes for investigating the binding sites of a new drug molecule in a biological system. Explain the rationale behind your approach.
7. Design an experiment to study the kinetics of a chemical reaction using a radioisotope as a tracer. Outline the parameters to be measured and the data analysis methods.
8. Evaluate the potential sources of contamination in a sample for radio-carbon dating. Suggest strategies to minimize contamination and ensure the reliability of results.
9. Assess the radiation safety measures in a nuclear medicine facility where radioactive tracers are routinely used. Identify key practices and equipment to protect staff and patients.
10. Develop a training program for laboratory personnel working with radioisotopes. Highlight the essential elements, including theoretical knowledge, practical skills, and emergency response training.

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Module III: Periodic Table

Unit 7 ❐ Periodic Table

Contents

7.1 Objectives

7.2 Introduction

7.3 Periodic Table

7.4 Trends and Periodic Trends in Physical Properties

7.5 Classification of Elements on The Basis of Electronic Configuration

7.6 Modern IUPAC Periodic Table

7.7 General Characteristic of s, p, d and f Block Elements

7.8 Position of Hydrogen in Periodic Table

7.9 Position of Noble Gases in Periodic Table

7.10 Summary

7.11 References

7.1 Objectives

- Explore the organization of elements in the Periodic Table.
- Identify and comprehend the significance of periods and groups.
- Investigate the trends within groups (columns) of the Periodic Table.
- Analyze the similarities and variations in properties among elements within a group.
- Examine and comprehend periodic trends in atomic size.
- Explore trends in ionization energy and electronegativity across periods.
- Classification of Elements Based on Electronic Configuration:
- Investigate the relationship between electronic configuration and an element's position in the Periodic Table.

E-Copy

- Understand how electron configuration influences an element's chemical behavior.
- Familiarize yourself with the modern IUPAC (International Union of Pure and Applied Chemistry) version of the Periodic Table.
- Recognize the systematic arrangement of elements based on atomic number.
- Explore the properties and behaviors of elements in the s, p, d, and f blocks.
- Understand the implications of electron filling in different subshells on the characteristics of these elements.
- Investigate the unique position of hydrogen in the Periodic Table.
- Understand the reasons behind hydrogen's placement and its distinct characteristics.
- Explore the characteristics and properties of noble gases.
- Understand the reasons for the placement of noble gases in the Periodic Table and their lack of reactivity.
- Examine how the electronic structure of elements influences their chemical properties.
- Identify patterns in chemical behavior based on the arrangement of electrons in different orbitals.
- Explore real-world applications of periodic trends in various fields, such as chemistry, materials science, and medicine.
- Understand how knowledge of periodic trends contributes to predicting and explaining the behavior of elements and compounds.

7.2 Introduction

The Periodic Table stands as one of the foundational pillars in the realm of chemistry, offering a systematic and comprehensive arrangement of the elements. This iconic tabular representation not only organizes elements based on their atomic numbers but also provides invaluable insights into the relationships between their properties. Exploring the Periodic Table involves unraveling intricate patterns, such as group trends and periodic trends in physical properties, which shed light on the behavior of elements.

One of the captivating dimensions of the Periodic Table lies in its groups, or columns, where elements with similar chemical characteristics reside. Delving into group trends

unveils a symphony of shared attributes among elements, offering a glimpse into the predictable variations within a given column. Simultaneously, periodic trends in physical properties, such as atomic size, ionization energy, and electronegativity, provide a dynamic perspective across periods, revealing the subtle shifts in elemental characteristics as one moves horizontally across the table.

The classification of elements based on electronic configuration emerges as a crucial key to deciphering the mysteries of the Periodic Table. This classification not only aids in understanding an element's place in the table but also serves as a guide to predicting its chemical behavior. By unraveling the intricacies of electron arrangement, we gain insights into the underlying principles that govern the diverse properties exhibited by elements.

The evolution of the Periodic Table has seen refinements over time, with the Modern IUPAC Periodic Table emerging as the standardized version. This contemporary rendition aligns elements based on their atomic numbers, providing a more accurate representation of the relationships between elements and their properties. Exploring this modern framework deepens our understanding of the fundamental principles that govern the organization of elements.

Further, the Periodic Table introduces us to the unique characteristics of s, p, d, and f block elements, each contributing distinct qualities to the tableau of the elements. Understanding the general traits associated with these blocks unravels the richness of chemical diversity present within the Periodic Table.

In this exploration, we also turn our attention to the singular positioning of hydrogen and the noble gases. Hydrogen, with its solitary position at the top of the table, challenges traditional classification methods, while the noble gases, occupying the far-right column, stand as a testament to their exceptional stability and lack of reactivity. Examining the placement of these elements adds intriguing dimensions to our comprehension of the periodic landscape.

Embarking on this journey through the Periodic Table and its associated concepts promises a fascinating expedition into the heart of chemical organization, where patterns and principles converge to unlock the secrets of the elements.

7.3 Periodic Table

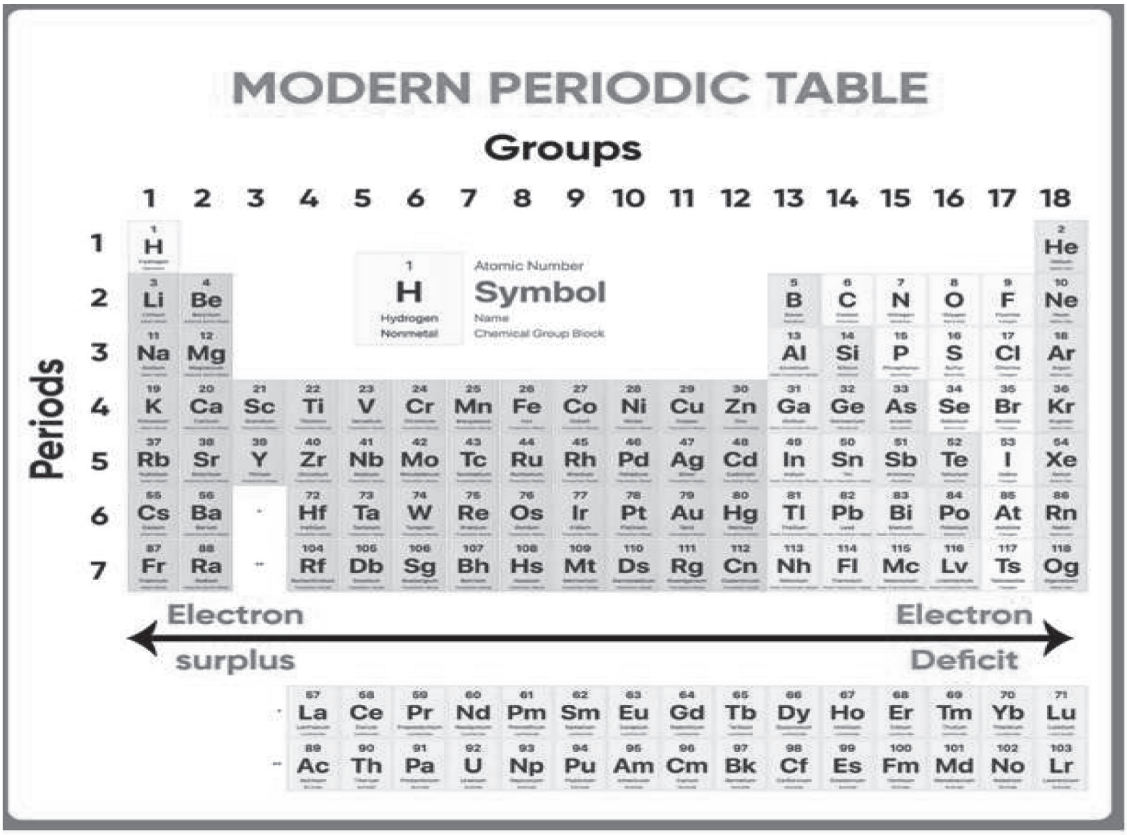
The periodic table is a fundamental tool in chemistry, serving as a systematic arrangement of chemical elements based on their atomic number, electron configuration, and recurring chemical properties. Developed by Dmitri Mendeleev in 1869, the table organizes elements into rows and columns, facilitating the understanding of their relationships and behaviors. Elements are grouped into periods (horizontal rows) and groups or families (vertical columns), with each element uniquely identified by its atomic number, which represents the number of protons in its nucleus. The periodic table not only provides a concise summary of the building blocks of matter but also serves as a predictive guide for understanding the properties and reactivity of elements, forming a cornerstone for the study and application of chemistry.

Period: In the context of the periodic table, a period refers to a horizontal row of elements. The periodic table is organized into rows and columns. Each horizontal row is called a period, and there are seven periods in the periodic table. The elements within a period have the same number of electron shells.

As you move across a period from left to right, the atomic number of the elements increases, and there is a gradual filling of electron shells. The properties of elements within a period can exhibit trends and variations based on the changing electron configurations.

Modern Periodic Table

In the modern periodic table elments are arranged sequentially by atomic number in rows and columns. In 1913, Henry Moseley's work established the concept of atomic number, the number of protons in the nucleus, as the key for determining an element's position in the periodic table. Rows in the periodic table are referred to as periods, and columns are called groups. The periods run left to right, and the groups from top to bottom. A goup may also comprise a chemical family. Groups are numbered across the top of the table. In recent years, scientists have suggested using the Arabic



Group: A periodic group, in the context of the periodic table, refers to a vertical column of elements that share similar chemical properties. These columns are also known as groups or families. Elements within the same group typically exhibit comparable outer electron configurations and, consequently, similar patterns of chemical behavior.

The periodic table is divided into several groups numbered from 1 to 18. Elements in the same group often have the same number of valence electrons, which are the electrons in the outermost shell of an atom. As a result, they tend to react in similar ways and exhibit analogous chemical properties. For example, Group 1 elements (alkali metals) all have one valence electron, and Group 17 elements (halogens) have seven valence electrons.

Understanding the arrangement of elements into groups is fundamental to comprehending the periodic trends and behaviors of elements, making the periodic table a valuable tool for chemists and researchers.

7.4 Trends and Periodic Trends in Physical Properties

The periodic table serves as a roadmap to the properties of elements, providing a systematic organization that reveals trends and patterns in their behavior. In this section, we will delve into the fundamental physical properties of elements and explore the intriguing patterns that emerge across periods and groups.

I. Atomic Size and Radius:

Understanding the size of an atom is crucial in comprehending its physical behavior. As we progress across a period from left to right, the atomic radius generally decreases. This phenomenon is attributed to the increasing effective nuclear charge, drawing electrons closer to the nucleus. Conversely, moving down a group, the atomic radius increases due to the addition of electron shells.

II. Density Trends:

Density, the mass of an element per unit volume, exhibits notable trends across the periodic table. Generally, metals, found on the left side, have higher densities compared to nonmetals on the right. Transition metals, located in the middle, often have intermediate densities.

III. Melting and Boiling Points:

The melting and boiling points of elements also display intriguing periodic trends. Across a period, these points generally increase due to stronger atomic bonding resulting from higher effective nuclear charge. Down a group, melting and boiling points decrease as a consequence of weaker atomic bonding from increased atomic radius.

IV. Electrical Conductivity:

Electrical conductivity is a crucial physical property, especially in metals. Metals, found on the left side, are excellent conductors of electricity due to the presence of free electrons. Nonmetals, on the other hand, are typically poor conductors. Transition metals often exhibit variable conductivity.

V. Trends in Metallic Character:

Metallic character encompasses properties like luster, malleability, and ductility. As we move from left to right across a period, metallic character generally decreases, with

nonmetals dominating the right side. Down a group, metallic character increases, with alkali and alkaline earth metals exhibiting pronounced metallic properties.

VI. Trends in Physical State:

The physical state of elements at room temperature varies systematically across the periodic table. Most elements are solids, with a few gases and liquid elements. Metals are predominantly solids, while nonmetals can exist in all three states.

VII. Trends in Electron Configuration:

The arrangement of electrons in atoms influences physical properties. Exploring trends in electron configuration provides insights into the periodicity of elements and their behavior in chemical reactions.

Periodic trends in physical properties offer a powerful tool for understanding the behavior of elements and predicting their properties. This knowledge serves as a foundation for further exploration in chemistry, materials science, and various engineering disciplines, enabling scientists and researchers to design and manipulate materials with specific physical characteristics.

7.5 Classification of Elements on The Basis of Electronic Configuration

The overall elements are classified in the following ways.

1. Alkali metals
2. Alkaline earth metals
3. Transition metals
4. Post-transition metals
5. Metalloids
6. Other non-metals
7. Halogens
8. Noble gases
9. Lanthanides
10. Actinides
11. Unknown chemical properities

Alkali metals : This "group I" of metals occupies the far-left column of the periodic table. They are all soft, but solid metals at room temperature, and are highly reactive *Elements Include* : Li, Na, K, Rb, Cs, and Fr.

Alkaline earth metals : The alkaline earth metals are silver-white metals at room temperature. The name is a term that refers to the naturally occurring oxides of these elements. For example, lime is the alkaline oxide of calcium. *Elements Include :* Be, Mg, Ca, Sr., Ba, and Ra.

Transition metals : The transition metals occupy a broad area in the centre of the periodic table. They are harder than the alkali metals less reactive and are generally good conductors of both heat and electrical current.

Elements Include : Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Rf, Db, Sg, Bh, Hs, and Cn.

Post-transition metals : Lying in a triangular region to the right of the transition metals, the post-transition metals are soft metals that mostly have low melting and boiling points. They also include mercury, which is liquid at room temperature. *Elements Include :* Al, Ga, In, Sn, Tl, Pb, and Bi.

Metalloids : The metalloid elements from a line between the metals and nonmetals in the periodic table. Their electrical conductivity in intermediate between the two grops, leading to their use in semiconductor electronics. *Elements Include :* B, Si, Ge, As, Sb, Te, and Po.

Other non-metals : In addition to halogens and noble gases, there are other elements that are simply classified as "other non-metals." They display a wide range of chemical properities and reactivities. They have high ionization energies and electronegativities, and are generally poor conductors of heat and electricity. Most non-metals have the ability to gain electrons easily. They have lower melting points, boiling points and densities than the metal elemtns. *Elements Include :* H, C, N, O, P, S, and Se.

Halogens : The halogens, known as group 17, are the only group to contain all three principal states of matter at room temperature : gas (fluorine and chlorine), liquid (bromine) and solid (iodine and astatine)–all non-metals. *Elements Include :* F, Cl, Br., I, and At.

Noble gases : The noble gases are non-metals occupying group 18 of the table. They are all gaseous at room temperature and share the properties of being colourless, odourless and unreactive. Including neon, argon and xenon, they have applications in lighting and welding *Elements Include :* He, Ne, Ar, Kr, Xe, and Rn.

Lanthanides : The lanthanide elements occupy a horizontal strip normally appended at the foot of the periodic table. Named after lanthanum, the first element in the series, they are generally found in less common mineral rocks, such as monazite and bastnasite. *Elements Include :* La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

Actinides : The actinides fill the second horizontal strip at the foot of the table. Named after their first element, actinium, they are all highly radioactive. So much so, that natural reserves of many of these elements have decayed away to nothing. *Elements Include :* Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr.

Unknown chemical properties : This is a label reserved for elements that can only be manufactured in a laboratory. Very often, only minute quantities of such elements have been created—making it impossible to ascertain their exact chemical classification. *Elements Include :* Mt, Ds, Rg, Uut, Fl, Uup, Lv, Uus, and Uuo.

7.6 Modern IUPAC Periodic Table

The International Union of Pure and Applied Chemistry (IUPAC) periodically updates its recommendations for the periodic table. The periodic table is a tabular arrangement of chemical elements based on their atomic number, electron configuration, and recurring chemical properties.

Here are some general features and principles that are typically considered in the modern **IUPAC periodic table:**

Arrangement by Atomic Number: Elements are arranged in order of increasing atomic number, which corresponds to the number of protons in an atom.

Groups and Periods: Elements are organized into groups (columns) and periods (rows).

Groups generally share similar chemical properties, while periods indicate the energy levels of the electron shells.

Block Classification: Elements are categorized into s-block, p-block, d-block, and f-block based on the subshells in which the last electron is added. The blocks are often represented by different regions in the table.

Transition Metals: The transition metals are typically found in the d-block, and they exhibit a variety of oxidation states and complex chemistry.

Lanthanides and Actinides: The f-block elements are often shown separately at the bottom of the periodic table, representing the lanthanides and actinides.

Metalloids: Metalloids, elements with properties between metals and nonmetals, are often found along the diagonal line between metals and nonmetals.

Noble Gases: Noble gases are placed in Group 18 and are known for their stable and inert nature due to their full outer electron shells.

Colour Coding: Different colours may be used to distinguish between categories of elements, such as metals, nonmetals, and metalloids.

It's important to note that the periodic table is subject to periodic updates and revisions by the scientific community. I recommend checking the latest IUPAC recommendations or reliable scientific sources for the most up-to-date information on the periodic table, as developments may have occurred after my last update in January 2022.

7.7 General Characteristic of s, p, d and f Block Elements

s-block elements:

The s-block elements, located in groups 1 and 2 of the periodic table, exhibit several general properties that are characteristic of this group of elements. Here are some of the key general properties of s-block elements:

Valence Electrons:

The outermost electron(s) of s-block elements are located in the s orbital.

Group 1 elements (alkali metals) have one valence electron, and Group 2 elements (alkaline earth metals) have two valence electrons.

Atomic Size:

Generally, s-block elements have larger atomic sizes compared to elements in other blocks.

Atomic size increases down a group due to the addition of electron shells.

Ionization Energy:

S-block elements have relatively low ionization energies, especially in group 1.

Ionization energy decreases down a group due to increased distance of the outermost electron from the nucleus.

Reactivity:

Alkali metals (Group 1) are highly reactive due to their low ionization energies and a strong desire to lose their single valence electron.

Alkaline earth metals (Group 2) are also reactive but less so than alkali metals.

Formation of Cations:

S-block elements readily form positive ions (cations) by losing their valence electrons.

Alkali metals form +1 ions, and alkaline earth metals form +2 ions.

Physical State:

Alkali metals are typically soft and have low melting points.

Alkaline earth metals are generally harder and have higher melting points than alkali metals.

Density:

Alkali metals have low densities, gradually increasing down the group.

Alkaline earth metals have higher densities compared to alkali metals.

Flame Test:

Alkali metals exhibit characteristic flame colors when they are heated.

For example, sodium produces a yellow flame, and potassium produces a violet flame.

Formation of Salts:

Alkali metals react with nonmetals to form salts.

Alkaline earth metals also form salts, but their reactivity is generally lower than that of alkali metals.

Hydration Energy:

S-block elements show significant hydration energies, especially for alkali metals, which form highly soluble hydroxides.

Alloy Formation:

S-block elements, particularly alkaline earth metals, are involved in the formation of alloys, contributing to the mechanical properties of materials.

p-block elements:

The p-block elements are a group of elements in the periodic table that belong to groups 13 to 18. These elements include nonmetals, metalloids, and metals. Here are some general properties of p-block elements:

Electron Configuration: P-block elements have their outermost electrons in the p subshell. The general electron configuration for these elements is ns^2np^1-v, where n is the principal quantum number.

Metallicity: P-block elements include metals, metalloids, and nonmetals. Elements to the left (group 13-15) tend to be metals, while those to the right (group 16-18) are generally nonmetals.

Atomic Size: Atomic size generally decreases from left to right across a period due to increasing effective nuclear charge. However, within a group, atomic size increases from top to bottom.

Ionization Energy: Ionization energy generally increases from left to right across a period due to increased nuclear charge. Within a group, ionization energy decreases from top to bottom.

Electronegativity: Electronegativity values generally increase from left to right across a period and decrease from top to bottom within a group. The elements in the upper right corner of the periodic table (group 17) have the highest electronegativity.

Melting and Boiling Points: These properties vary widely among p-block elements. Generally, metals have lower melting and boiling points compared to nonmetals. Metalloids often have intermediate values.

Metallic Character: Metallic character decreases from left to right across a period and increases from top to bottom within a group. Metals are typically found on the left side of the p-block, while nonmetals are on the right side.

Oxidation States: P-block elements can exhibit various oxidation states. However, the tendency to show multiple oxidation states is more pronounced for transition metals. Elements in groups 13 and 14 usually exhibit +4 oxidation state, while those in groups 15, 16, and 17 can show multiple oxidation states.

Chemical Reactivity: P-block elements participate in a wide range of chemical reactions. The reactivity is often influenced by the number of valence electrons and the ability to gain or lose electrons.

Allotropy: Some p-block elements exist in different structural forms called allotropes. For example, carbon has allotropes such as diamond, graphite, and graphene.

It's important to note that these properties can vary within a group due to differences in atomic structure and bonding tendencies.

d-block Elements

The d-block, also known as the transition metals, is a set of elements in the periodic table that spans groups 3 to 12. These elements share some general properties:

Metallic Character:

Transition metals are generally good conductors of heat and electricity.

They have a metallic luster and are malleable and ductile.

Variable Oxidation States:

Transition metals often exhibit multiple oxidation states due to the availability of d orbitals for electron transfer.

The range of oxidation states can vary widely within a single element.

Formation of Colored Compounds:

Transition metal compounds often display vibrant colours due to electronic transitions involving d orbitals.

The colour of the compounds is sensitive to the oxidation state of the metal ion.

Formation of Complex Ions:

Transition metals have a tendency to form complex ions by combining with ligands (molecules or ions that donate electrons).

These complexes often have distinct colours and enhanced stability.

High Melting and Boiling Points:

Transition metals generally have higher melting and boiling points compared to s-block elements. These are attributed to the strong metallic bonding resulting from the presence of partially filled d orbitals.

Catalytic Activity:

Many transition metals and their compounds exhibit catalytic activity.

They are often used as catalysts in various chemical reactions due to their ability to change oxidation states easily.

Formation of Alloys:

Transition metals readily form alloys with other metals, which often results in improved mechanical and chemical properties. Common alloys include steel (iron with carbon and other elements) and brass (copper with zinc).

Magnetic Properties:

Some transition metal ions and compounds exhibit magnetic properties due to the presence of unpaired electrons in their d orbitals.

Magnetic behavior can vary, including paramagnetism and ferromagnetism.

Density:

Transition metals generally have high densities, especially when compared to s-block elements.

Tendency to Form Coordination Compounds:

Transition metals have a high affinity for forming coordination compounds where metal ions are surrounded by ligands.

These compounds often exhibit interesting chemical and physical properties.

It's important to note that while these general properties apply to the transition metals as a group, individual elements within the d-block may have unique characteristics and exceptions to these trends.

f-block Elements

The f-block elements, also known as inner transition elements, consist of two series: the lanthanides and actinides. These elements have partially filled f orbitals and are placed at the bottom of the periodic table. Here are some general properties of f-block elements:

Electron Configuration: The f-block elements have electrons filling the f orbitals. The lanthanides have electrons filling the 4f orbitals, while the actinides have electrons filling the 5f orbitals.

Position in the Periodic Table: The f-block elements are located at the bottom of the periodic table, below the main body of the table. The lanthanides are found in the sixth and seventh periods, and the actinides are located in the seventh period.

Atomic Size: Generally, the f-block elements are large atoms due to the filling of inner f orbitals. There is a gradual increase in atomic size as you move from the beginning to the end of the lanthanide or actinide series.

Metallic Nature: Most f-block elements are metals, and they exhibit typical metallic properties such as conductivity, malleability, and ductility.

Magnetic Properties: Many f-block elements are magnetic, especially those with unpaired electrons. The magnetic behavior is influenced by the presence of magnetic moments arising from the orientation of the electron spins.

High Atomic and Ionic Radii: Due to the presence of additional inner f orbitals, f-block elements generally have larger atomic and ionic radii compared to the elements in the s- and p-blocks.

Variable Oxidation States: f-block elements exhibit a wide range of oxidation states, although the +3 oxidation state is the most common. The presence of f orbitals allows for multiple oxidation states, contributing to the complex chemistry of these elements.

Chemical Reactivity: f-block elements are chemically reactive, and their reactivity is

influenced by the availability of f orbitals for bonding. They often form coordination compounds and complexes with ligands.

Lanthanide Contraction: This is a phenomenon observed in the lanthanide series where there is a gradual decrease in atomic and ionic radii across the series. This is primarily due to poor shielding of outer electrons by the inner f electrons.

Radioactivity: Many of the actinide elements are radioactive, and their isotopes are often used in nuclear reactions and applications.

Complex Formation: f-block elements have a tendency to form stable complexes with various ligands due to the availability of inner f orbitals.

These general properties highlight the unique characteristics of the f-block elements, making them distinct from the other elements in the periodic table.

7.8 Position of Hydrogen in periodic Table

The location of hydrogen in the periodic table has been a subject of discussion and debate among scientists. Although conventionally placed in Group 1 above alkali metals due to its $1s^1$ electronic configuration and a single valence electron, hydrogen's properties differ significantly from those of typical Group 1 elements.

Key considerations regarding hydrogen's position in the periodic table include:

Electronic Configuration: Hydrogen shares a single valence electron with Group 1 elements ($1s^1$), but unlike alkali metals, it is a non-metal.

Chemical Properties: Hydrogen can either gain or lose electrons to attain a stable configuration, resembling alkali metals and halogens. It can form positive ions (H^+) or negative ions (H^-) based on reaction conditions.

Isotopes: Hydrogen possesses three isotopes (protium, deuterium, and tritium), a feature absent in other Group 1 elements.

Occurrence: While hydrogen is abundant in the universe, on Earth, it is predominantly found in compounds like water (H2O) and hydrocarbons, rarely occurring in its elemental form.

Hydrogen Bonding: Exhibiting a unique form of bonding known as hydrogen bonding, hydrogen plays a crucial role in phenomena such as water behavior and biological processes.

Metallic and Non-metallic Behavior: Hydrogen displays characteristics of both metals and nonmetals. Under standard conditions, it behaves more like a non-metal, but under extreme pressure, it can exhibit metallic properties.

Positional Ambiguity: The placement of hydrogen varies among periodic tables, with some depicting it separately at the table's top and others positioning it in Group 1. The IUPAC officially designates hydrogen as a Group 1 element.

Anomalous Nature: Hydrogen is often regarded as an anomalous element due to its unique traits, and its behavior cannot be entirely predicted based on its location in the periodic table.

In summary, hydrogen's inclusion in Group 1 reflects its distinct characteristics and peculiar nature. While traditionally associated with alkali metals, its non-metallic attributes, isotopic variety, and individual behavior set it apart as an exceptional element with characteristics deviating from those of typical Group 1 elements.

7.9 Position of Noble Gases in Periodic Table

The noble gases occupy Group 18 (VIII A) of the periodic table. This group is located on the far right-hand side of the table, to the right of the halogens (Group 17) and just above the inert gases (Group 0). The noble gases consist of helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn).

Key characteristics of noble gases and their position in the periodic table include:

Stability: Noble gases are known for their high stability due to a complete set of electrons in their outermost energy level. This full complement of electrons results in a stable electron configuration, making them chemically inert. They generally do not readily form compounds with other elements.

Full Outer Shell: Each noble gas has a full outer electron shell, which is why they are relatively unreactive. This stable electron configuration is a result of having the maximum number of electrons allowed in their outermost energy level.

Gaseous State: At room temperature and pressure, all noble gases exist in the gaseous state. They have relatively low boiling and melting points compared to other elements, and they lack colour, taste, and odour.

Increasing Atomic Size: Moving down the group, the atomic size of the noble gases

increases. This trend is due to the addition of energy levels as you go from helium to radon.

Nonmetals: Noble gases are considered nonmetals, and they are situated to the right of the metalloids on the periodic table.

Use in Lighting: Some noble gases find practical applications, particularly in lighting. For example, argon is used in fluorescent lights, and neon is used in neon lights. Xenon and krypton are used in certain types of high-intensity discharge lamps.

In summary, the noble gases are a unique group of elements with distinctive properties, primarily characterized by their inertness and stability. Their position in Group 18 reflects their shared characteristics and the fact that they have a complete set of electrons in their outermost energy level, making them relatively unreactive compared to other elements in the periodic table.

7.10 Summary

The periodic table is a systematic arrangement of chemical elements based on their atomic number, electron configuration, and recurring chemical properties. It consists of periods (horizontal rows) and groups (vertical columns). Group trends refer to the similarities and patterns in the chemical behavior of elements within a specific group, while periodic trends involve the variations in physical and chemical properties across periods.

Group Trends:

1. Alkali Metals (Group 1): Highly reactive metals with a single valence electron.
2. Alkaline Earth Metals (Group 2): Reactive metals with two valence electrons.
3. Halogens (Group 17): Highly reactive nonmetals with seven valence electrons.
4. Noble Gases (Group 18): Inert gases with a full valence shell, exhibiting minimal reactivity.

Periodic Trends in Physical Properties:

1. Atomic Radius: Increases down a group and decreases across a period.
2. Ionization Energy: Decreases down a group and increases across a period.
3. Electronegativity: Decreases down a group and increases across a period.

Classification of Elements Based on Electronic Configuration: Elements are categorized into s, p, d, and f blocks based on the subshells being filled in their electron configurations.

1. s Block (Groups 1 and 2): Alkali and alkaline earth metals with electrons filling the s subshell.
2. p Block (Groups 13 to 18): Mainly nonmetals and metalloids with electrons filling the p subshell.
3. d Block (Transition Metals): Metals with electrons filling the d subshell.
4. f Block (Inner Transition Metals): Lanthanides and actinides with electrons filling the f subshell.

Modern IUPAC Periodic Table: The International Union of Pure and Applied Chemistry (IUPAC) periodic table is a standard representation, organized by increasing atomic number.

General Characteristics of s, p, d, and f Block Elements:

1. s Block: Typically alkali and alkaline earth metals, generally reactive.
2. p Block: Diverse properties, including nonmetals, metalloids, and metals.
3. d Block: Transition metals with variable oxidation states and metallic properties.
4. f Block: Lanthanides and actinides, often characterized by inner electron transitions.

Position of Hydrogen and Noble Gases:

- Hydrogen: Positioned in the top-left corner, it is a non-metal with unique properties.
- Noble Gases: Found in Group 18, they are inert, monatomic gases with complete valence shells.

In summary, the periodic table provides a structured framework for understanding the relationships between elements based on their electronic configuration, leading to the identification of group and periodic trends in physical properties.

7.11 Model Questions

A. Multiple Type Questions

1. What is the main factor determining the placement of elements in the modern IUPAC periodic table?

a. Atomic mass
b. Atomic number
c. Valence electrons
d. Electronegativity

2. Which group of elements is known for having a single valence electron and extreme reactivity?

a. Alkali Metals (Group 1)
b. Halogens (Group 17)
c. Noble Gases (Group 18)
d. Alkaline Earth Metals (Group 2)

3. The trend of increasing atomic radius is observed:

a. Across a period from left to right
b. Across a period from right to left
c. Down a group
d. Up a group

4. Which block of elements is characterized by filling the s subshell?

a. s Block b. p Block
c. d Block d. f Block

5. Elements in the p block of the periodic table include:

a. Alkali metals
b. Noble gases
c. Transition metals
d. Halogens

6. Which group of elements is known for having two valence electrons and is less reactive than alkali metals?

a. Alkali Metals (Group 1)
b. Halogens (Group 17)
c. Noble Gases (Group 18)
d. Alkaline Earth Metals (Group 2)

7. What is the general trend in ionization energy as you move from left to right across a period?

a. Increases
b. Decreases
c. Remains constant
d. Unpredictable

8. The transition metals, characterized by filling the d subshell, are found in which block of the periodic table?

a. s Block b. p Block
c. d Block d. f Block

9. Which group of elements is known for their inertness and is found in Group 18 of the periodic table?

a. Alkali Metals
b. Halogens
c. Noble Gases
d. Alkaline Earth Metals

10. Where is hydrogen located in the modern IUPAC periodic table?

a. Group 1
b. Group 2
c. Group 17
d. Not in any specific group

B. Short Type Questions

1. What is the primary criterion for the arrangement of elements in the modern IUPAC periodic table?
2. Which group of elements is known for having a complete valence shell and minimal reactivity?
3. Describe the trend of electronegativity as you move from left to right across a period.
4. In which block of the periodic table are transition metals located, and what subshell do they fill?
5. Define the term "group trends" in the context of the periodic table.
6. Which group of elements is characterized by filling the s subshell, and what are their general characteristics?
7. Explain the variation in atomic radius as you move down a group in the periodic table.
8. Identify the elements found in the p block of the periodic table and mention one notable property of this block.
9. What is the electronic configuration of alkali metals, and why are they highly reactive?
10. Where is hydrogen located in the modern IUPAC periodic table, and what makes its placement unique?

C. Assay Type Questions

1. Discuss the historical development of the periodic table and the contributions of key scientists in its creation.
2. Explain the concept of group trends in the periodic table, providing examples and discussing the underlying reasons for observed patterns.
3. Compare and contrast the properties of alkali metals and alkaline earth metals, highlighting their similarities and differences.
4. Elaborate on the factors influencing ionization energy and electronegativity across a period in the periodic table.
5. Describe the characteristics of transition metals, including their electronic configuration, variable oxidation states, and common physical properties.

6. Explore the significance of the s, p, d, and f blocks in the periodic table, emphasizing the types of elements found in each block and their general properties.
7. Discuss the unique characteristics of noble gases, explaining why they are classified as inert and providing examples of their applications.
8. Examine the position of hydrogen in the periodic table, considering its ambiguous classification and the reasons for its placement.
9. Explore the concept of atomic radius and its variation across periods and groups, providing insights into the factors influencing this trend.
10. Investigate the electronic configuration of halogens, discussing their role in chemical reactions and their significance in various industrial processes.

7.12 References

1. **"Concise Inorganic Chemistry"** – J.D. Lee

   Covers periodic trends, classification of elements, electronic configurations, and theproperties of different blocks of elements.

2. **"Inorganic Chemistry"** – Gary L. Miessler, Paul J. Fischer, and Donald A. Tarr

   Provides in-depth discussions on periodic trends, periodic classification, and modern periodic table arrangements.

3. **"Chemistry: The Central Science"** – Theodore L. Brown, H. Eugene LeMay, Bruce E. Bursten

   Explains periodic trends, physical properties of elements, and classification based on electronic configuration.

4. **"Principles of Inorganic Chemistry"** – Puri, Sharma, and Kalia

   Covers the modern periodic table, position of hydrogen and noble gases, and characteristics of s, p, d, and f block elements.

5. **"Advanced Inorganic Chemistry"** – F. Albert Cotton and Geoffrey Wilkinson

   Discusses periodicity, classification of elements, and the properties of different element groups in detail.

Unit 8: Chemical periodicity

Contents

8.1 Objectives

8.2 Introduction

8.3 Atomic Radii

8.4 Ionic Radii (Pauling's Univalent)

8.5 Covalent Radii

8.6 Ionization Potential

8.7 Electron Affinity

8.8 Electronegativity (Pauling's, Mulliken's and Allred-Rochow's Scales) and Factors Influencing these Properties

8.9 Inert Pair Effect

8.10 Group trends and periodic trends in these properties in respect of s-, p- and d-block elements

8.11 Summary

8.12 Model Questions

8.13 Further Reading

8.1 Objectives

- Define atomic radii and explain the factors influencing the size of atoms.
- Describe the trends in atomic radii across periods and down groups in the periodic table.
- Define ionic radii and Pauling's scale for univalent ions.

- Discuss the factors affecting the size of ions and how ionic radii vary across the periodic table.
- Define covalent radii and explain the concept of bond length in covalent compounds.
- Discuss the trends in covalent radii based on the nature of the bonded atoms.
- Define ionization potential and its significance.
- Discuss the trends in ionization potential across periods and down groups.
- Explain the factors influencing ionization potential.
- Define electron affinity and its significance.
- Discuss the trends in electron affinity across periods and down groups.
- Explain the factors influencing electron affinity.
- Define electronegativity and compare Pauling's, Mulliken's, and Allred-Rochow's scales.
- Discuss the trends in electronegativity across periods and down groups.
- Explain the factors influencing electronegativity.
- Explore the various factors influencing atomic and ionic radii, ionization potential, electron affinity, and electronegativity.
- Relate these factors to the nature of the electronic configuration and effective nuclear charge.
- Define the inert pair effect and its significance.
- Explain how the inert pair effect influences the chemical behavior of certain elements.
- Analyze the group trends in atomic and ionic radii, ionization potential, electron affinity, and electronegativity.
- Discuss similarities and differences among elements within a group.

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- Explore the periodic trends in atomic and ionic radii, ionization potential, electron affinity, and electronegativity for s-, p-, and d-block elements.
- Discuss the variations in these properties within a period and across different blocks.

8.2 Introduction

Understanding the physical and chemical properties of elements is fundamental to unraveling the mysteries of the periodic table. The properties of atoms and ions play a crucial role in determining their behavior in various chemical reactions. In this comprehensive study, we delve into the intricacies of atomic radii, ionic radii (as per Pauling's univalent scale), and covalent radii, unraveling the dimensions that define the spatial extent of atoms and ions. Simultaneously, we explore the energetics associated with the electronic structure of atoms, investigating ionization potential, electron affinity, and electronegativity using scales devised by luminaries like Pauling, Mulliken, and Allred-Rochow.

As we embark on this exploration, we aim to elucidate the periodic trends that govern these properties, discerning the variations across periods and down groups. The inert pair effect, a phenomenon affecting the reactivity of certain elements, will be scrutinized for its impact on chemical behavior. Additionally, we will analyze the group trends within the periodic table, considering how elements within a group exhibit similarities and differences in their atomic and molecular characteristics.

This journey through the microscopic realm of atomic and molecular properties will not only provide a deeper understanding of the periodic table but will also lay the foundation for predicting the chemical behavior of elements and compounds. The interplay between atomic structure and chemical reactivity is a fascinating tapestry, and our exploration aims to unravel the threads that weave it together. Join us as we navigate the intricate landscape of atomic and

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molecular dimensions, ionization energies, and the captivating world of electronegativity, unveiling the secrets that govern the behavior of elements in the periodic table.

8.3 Atomic Radii

One of the most systematic periodic properties is atomic radius. Because the electrons can be defined only in terms of probability, there is no real boundary to an atom. We cannot directly measure the actual size of an atom. What we can do is to measure the inter nuclear distance between two atoms; this is obtained from spectroscopic or x-ray electron diffraction studies. The outer part of the atom is made up of diffuse "electron clouds" – the density of this cloud falls exponentially with the radius. So there cannot be any well-defined boundary of an atom and the radius of an isolated atom has no meaning. We can calculate the effective volume occupied by an atom in the solid and liquid state in an environment of other atoms. Even then, the situation is not simple because the nature of packing differs from one element to another. In a compound, the outer electrons of an atom are subject to the field of all the neighbouring atoms and so its "size" will depend on the chemical environment. Experimentally it is possible to measure the distances oetween atoms in a close-packed aggregate or in a compound. This gives us an idea of radius of an atom which will of course differ in different environments. Different sets of radii of atoms have been worked out depending on their environment like Vander Waals radii, covalent radii etc.

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■ ***Group Trend***:- Increases down a group (Caused by an increase in Shells)

■ ***Period Trend***:- Decreases across a period(As nuclear strength increases the nucleus pulls the outer electrons closer)

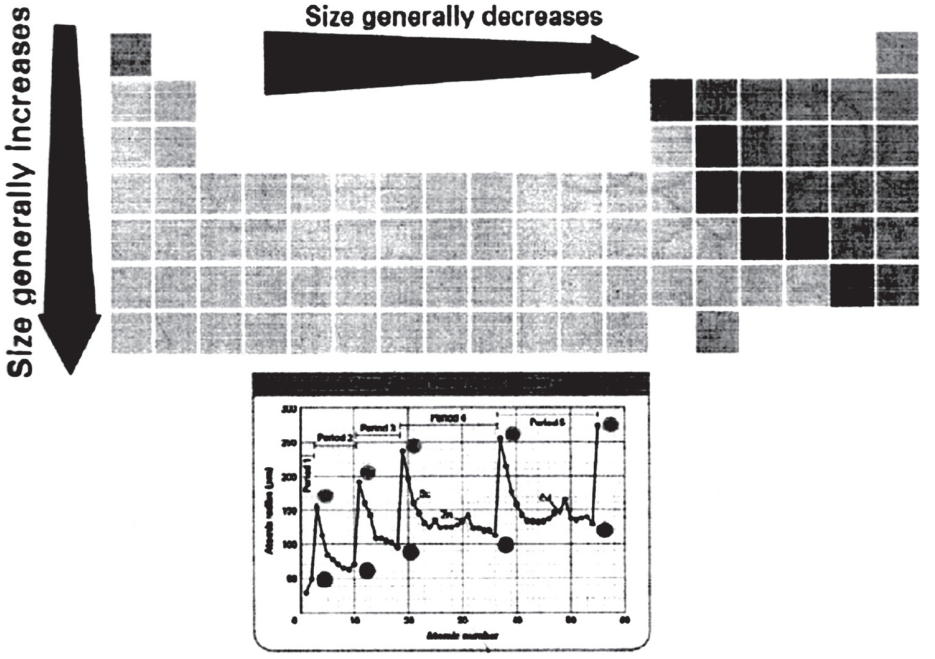


Fig. 2 : Periodic trend of atomic size

As a general rule, the radius of an atom will increase down and to the left in the periodic table. The radius of an atom depends on its electron probability. Across a period, the principal quantum number remains essentially the same, whereas the effective nuclear charge is increasing as more and more protons are added to the nucleus. This larger value of Z_{eff} exerts a stronger pull on the electrons, shrinking the atomic radius. Down a column or group in the periodic table, Z_{eff} varies only slightly, while n is increasing. As n increases, the outer-most electron will be added to an orbital having a larger average radial probability. Thus, the atomic radius increases down a column.

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3.5.1. ***Vander Waals radii :*** The *vander Waals radius,* is defined as the half-distance between the nuclei of two atoms of neighboring molecules (Figure 3), more specifically, it is the shortest distance to which two non bonded atoms can approach before repulsion between their electron clouds comes into action. In solid xenon, for

example, the measured inter atomic distance is 436 pm. The Vander Waals radius of xenon is thus estimated to be 218 pm. Steric effects between different parts of a molecule are governed mainly by this radius.

3.5.2. ***Covalent radii :*** The covalent radius of an element may by taken as half the inter nuclear distance between two atoms of the same element joined by a single bond. For elements forming single bonded units, the experimental inter nuclear distance may by halved to obtain the covalent radius (Fig.3).

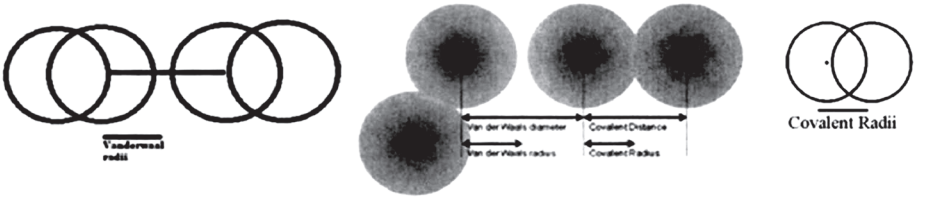


Fig.3: Atomic radii

8.4 Ionic Radii (Pauling's Univalent)

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The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals. Although from a wave-mechanical viewpoint, the radius of an individual ion has no precise physical significance, for purposes of descriptive crystallography, it is convenient to have a compilation of values obtained by partitioning measured interatomic distances in 'ionic' compounds. Values of the ionic radius (r_{ion}) may be derived from X-ray diffraction data. However, experimental data only give the internuclear distance and we generally take this to be the sum of the ionic radii of the cation and anion Internuclear distance between a cation and the closest anion in a lattice = $r_{catlon} + r_{anion}$ A positive ion is always smaller than the corresponding atom, and the more electrons which are removed. Metallic radius of Na is 1.86A , whereas Ionic radius of Na^+ is 1.02A. When a negative ion is formed, one or more electrons are added to an atom, the effective nuclear charge is reduced and hence the electron cloud expands. Negative ions are bigger than the corresponding atom. Covalent radius of Cl is 0. 99 A, whereas, Ionic radius of Cl^- is 1.84A.

Trends in ionic radii :

Irrespective of which set of ionic radii are used, the following trends are observed :

1. In the main groups, radii increase on descending the group, e.g. Li^+ = 0.76A, Na^+ = 1.02A, K^+ = 1.3 8 A, because extra shells of electrons are added.

2. The ionic radii decrease moving from left to right across any period in the periodic table, e.g. Na^+ = 1.02A, Mg^{2+} = 0.720Aand Al^{3+} = 0.535 A. This is partly due to the increased number of charges on the nucleus, and also to the increasing charge on the ions.

3. The ionic radius decreases as more electrons are ionized off, that is as the valency increases, e.g. Cr^{2+} = 0.80 , Cr^{3+} = 0.615 A, Cr^{4+} = 0.55 A, and Cr^{6+} = 0.44A.

4. The *d* and *f* orbitals do not shield the nuclear charge very effectively. Thus there is a significant reduction in the size of ions just after *10d* or 14f electrons have been filled in. The latter is called the lanthanide contraction, and results in the sizes of the second and third row transition elements being almost the same.

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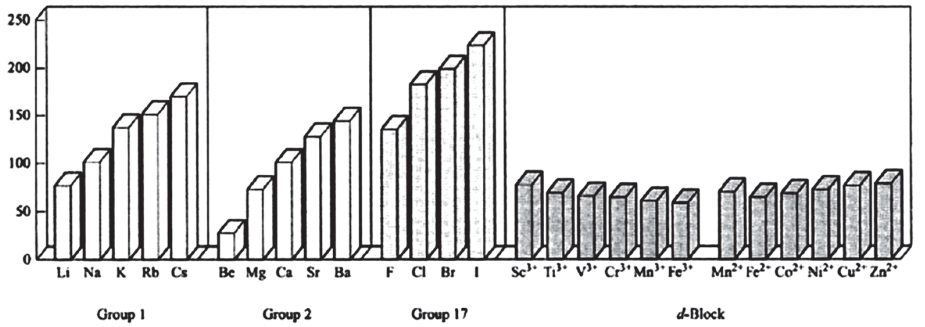


Fig.4 : Trends in ionic radii, r_{ion}, within the metal ions of groups 1 and 2, the anions of group 17, and metal ions from the first row of the d-block.

The right-hand side of Figure 4 illustrates the small variation in size for M^{3+} and M^{2+} ions of the d-block metals. As expected, the decrease in nuclear charge in going from Fe^{3+} to Fe^{2+}, and from Mn^{3+} to Mn^{2+}, causes an increase in r_{ion}. The cation size increases on descending groups 1 and 2, as does the anion size on descending group 17.

3.6.1. ***Pauling's method for determining univalent ionic radii :***

Pauling used a theoretical model to calculate ionic radii. Recognizing that there is an inverse relationship between the radius and the effective nuclear charge, Pauling set up the ratio in Equations, where r_0 is the inter ionic distance between the cation and anion. r_+ and r_-. are radius of cation and anion respectively. Z_{eff}^+ and Z_{eff}^- are effective nuclear charge of cation and anion respectively.

$$r_+ / r_- = Z_{eff}^- / Z_{eff}^+ \text{ and } r_0 = r_+ + r_-.$$

■ ***Question : calculate the univalent radii of Na^+ and F^- if the inter ionic distance in NaF is 231pm.***

Solution : Using Slater's rule we can find out $S_{Na^+} = S_{F^-} = 4.5$; Therefore $r_{Na^+}/r_{F^-} = (9 - 4.5)/ (11–4.5) = 4.5/ 6.5$; $r_{Na^+} + r_{F^-} = 231$,

Solving above two equations, we get $r_{Na^+} = 194$ pm and $r_{F^-} = 136$ pm

8.5 Covalent Radii

Covalent radii refer to the sizes of atoms as determined by the distances between the nuclei of atoms involved in covalent bonds. In a covalent bond, two atoms share electrons, and the distance between their nuclei is influenced by factors such as the size of the atoms and the number of electron pairs being shared. The covalent radius is often considered as half the distance between the nuclei of two identical atoms that are bonded together.

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Here are some key points about covalent radii:

Nature of Covalent Bonds:

- Covalent bonds form when atoms share electrons to achieve a more stable electron configuration.
- The distance between the nuclei of the two bonded atoms is determined by the balance between attractive forces (nucleus-electron and electron-electron) and repulsive forces (electron-electron and nucleus-nucleus).

Factors Influencing Covalent Radii:

- Atomic size: Larger atoms generally have larger covalent radii.
- Effective nuclear charge: The effective nuclear charge experienced by electrons also affects the covalent radius.
- Electron-electron repulsion: Repulsion between electrons in the valence shell can cause the covalent radius to increase.

Comparison with Metallic and Ionic Radii:

- Covalent radii are intermediate between metallic radii (for metallic bonds) and ionic radii (for ionic bonds).
- Metallic radii are larger than covalent radii because metallic bonds involve the sharing of electrons in a "sea" of delocalized electrons.
- Ionic radii are generally larger or smaller than covalent radii, depending on whether an atom gains or loses electrons to form ions.

Trends in the Periodic Table:

- Covalent radii exhibit trends across a period and down a group on the periodic table.
- Across a period, covalent radii generally decrease due to increased effective nuclear charge.

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- Down a group, covalent radii increase as you move to higher energy levels, leading to larger atomic sizes.

Applications:

- Understanding covalent radii is crucial in predicting the sizes of molecules and their geometries.
- It is used in molecular geometry predictions, which are essential in fields such as chemistry, biology, and materials science.

It's important to note that covalent radii are theoretical values and can vary depending on the method used to determine them. Different methods, such as X-ray diffraction or spectroscopy, can provide slightly different values for covalent radii.

8.6 Ionization Potential

The ionization energy is defined as the amount of energy required to remove an electron from an atom in the gas phase to a distance of infinity away from the uncleus. It is generally represented as I or IP (Ionization potential) or IE and is measured in electron volt or KJ/mole.

$$M(g) + E_1 \rightarrow M^+(g) + e$$

The first ionization energy for an atom is represented by E_1 and it is the one that removes the outer-most (or valence) electron from the electrostatic attraction of the uncleus. The second ionization energy is the additional amount of energy required to remove the second electron, and so on. Because it will always take energy to remove an electron, ionization energies are always positive.

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3.9.1. *Factors upon which IE depends :*

1. **Charge of the nucleus** : The greater the charge on the nucleus of an atom it will be more difficult to remove an electron from the atom and hence greater would be the value of ionization potential. Thus the value of ionization potential generally increases from left to right in a period and decreases along a group from top to bottom.
2. **Completely filled and half filled orbitals** : According to Hund's rule, atoms having half filled or completely filled orbitals, are comparatively more stable hence more energy required to remove an electron from the atom. The ionisation potential of such atoms is therefore relatively higher than expected normal value from their position in the periodic table.
3. **Atomic radius :** With increasing the atomic radius, IE decreases. This is because of the fact that in case of larger atoms the attraction between the nucleus and outermost electron is less an hence it is easier to remove.
4. **Principal quantum number :** Principal quantum number(n) determine the location of an electron from the nucleus. Higher the value of n the lower will be the IE.

3.9.2. Variation of Ionisation Energy in the periodic table :

In general Ionisatin energy increases along a period and reaches a maximum value in the noble gas with minor fluctuation. On moving across a group from top to bottom IE of the elements decreases.

3.9.3. Variation of IE along transition elements :

Variation of IE along a transition series is not so much because with increase in atomic number, elements enters successfully into the inner d orbital with little penetrating ability. The first IE involves the removal of the outermost s orbital electrons. So the first IE of the transition elements increases very slightly due to increase in the effective nuclear charge. As the variation is not so much prominent, so it may be considered that 1^{st} IE of the elements of a transition series remain almost constant. But on desending a group of transitin elements, there will be normal decrease in 1^{st} IE from 1^{st} to 2^{nd} elements, but increase of the third elements. The value increases due to the effect of lanthanide contraction.

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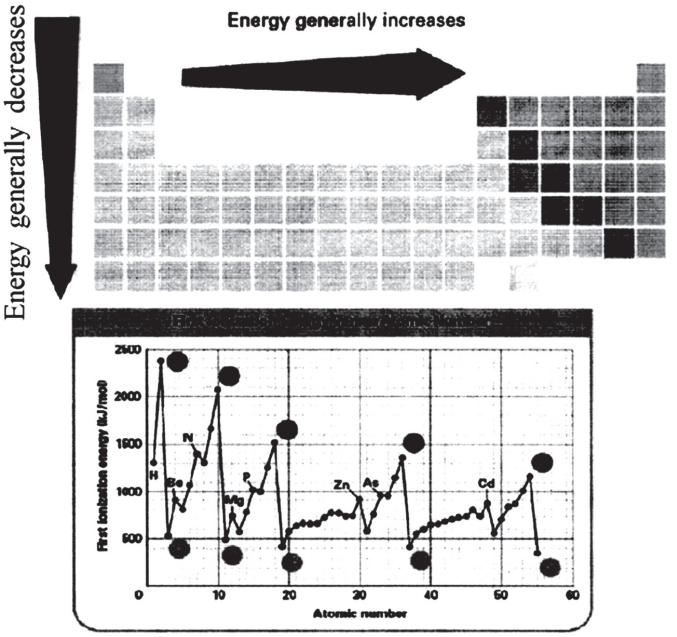


Fig.6 : Variation of Ionisation energies in the periodic table.

8.7 Electron Affinity

The amount of energy released when an electron is added to an isolated neutral gaseous atom in its lowest energy state (ground state) to produce an anion ia called its electron affinity. It is generally representd by EA or E and is measured in electron volt (ev) or K. Cal per gm atom. Thus the electron affinity can be defined by the following equation.

$$\underset{\text{Neutral gaseous atom}}{A(g)} + e \rightarrow \underset{\text{Anion}}{A^-(g)} + \text{Energy relased (EA)}$$

Since EA represents the energy released, it is represented with a negative sign. First EA represented by E_1 and it corresponds to the addition of one electron only. In the case of 2nd EA, electron is added to an anion against the electrostatic repulsion between the electron being added and the negative charge ion $A^-(g)$. Hence, the energy instead of being relased is supplied to A^- (g) to form $A^{2-}(g)$

3.10.1. Factors upon which EA depends :

1. Atomic Size
2. Effective nuclear charge
3. Screening effect by inner electrons.

In general E value decreases with the increasing atomic radius and increases with decreased screening effect by the inner electrons. Besides these factors E value also depends on the type of the orbitals into which the electron is added. When other factors remain constant, E value is the greatest for an electron entering an s orbital and decreases for p, d, and f orbitals.

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3.10.2. Variation of EA in the Periodic Table :

♦ **In a group :** In moving down a group EA values generally decrease due to the steady increase in the atomic radius of the elements.

♦ **In a period :** EA values generally increase on moving from left to right in a period in the periodic table.

Exceptions : Nitrogen and Phosphorus have unexpected lower values of EA. This is because of the presence of the half-filled 2p orbitals which are relatively more stable and hence it is very difficult to add an additional electron.

3.10.3. Difference between Electronegativity and Electron affinity

Sl.No.	Electronegativity	Electron affinity
1.	It refer to the attraction of the bonding electrons.	It refers to the attractin of the free electrons by an isolated gaseous atom.
2.	Only shifting of the bonding electrons towards the more electronegative atom occurs	Outright gain of the electrons occur
3.	The covalent bond becomes polar	Anion is formed
4.	It is the relative property of the atom	It is the inherent property of the atom

8.8 Electronegativity (Pauling's, Mulliken's and Allred-Rochow's Scales) and Factors Influencing these Properties

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Electronegativity is the ability of an atom in a molecule to attract the shared electrons closer to itself, as defined by Linus Pauling. Unlike most of the other periodic laws, such as radius, ionization energy, and E.A., electronegativity has no meaning outside the context of a chemical bond.

3.8.1. *Factors upon which Electronegativity depends* :

1. Valence state and oxidation state : Electronegativity increases with increasing + ve oxidation state and decreases with increasing -ve oxidation state.
2. Size of the atom : Electronegativity decreases with increasing the size of the atom and vice-versa.
3. Nature of hybridization : Electronegativity increases with increase the s character of the hybrid orbital i, e, $sp > sp^2 > sp^3$

3.8.2. *Variation of electronegativity in the periodic table* :

■ ***In a period :*** Electronegativity increases on moving a period in the periodic table from left to right. This is due to increase in nuclear charge as a result of which the added electrons can be held more tightly.

■ ***In a group :*** On moving down through a group of the periodic table, the size of the elements gradually increases. Since small atoms attract the electron more strongly than large ones and therefore more electronegative. Consequently a lower element of a group is less electronegative than upper elements.

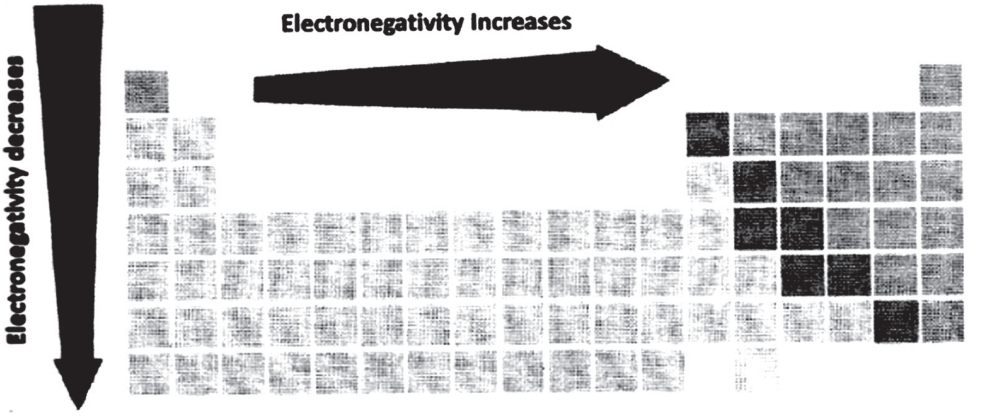


Fig. 5 : Periodic trend of electronegativity

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The absolute magnitude of the electronegativity vales of an element is however not fixed , different values may be assigned to the same element from different theoretical approaches i,e different electronegativity scale.

3.8.3. *Pauling scale of Electronegativity* :

The Pauling scale of electronegativity was developed in 1932 and is still the most widely used. Let us consider two covalent molecules A-A & B-B. It is generally observed that rections of the type A-A + B-B - $\rightarrow$ A-B + A-B are almost always exothermic and bond A-B is thus more stable than A-A or B-B bonds. The extra stability was derived from unequal sharing of bonding electrons between A & B giving rise to some ionic character. Bond stabilities are measured in terms of bond energy so, we may express the extra stability of the bond A-B in the following way,

$\Delta = E_{A-B}$ – Energy of 100% covalent bond; where E_{A-B} is the observed bond energy of A–B. Pauling suggested that Δ is related to the difference of electronegativity between A & B ($\chi_A - \chi_B$) by the relation $\chi_A - \chi_B = 0.208\sqrt{\Delta}$; where Δ is expressed in Kcal/mol. The energy of 100% covalent bond is $E_{100\%covalent} = \sqrt{(E_{A-A}\ E_{B-B})}$

Finally we have = $0.208\sqrt{\{E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}\}}$.....1

(Converting the equation to SI units gives $0.1017\sqrt{\Delta}$, where Δ is measured in kJ/mol).....(2)

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Pauling next arbitrarily assumed $\chi_H = 2.1$ as a standard and framed his electronegativity scale. In this scale F is the most electronegative with a value of 4.0

■ ***Question : Calculate the electronegativity of Cl given that the bond dissociation energies for Cl_2, F_2, and ClFare 242, 158, and 255 kJ/mol, respectively.***

Solution. according to Pauling scale, $\Delta = 255 - \sqrt{(242 \times 158)}$

$= 59.45$ kJ/mol

The difference in electronegativity between F and Cl can be calculated from Equation 2 :

$$\chi_F - \chi_{Cl} = 0.101\sqrt{59.45} = 0.77 \text{ kJ/mol}$$

3.8.4. *Mulliken's scale of electronegativity* (χ_M) :

The Mulliken-Jaffe scale defines electronegativity on the basis of atomic parameters, namely the average of the valence ionization energy and E.A., as shown in Equation 3. The *v* subscripts indicate that the valence configuration must be used. Thus, for example, boron forms three equivalent bonds by hybridizing its valence 2*s* and 2p orbitals to make sp^2 hybrid orbitals. The theoretical ionization energy and

E.A. for the sp^2 hybrid orbitals must be used in Equation 2 in place of those for an unhybridized 2*p* orbital. Hence, the original Pauling definition of electronegativity as a property of an atom within a molecule still rings true. Mulliken-Jaffe electronegativities are typically expressed in units of electron volts. However, the Pauling scale has been so firmly entrenched that more often than not the Mulliken-Jaffe scale is converted to the Pauling scale through a simple conversion factor. One advantage of the Mulliken-Jaffe scale is that it correctly predicts the periodic trend for electronegativity. Because the periodic trends for both first ionization energy and E.A. increase up and to the right in the periodic table, the average of these two values should also follow this trend. Indeed, the periodic trend for electronegativity is that it increases toward the upper right-hand corner of the periodic table. When comparing the electronegativities of the elements, there is a very clear demarcation line between the metals and the nonmetals. The metals have only a small difference in energy between their s and *p* orbitals, whereas the nonmetals have a much larger gap. Electronegativity in Mulliken scale (χ_M) can be extressed in the following way, $\chi_M = (I.E + E.A.)/2$; .....(3) hvhere IE & EA are the lonisation energy and Elcetron affinity respectively. χm may be related with Pauling electronegativity value (χ_P) through a relation, $\chi_P = 1.35\sqrt{\chi_M} - 1.37$

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densities of the two nearest noble gas atoms. Sanderson is also responsible for the concept of electronegativity equalization. When two or more atoms having different initial electronegativities combine to make a bond, they adjust to have the same intermediate electronegativity in the molecule. The electronegativities of ions and of groups of atoms, such as CF_3, NH_2, or COOH, have also been calculated using the

3.8.5. *Allred-Rochow electronegativity values,* (χ_{AR}) :

Allred and Rochow chose as a measure of electronegativity of an atom the electrostatic force exerted by the effective nuclear charge Z_{eff} (estimated from Slater's rules) on the valence electrons. Allred-Rochow electronegativity can be calculated by the following way,

$\chi_{AR} = (0.359 \times Z_{eff})/ r_{cov}^2 + 0.744$ (when r_{cov} is measured in Angstrom)

$xar = (3590 \times Z_{eff})/ r_{cov}^2 + 0.744$ (when r_{cov} is measured in pm)

However, Slater's rules are partly empirical and covalent radii are unavailable for some elements, the Allred-Rochow scale is no more rigid or complete than the Pauling one. The Allred-Rochow scale is based on the electrostatic force exerted by the nucleus on the valence electrons, whereas the Sanderson scale represents a ratio of the experimental electron density to that predicted by interpolation of the electron densities of the two nearest noble gas atoms. Sanderson is also responsible for the concept of electronegativity equalization. When two or more atoms having different initial electronegativities combine to make a bond, they adjust to have the same intermediate electronegativity in the molecule. The electronegativities of ions and of groups of atoms, such as CF_3, NH_2, or COOH, have also been calculated using the principle of A electronegativity neutrality. For example, the group electronegativity of CF_3 (3.47) is greater than that of CH_3 (2.31) as a result of the inductive effect of the F atoms. Likewise, the calculated group electronegativity of the electron

withdrawing group '-COOH' (3.04) is greater than that of the electron-donating group '-NH_2' (2.47)

Table-1

Element	x (Pauling)	Xmi (Mulliken)	Xspec (Allen)
H	2.20	2.25(*s*)	2.30
Li	0.98	0.97(*s*)	0.91
Be	1.57	1.54 (*sp*)	1.58
B	2.04	2.04 (sp^2)	2.05
C	2.55	2.48	2.54
N	3.04	3.04	3.07
O	3.44	3.68	3.61
F	3.98	3.91 (14% *s*)	4.19
Na	0.93	0.91 (*s*)	0.87
Mg	1.31	1.37 (*sp*)	1.29
Al	1.61	1.83 (sp^2)	1.61
Si	1.90	2.28	1.92
P	2.19	2.41	2.25
S	2.58	2.86	2.59
Cl	3.16	3.10 (14% *s*)	2.87
K	0.82	0.73 (s)	0.73
Ca	1.00	1.08 (*sp*)	1.03
Ga	1.81	2.01 (sp^2)	1.76
Ge	2.01	2.33	1.99
As	2.18	2.38	2.21
Se	2.55	2.79	2.42
Br	2.96	2.95 (14% *s*)	2.68
Kr	3.00	3.31	2.97
Rb	0.82	0.82 (*s*)	0.71
Sr	0.95	1.00 (*sp*)	0.96
In	1.78	1.76 (sp^2)	1.66
Sn	1.96	2.21	1.82
Sb	2.05	2.22	1.98
Te	2.10	2.57	2.16
I	2.66	2.95	2.36
Xe	2.60	3.01	2.58

Table 1 : Electronegativities of selected elements using the revised Pauling scale the Mulliken– Jaffe scale, and Allen's spectroscopic configuration energies. The

latter scales have been converted to the revised Pauling scale. The Mulliken–Jaffe values are listed for the *sp*3 valence hybridization, unless otherwise indicated.

■ ***Question : Calculate the electronegativity of bromine in the AR scale (r_{cov} = 114 pm)***

Solution : *Z_{eff} is calculated by taking into account the screening by all electrons* [Br = $(1s)^2(2s2p)^8(3s3p3d)^{18}(4s4p)^7$]; Z_{eff} = 35-[0.35×7+0.85×18+1×10]=7.25; χ_{AR} = $(3590\times7.25)/114^2+0.744$ = 2.75

3.8.6. *Grou Electronegativity* :

The overall effect of charge, substituents, hybridization of the bonding orbitals, etc. of a group on electronegativity may be summarily expressed in terms of its group electronegativity. The following table represents the electronegativity of some groups according to the Pauling scale.

Group	Electronegativity
$-CH_3$	2.34
$-CF_3$	3.35
$-CCl_3$	3.03
-COOH	2.8-3.5
$-NO_2$	3.4
C_6H_5	3

Table : 2 Group Electronegativity values of few groups

The values of Electronegativity of methyl group suggests that it should be slightly more electronegative than hydrogen. Yet the methyl group behaves as a better donor of Electron density presumably because of its larger size which makes it more easily polarizable.

3.8.7. *Electronegativity; final remarks :*

Despite the somewhat dubious scientific basis of these methods described above, the trends in electronegativities obtained by them are roughly in agreement as Figure 3 exemplifies. The most useful of the scales for application in inorganic chemistry is probably the Pauling scale which, being based empirically on thermochemical data, can reasobably be used to predict similar data. For example, if the electronegativities of two elements X and Y have been derived from the single

covalent bond enthalpies of HX, HY, X_2, Y_2 and H_2, we can estimate the bond dissociation enthalpy of the bond in XY with a fair degree of reliability.

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8.9 Inert Pair Effect

it costs these elements relatively more energy to achieve a higher oxidation state than their lighter group congeners. At the same time, less energy is gained as a result of bond formation because they also exhibit lower-than-predicted bond dissociation enthalpies.Weaker bond enthalpies are expected for the heavier elements as a result of the diffuse nature of orbital overlap with increasing orbital size. The larger-than-expected ionization energies for the post-transition series Group IIIA elements result from the fact that the valence s electrons are not shielded from the nucleus very effectively by the intervening d electrons. As the two s electrons are both held tighter by the nucleus in the post-transition series elements, the ionization energies for these two electrons are unusually large. The end result is that these elements prefer oxidation states that are two lower than their typical group valence. Relativistic effects, which are discussed in the above section, also contribute to the higher-than-expected ionization energies of the valence s electrons.

One of the more unusual periodic trends is known as the inert-pair effect. The elements that immediately follow the 4d and 5d transition series are considerably less reactive than their group properties might have predicted and they also prefer oxidation states that are two lower than the usual group valence. Consider, for example, the Group IIIA elements. The lighter elements, B, Al, and Ga take only the 3+ oxidation state predicted by their group valence. However, the heavier elements, In and Tl, take both the 3+ and 1+ oxidation states. The same trend is observed for the Group IVA elements. Again, the lighter elements C, Si, and Ge take the 4+ valence predicted by their period. However, Sn and Pb can exist in either the 4+ or the 2+ oxidation state. The relative stability of the lower oxidation states for the fifth and sixth series post-transition elements (In, Sn, Sb, Tl, Pb, Bi, and Po) has been attributed to the higher-than-expected ionization energies for these seven elements. Consequently,

8.10 Group trends and periodic trends in these properties in respect of s-, p- and d-block elements

s-block Elements

The s-block elements, located in groups 1 and 2 of the periodic table, exhibit certain trends in their physical properties. Here, we'll explore the group trends (vertical columns) and periodic trends (horizontal rows) in electronegativity, electron affinity, and ionization potential for s-block elements.

Electronegativity:

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Group Trend (Vertical):

- Electronegativity tends to decrease down a group in the s-block.
- This is because, as you move down a group, the outermost electrons are farther from the nucleus and are shielded by inner electron shells. As a result, there is less effective nuclear charge acting on the outer electrons, making it easier for them to be lost.

Periodic Trend (Horizontal):

- Electronegativity generally increases from left to right across a period in the s-block.
- This is due to the increasing effective nuclear charge as electrons are added to the same energy level. The stronger pull from the nucleus makes it more difficult for atoms to lose electrons.

Electron Affinity:

Group Trend (Vertical):

- Electron affinity generally decreases down a group in the s-block.
- As you move down, the atomic size increases, and electrons are farther from the nucleus. Therefore, the attraction for additional electrons decreases.

Periodic Trend (Horizontal):

- Electron affinity tends to increase from left to right across a period in the s-block.
- As you move across a period, the atomic size decreases, and electrons are added to the same energy level. This results in a stronger attraction between the electrons and the nucleus, making it more favorable for an atom to accept an additional electron.

Ionization Potential:

Group Trend (Vertical):

- Ionization potential (energy required to remove an electron) generally decreases down a group in the s-block.

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- As you move down, electrons are located in higher energy levels and are farther from the nucleus. The outer electrons experience less effective nuclear charge, making it easier to remove them.

Periodic Trend (Horizontal):

- Ionization potential tends to increase from left to right across a period in the s-block.
- As you move across a period, electrons are added to the same energy level, but the increasing effective nuclear charge makes it more difficult to remove electrons. Therefore, ionization potential generally increases across a period.

In summary, the s-block elements exhibit systematic trends in electronegativity, electron affinity, and ionization potential based on their position in the periodic table. Understanding these trends provides valuable insights into the behavior of these elements in chemical reactions.

8.11 Summary

Atomic Radii: Atomic radius is the measure of the size of an atom, typically defined as the distance from the nucleus to the outermost electron cloud. Atomic radii increase down a group due to the addition of electron shells and decrease across a period due to increased effective nuclear charge.

Ionic Radii (Pauling's Univalent): Ionic radius refers to the size of ions, and Pauling's scale is commonly used for monovalent ions. Cations are smaller than their parent atoms, while anions are larger. Ionic radii trends follow atomic size trends, with cations decreasing and anions increasing across a period and the opposite down a group.

Covalent Radii: Covalent radius is a measure of the size of atoms in covalent compounds. It is half the distance between the nuclei of two identical atoms when they are joined by a covalent bond. Covalent radii follow similar trends as atomic radii.

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Ionization Potential: Ionization potential is the energy required to remove an electron from an atom or a positive ion. It generally increases across a period and decreases down a group due to the shielding effect of inner electrons.

Electron Affinity: Electron affinity is the energy change associated with gaining an electron. Trends in electron affinity are not as regular as ionization potential. Generally, electron affinity increases across a period and decreases down a group.

Electronegativity (Pauling's, Mulliken's, and Allred-Rochow's scales): Electronegativity is a measure of an atom's ability to attract and hold electrons in a chemical bond. Different scales, such as Pauling's, Mulliken's, and Allred-Rochow's, provide slightly different values. Electronegativity generally increases across a period and decreases down a group.

Factors Influencing Properties: Factors influencing these properties include effective nuclear charge, electron-electron repulsion, distance from the nucleus, and shielding effect. Effective nuclear charge is crucial in determining ionization potential, electron affinity, and electronegativity.

Inert Pair Effect: The inert pair effect refers to the reluctance of heavier elements, particularly in the p-block, to participate in chemical reactions due to the stability of s electrons over p electrons. This effect is more prominent in lower oxidation states.

Group and Periodic Trends:

- Atomic Radii: Increase down a group, decrease across a period.
- Ionization Potential: Increase across a period, decrease down a group.
- Electron Affinity: Increase across a period, decrease down a group.
- Electronegativity: Increase across a period, decrease down a group.

These trends vary within s-, p-, and d-block elements due to differences in electron configurations and subshell filling. Transition metals, in particular, exhibit unique behavior due to their partially filled d-subshells.

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8.12 Model Questions

A. Multiple Choice Type Questions

1. What is the trend of atomic radii across a period in the periodic table?
    a. Increase
    b. Decrease
    c. Remain constant
    d. No specific trend
2. Which scale is commonly used for monovalent ions in determining ionic radii?
    a. Bohr's scale
    b. Pauling's scale
    c. Thomson's scale
    d. Rutherford's scale
3. What is the inert pair effect related to?
    a. Ionization potential
    b. Electron affinity
    c. Reactivity of heavier elements
    d. Atomic radius
4. What is the electron affinity trend down a group in the periodic table?
    a. Increase

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b. Decrease

c. Remain constant

d. No specific trend

5. Which property is measured as the energy required to remove an electron from an atom or a positive ion?

a. Atomic radius

b. Ionization potential

c. Electron affinity

d. Electronegativity

6. Which electron scale considers the average position of an electron in a multi-electron atom?

a. Pauling's scale

b. Mulliken's scale

c. Allred-Rochow's scale

d. Bohr's scale

7. What is the covalent radius defined as?

a. Distance between nuclei of two identical ions

b. Distance between nuclei of two identical atoms in a covalent bond

c. Distance between an atom and its outermost electron cloud

d. Distance between cations and anions

8. Which trend is observed for electronegativity across a period in the periodic table?

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a. Increase

b. Decrease

c. Remain constant

d. No specific trend

9. What factor contributes to the decrease in ionization potential down a group?

a. Increased effective nuclear charge

b. Decreased electron-electron repulsion

c. Increased shielding effect

d. Decreased distance from the nucleus

10. In which group of elements is the inert pair effect commonly observed?

a. Alkali metals

b. Halogens

c. Transition metals

d. Noble gases

B. Short Type Questions

1. Define atomic radius and explain how it changes across a period in the periodic table.
2. What is the inert pair effect, and how does it influence the reactivity of heavier elements?
3. Briefly describe Pauling's scale and its significance in determining electronegativity.

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4. What is the covalent radius, and how does it differ from atomic radius?
5. Explain the trend of ionization potential across a period and down a group.
6. How does electron affinity vary across a period in the periodic table?
7. What is the effective nuclear charge, and how does it impact ionization potential?
8. Differentiate between cations and anions in terms of ionic radii.
9. Describe the factors that influence the properties of atoms, such as ionization potential and electronegativity.
10. Discuss the significance of the shielding effect in determining atomic properties.

C. Assay Type Questions

1. Explain the concept of atomic radius. How does it change as you move across a period and down a group in the periodic table?
2. Discuss the inert pair effect. How does it manifest in the behavior of heavier elements, and what implications does it have for their chemical reactivity?
3. Elaborate on Pauling's scale for electronegativity. How is it determined, and what are its applications in understanding chemical bonding?
4. Define covalent radius and compare it with atomic radius. How are covalent radii useful in understanding the size of atoms in covalent compounds?

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5. Explore the trends of ionization potential across periods and down groups in the periodic table. What factors contribute to these trends?
6. Examine the variations in electron affinity across the periodic table. How is electron affinity related to the stability of atoms?
7. Define effective nuclear charge. How does it impact the ionization potential of an atom, and what role does it play in periodic trends?
8. Compare and contrast ionic radii of cations and anions. How do they change across a period and down a group?
9. Discuss the factors that influence atomic properties such as ionization potential, electron affinity, and electronegativity. Provide examples to illustrate these influences.
10. Examine the significance of the shielding effect in the determination of atomic properties. How does the presence of inner electrons affect the behavior of outer electrons in an atom?

8.13 Further Reading

1. "The Periodic Table: A Visual Guide to the Elements" by Paul Parsons, ISBN-13: 978-1623651107
2. "The Disappearing Spoon: And Other True Tales of Madness, Love, and the History of the World from the Periodic Table of the Elements" by Sam Kean,
3. ISBN-13: 978-0316051644
4. "The Elements: A Visual Exploration of Every Known Atom in the Universe" by Theodore Gray, ISBN-13: 978-1579128951

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5. "The Periodic Table: Its Story and Its Significance" by Eric R. Scerri, ISBN-13: 978-0195305739
6. "Nature's Building Blocks: An A-Z Guide to the Elements" by John Emsley, ISBN-13: 978-0199605637
7. "The Periodic Table: Elements with Style!" by Simon Basher, ISBN-13: 978-0753460854
8. "Chemistry: The Central Science" by Theodore L. Brown, H. Eugene LeMay, and Bruce E. Bursten, ISBN-13: 978-0321910417
9. "The Periodic Table: A Field Guide to the Elements" by Paul Parsons and Gail Dixon, ISBN-13: 978-1623654504
10. "Periodic Tales: A Cultural History of the Elements, from Arsenic to Zinc" by Hugh Aldersey-Williams, ISBN-13: 978-0061824722
11. "Molecules: The Elements and the Architecture of Everything" by Theodore Gray, ISBN-13: 978-0316480581

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Unit 9: Chemistry of s-block elements: Li-Na-K, Be-Mg-Ca-Sr-Ba

Contents

9.1 Objectives
9.2 Introduction
9.3 Li-Na-K
- 9.3.1 General Chemistry of Li
- 9.3.2 Some Important Properties of Li
- 9.3.3 General Chemistry of Na
- 9.3.4 General Chemistry of K
- 9.3.5 Comparative Properties of Li. Na And K
- 9.3.6 Detail Chemical Properties of Li, Na And K
- 9.3.7 Some Important Compounds of Sodium
- 9.3.8 Important Term: Diagonal Relationship
- 9.3.9 Comparative Anomalous Behaviours of Li, Na & K

9.4 Be-Mg-Ca-Sr-Ba
- 9.4.1 Introduction
- 9.4.2 Physical Properties
- 9.4.3 Chemical Properties
- 9.4.4 Behaviour of Beryllium Different from Other Alkaline Earth Metals
- 9.4.5 Important Compounds

9.5 Summary
9.6 Model Questions
9.7 Further Reading

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9.1 Objectives

- Provide an overview of the S-block elements with a focus on the alkali metals (Li, Na, K) and alkaline earth metals (Be, Mg, Ca, Sr, Ba).
- Explore their general properties, electronic configurations, and their significance in the periodic table.
- Examine the electronic structure of s-block elements, emphasizing the trends in atomic and ionic sizes, ionization energies, and electron affinities.
- Explore the bonding characteristics, including the formation of metallic bonds and ionic compounds, to understand the chemical behavior of these elements.
- Investigate the reactivity patterns of alkali metals, focusing on lithium (Li), sodium (Na), and potassium (K).
- Analyze their reactions with water, oxygen, and other common substances, and understand the underlying principles that govern their chemical behavior.
- Explore the reactivity patterns of alkaline earth metals, including beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba).
- Examine their reactions with various elements and compounds, highlighting trends in reactivity and the factors influencing their chemical behavior.
- Investigate the practical applications of s-block elements in various industries and daily life.

9.2 Introduction

The s-block elements represent the first two groups of the periodic table, specifically Group 1 (alkali metals) and Group 2 (alkaline earth metals). These elements are characterized by the filling of their outermost electron shell, which consists of the s orbitals. As we move down the

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periodic table within these groups, the elements exhibit distinct trends in their physical and chemical properties.

The alkali metals in Group 1, including lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr), are highly reactive metals with a single electron in their outermost s orbital. This lone electron imparts unique chemical reactivity, leading to the alkali metals' tendency to readily form ionic compounds and react vigorously with water.

On the other hand, the alkaline earth metals in Group 2, such as beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra), also possess distinct characteristics. They have two electrons in their outer s orbital, making them less reactive than alkali metals but still quite reactive compared to other elements. Alkaline earth metals commonly form ionic compounds and are essential constituents of various minerals.

Understanding the properties and behaviours of s-block elements is crucial in elucidating the principles governing chemical reactivity and the formation of compounds. Their applications extend across diverse fields, including metallurgy, medicine, and everyday materials. This introduction sets the stage for a comprehensive exploration of the fascinating world of s-block elements.

9.3.1 General chemistry of Li

Lithium (Li) is a chemical element that belongs to Group 1 (alkali metals) in the periodic table. Here are some details about the chemistry of lithium:

1. Atomic and Physical Properties:

Atomic Number: 3

Atomic Mass: 6.94 u

Electron Configuration: [He] $2s^1$

Density: 0.534 g/cm³ (at 20°C)

Melting Point: 180.5°C

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Boiling Point: 1,342°C

2. Reactivity:

Lithium is the least dense and lightest metal in the alkali metal group.

It is highly reactive due to its single valence electron in the 2s orbital, which it readily loses to achieve a stable electron configuration.

Lithium's reactivity with water is less vigorous compared to sodium and potassium, but it still produces hydrogen gas and lithium hydroxide:

$2Li+2H_2O \rightarrow 2LiOH+H_2$

$2Li(s)+2H_2O(l) \rightarrow 2LiOH(aq)+H_2(g)$

3. Compounds:

Lithium Oxide (Li_2O): Formed by the reaction of lithium with oxygen.

$4Li(s)+O2(g) \rightarrow 2Li_2O(s)$

Lithium Hydroxide (LiOH): Formed in the reaction of lithium with water.

$Li(s)+H_2O(l) \rightarrow LiOH(aq)+H_2(g)$

Lithium Carbonate (Li_2CO_3): A stable lithium compound used in the production of lithium chemicals and as a medication for certain psychiatric conditions.

$LiOH(aq)+CO_2(g) \rightarrow Li_2CO_3(s)+H_2O(l)$

4. Applications:

Lithium and its compounds find extensive use in various industries and technologies.

Lithium-ion batteries: Lithium is a crucial component in rechargeable batteries used in electronic devices, electric vehicles, and renewable energy storage systems.

Pharmaceuticals: Lithium carbonate is used in the treatment of bipolar disorder and certain mental health conditions.

While lithium is not considered an essential element for humans, some studies suggest that low doses of lithium may have neuroprotective and mood-stabilizing effects.

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Lithium's unique combination of properties, including its low density, high reactivity, and versatile compounds, makes it a valuable element in both technological and medical applications. The increasing demand for lithium, particularly in the context of battery technologies, has led to a growing interest in lithium extraction and processing methods.

9.3.2 Some important properties of Li

(i) Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.

(ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air, it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals. (iii) LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates (iv) Lithium hydrogen carbonate is not obtained in the solid form while all other elements form solid hydrogen carbonates. (v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne. (vi) Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give

Corresponding nitrite.

$$4\,LiNO_3 \rightarrow 2\,Li_2O + 4\,NO_2 + O_2$$

$$2\,NaNO_3 \rightarrow 2\,NaNO_2 + O_2$$

(vii) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

9.3.3 General Chemistry of Na

Sodium, symbolized as Na on the periodic table, is a chemical element with the atomic number 11. Here, we'll discuss some key aspects of the general chemistry of sodium.

1. Atomic Structure:

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Sodium has an atomic number of 11, indicating that it has 11 protons in its nucleus. It belongs to Group 1 (alkali metals) in the periodic table.

Its electronic configuration is [Ne] $3s^1$, which means it has one valence electron in its outermost electron shell.

2. Physical Properties:

Sodium is a soft, silvery-white, highly reactive metal at standard conditions.

It has a melting point of 97.79 degrees Celsius (208.02 degrees Fahrenheit) and a boiling point of 882.9 degrees Celsius (1621.22 degrees Fahrenheit).

3. **Chemical Properties:**

Sodium is highly reactive and tends to lose its lone valence electron to achieve a stable electron configuration.

It readily reacts with water, producing sodium hydroxide and hydrogen gas:

$2Na + 2H2O \rightarrow 2NaOH + H2$

$2Na+2H2O \rightarrow 2NaOH+H2.$

Sodium reacts vigorously with oxygen, forming sodium oxide ($2Na + O2 \rightarrow 2Na2O$)

It forms various compounds with other elements due to its reactivity.

4. Common Compounds:

Sodium Chloride (NaCl): Commonly known as table salt, it is a crucial compound for biological processes and is widely used in food preparation.

Sodium Hydroxide (NaOH): A strong base, also known as caustic soda, used in industries for cleaning and as a chemical reagent.

Sodium Bicarbonate ($NaHCO_3$): Also known as baking soda, it is used in cooking, cleaning, and as a leavening agent.

5. Occurrence:

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Sodium is not found in its elemental form in nature due to its high reactivity. Instead, it is commonly found as various salts, especially sodium chloride (table salt).

6. Importance in Biology:

Sodium is an essential element for living organisms. It plays a crucial role in nerve impulse transmission, muscle contraction, and the balance of fluids in and around cells.

7. Commercial Production:

Sodium is commercially produced by the electrolysis of molten sodium chloride (Downs process).

8. Isotopes:

Sodium has several isotopes, but only one is stable and naturally occurring, which is ^{23}Na.

In summary, sodium is a highly reactive alkali metal with important roles in both chemistry and biology. Its compounds are widely used in various industries and have significant biological functions.

9.3.4 General Chemistry of Potassium (K)

Potassium (K) is a chemical element with the symbol K and atomic number 19. It belongs to the alkali metal group, which is located in Group 1 of the periodic table. Here are some general aspects of the chemistry of potassium:

1. **Atomic Structure:**
    - Atomic Number: 19
    - Atomic Mass: 39.10 g/mol
    - Electronic Configuration: [Ar] $4s^1$
2. **Physical Properties:**
    - Potassium is a soft, silvery-white metal that is highly reactive.
    - It has a low density and melts at a relatively low temperature.

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- It is a good conductor of electricity.

3. **Chemical Properties:**
   - **Reactivity:** Potassium is highly reactive due to its position in Group 1 of the periodic table. It readily reacts with water, oxygen, and many other substances.
   - **Water Reaction:** When exposed to water, potassium reacts vigorously, producing hydrogen gas and forming potassium hydroxide (KOH).

     $2K+2H_2O \rightarrow 2KOH+H_2$

     $2K(s)+2H_2O(l) \rightarrow 2KOH(aq)+H_2(g)$
   - **Oxidation States:** Potassium typically exhibits an oxidation state of +1 in its compounds.
4. **Compounds:**
   - **Potassium Chloride (KCl):** This is a common salt and is often used in fertilizers and as a seasoning in food.
   - **Potassium Hydroxide (KOH):** A strong base, it is used in the production of soap and detergents.
   - **Potassium Nitrate (KNO_3):** This salt is used in fertilizers and fireworks.
   - **Potassium Carbonate (K_2CO_3):** It is used in the production of glass and soap.
5. **Biological Importance:**
   - Potassium ions are essential for various biological processes, including nerve function and muscle contraction.
   - Adequate potassium intake is important for maintaining electrolyte balance in the body.
6. **Flame Test:**
   - Potassium ions can be identified by the characteristic lilac or light purple flame color they produce when burned.

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Overall, potassium plays a crucial role in various chemical and biological processes, and its compounds have widespread applications in industry and everyday life.

9.3.5 Comparative Properties of Li. Na and K

1. Atomic Radius:
   - Increases down the group, so K > Na > Li.
2. Density:
   - Density of Na is more than that of K. Density order is: Li < K < Na
3. Reactivity:
   - Increases down the group, so K is more reactive than Na, which is more reactive than Li.
   - All three metals are highly reactive and readily form compounds with oxygen and water.
4. Melting point and Boiling Point:
   Their melting and boiling points are low due to weak metallic bonds. Strength of metallic bond decreases in the group from Li to K, due to which hardness from Li to K.
   Li > Na > K
5. Reaction with Water:
   - Li reacts slowly with water, Na reacts more vigorously, and K reacts even more violently.
6. Oxidation States:
   - They typically exhibit an oxidation state of +1 in compounds.
   - Li can also exhibit an oxidation state of -1 in certain compounds.
7. Hydration Energy: Hydration energy decreases on going downwards in the group, due to increase in the size of metal ion. Li > Na > K
   Lithium gets more hydrated due to high hydration energy of Li^+ and the charge present on it gets protected.
   Thus, Hydration energy $\propto$ 1/ Ionic size
8. Flame Test:
   - They all impart characteristic colors to flames: Li (red), Na (yellow), K (violet).
9. Halides (LiX, NaX, KX):
   - All form ionic halides (LiCl, NaCl, KCl) that are soluble in water.
10. Oxides (Li_2O, Na_2O, K_2O):
    - All form oxides that are basic in nature.
11. Hydroxides (LiOH, NaOH, KOH):
    - All form strongly alkaline hydroxides, with increasing solubility down the group.
12. Biological Importance:

Lithium: Used in the treatment of bipolar disorder.
Sodium and Potassium: Essential for nerve function, muscle contraction, and electrolyte balance in the body.

13. Industrial Applications:
    Lithium:

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- Used in batteries, especially lithium-ion batteries.

Sodium:

- Used in the production of various chemicals and as a coolant in nuclear reactors.

Potassium:

- Used in fertilizers and as a nutrient in plant growth.

14. Occurrence:

Lithium:

- Relatively rare and is usually found in pegmatite ores.

Sodium:

- Abundant in nature, especially in salt deposits (NaCl).

Potassium:

- Common in minerals like sylvite and carnallite.

Atomic and Physical Properties of Li, Na and K

Property	Lithium Li	Sodium Na	Potassium K
Atomic number	3	11	19
Atomic mass (g mol^{-1})	6.94	22.99	39.10
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$
Ionization enthalpy / kJ mol^{-1}	520	496	419
Hydration enthalpy/kJ mol^{-1}	−506	−406	−330
Metallic radius / pm	152	186	227
Ionic radius M^+ / pm	76	102	138
m.p. / K	454	371	336
b.p / K	1615	1156	1032
Density / g cm^{-3}	0.53	0.97	0.86
Standard potentials $E^{\ominus}$ / V for (M^+ / M)	−3.04	−2.714	−2.925
Occurrence in lithosphere†	18*	2.27**	1.84**

**ppm (part per million), ** percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle*

9.3.6 Detail Chemical Properties of Li, Na and K

Reducing nature:

The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful. The standard electrode potential (E^0) which measures the reducing power represents the overall change:

$$M(s) \rightarrow M(g) \quad \text{sublimation enthalpy}$$
$$M(g) \rightarrow M^+(g) + e^- \quad \text{ionization enthalpy}$$
$$M^+(g) + H_2O \rightarrow M^+(aq) \quad \text{hydration enthalpy}$$

With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative E^0 value and its high reducing power.

Solutions in liquid ammonia: The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

$$M^+_{(am)} + e^- + NH_3(l) \rightarrow MNH_{2(am)} + \tfrac{1}{2}H_2(g)$$

(where 'am' denotes solution in ammonia.) In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

Reactivity towards air: The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide O_2^- ion is stable only in the presence of large cations such as K, Rb, Cs.

$$4Li + O_2 \rightarrow 2Li_2O \text{ (oxide)}$$

$$2Na + O_2 \rightarrow Na_2O_2 \text{ (peroxide)}$$
$$M + O_2 \rightarrow MO_2 \text{ (superoxide)}$$
$$(M = K, Rb, Cs)$$

In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li_3N as well. Because of

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their high reactivity towards air and water, alkali metals are normally kept in kerosene oil.

Oxides and Hydroxides:

On combustion in excess of air, lithium forms mainly the oxide, Li_2O (plus some peroxide Li_2O_2), sodium forms the peroxide, Na_2O_2 (and some superoxide NaO_2) whilst potassium, rubidium and caesium form the superoxides, MO_2. Under appropriate conditions pure compounds M_2O, M_2O_2 and MO_2 may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions:

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$$

$$M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$$

$$2M_2O + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry. The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

Halides of Li, Na and K

The alkali metal halides, MX, (X=F, Cl, Br, I) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the Δ_fH^0 values for fluorides become less negative as we go down the group, whilst the reverse is true for Δ_fH^0 for chlorides, bromides and iodides. For a given metal Δ_fH^0 always becomes less negative from fluoride to iodide.

The melting and boiling points always follow the trend: fluoride > chloride > bromide > iodide. All these halides are soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy whereas the low solubility of CsI is due to smaller hydration enthalpy of its two ions.

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Other halides of lithium are soluble in ethanol, acetone and ethylacetate; LiCl is soluble in pyridine also.

9.3.7 Some Important Compounds of Sodium

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large-scale production of these compounds and their uses are described below:

Sodium Carbonate (Washing Soda), $Na_2CO_3 \cdot 10H_2O$:

Sodium carbonate is generally prepared by Solvay Process. In this process, advantage is taken of the low solubility of sodium hydrogen carbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogen carbonate. The latter is prepared by passing CO_2 to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogen carbonate are formed. The equations for the complete process may be written as:

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium hydrogen carbonate crystal separates. These are heated to give sodium carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

In this process NH3 is recovered when the solution containing NH_4Cl is treated with $Ca(OH)_2$. Calcium chloride is obtained as a by-product.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$$

It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogen carbonate is too soluble to be precipitated by the addition of ammonium hydrogen carbonate to a saturated solution of potassium chloride.

Properties: Sodium carbonate is a white crystalline solid which exists as a decahydrate, $Na_2CO_3 \cdot 10H2O$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its

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water of crystallisation to form monohydrate. Above 373 K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$$Na_2CO_3 \cdot 10H_2O \xrightarrow{375K} Na_2CO_3 \cdot H_2O + 9H_2O$$
$$Na_2CO_3 \cdot H_2O \xrightarrow{>373K} Na_2CO_3 + H_2O$$

Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

Uses: (i) It is used in water softening, laundering and cleaning. (ii) It is used in the manufacture of glass, soap, borax and caustic soda. (iii) It is used in paper, paints and textile industries. (iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

Sodium Chloride (NaCl)

Sodium chloride, commonly known as table salt, is a compound with the chemical formula NaCl. It is a fundamental and ubiquitous substance in chemistry and plays crucial roles in various biological, industrial, and geological processes. This detailed description of sodium chloride will cover its physical and chemical properties, its role in various applications, and its significance in the broader context of chemistry.

Physical Properties:

Molecular Structure:

Sodium chloride is an ionic compound composed of positively charged sodium ions (Na+) and negatively charged chloride ions (Cl-). It forms a crystalline structure in its solid state, with a cubic crystal lattice arrangement.

State at Room Temperature: At room temperature, sodium chloride is a white, crystalline solid.

It has a high melting point of 801 degrees Celsius (1,474 degrees Fahrenheit) and a boiling point of 1,413 degrees Celsius (2,575 degrees Fahrenheit).

Solubility: Sodium chloride is highly soluble in water, forming a clear and colourless solution.

The solubility of NaCl in water increases with temperature.

Density:

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The density of sodium chloride depends on its form (crystalline or amorphous) and can range between 2.16 to 2.17 g/cm^3.

Chemical Properties:

Ionic Bonding:

Sodium chloride is formed through ionic bonding, where sodium, a metal, donates an electron to chlorine, a non-metal.

The resulting electrostatic attraction between oppositely charged ions creates the stable NaCl compound.

Ionization: In aqueous solutions, sodium chloride dissociates into sodium ions (Na+) and chloride ions (Cl-). This ionization is crucial in various biological and chemical processes, such as nerve signal transmission.

Reaction with Acids and Bases:

Sodium chloride is neutral and does not react with most acids or bases under standard conditions. However, it can undergo reactions with strong acids or bases to produce different salts and water.

Applications:

Culinary Use:

Sodium chloride is a vital component in cooking and food preservation, enhancing flavor and acting as a natural preservative.

Chemical Industry:

It serves as a feedstock for the production of various chemicals, including chlorine and sodium hydroxide, through electrolysis.

Water Treatment:

Sodium chloride is used in water softening processes and as a de-icing agent in cold climates.

Biological Functions:

It plays a crucial role in maintaining electrolyte balance in living organisms.

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Nerve signal transmission and muscle contractions depend on the presence of sodium and chloride ions.

Significance in Chemistry:

Ionic Bonding Model:

Sodium chloride is often used as a model compound to illustrate the concept of ionic bonding in chemistry.

Electrolysis:

The electrolysis of molten sodium chloride is an essential process in the production of sodium and chlorine gas, showcasing the application of electrochemical principles.

Crystalline Structure Studies:

The study of sodium chloride's crystal lattice provides insights into crystallography and solid-state physics.

Preparation of NaCl:

Sodium chloride (NaCl), commonly known as table salt, can be prepared through different methods depending on the desired form (e.g., laboratory synthesis, extraction from natural sources, or industrial processes). Here are a few methods commonly used for preparing sodium chloride:

1. Laboratory Synthesis:

- **Neutralization Reaction:**
    1. Start with sodium hydroxide (NaOH), a strong base, and hydrochloric acid (HCl), a strong acid.
    2. Mix the solutions in stoichiometric proportions to ensure complete neutralization.
    3. The resulting reaction is: $NaOH+HCl \rightarrow NaCl+H2O$

2. Extraction from Natural Sources:

- **Salt Evaporation Ponds:**

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1. Seawater or brine from salt mines is collected in shallow ponds.
2. Allow the sun and wind to evaporate the water, leaving behind sodium chloride crystals.
3. The remaining solid is then harvested and processed to obtain pure sodium chloride.

3. Industrial Production:

- **Solution Mining:**
  1. Inject water into underground salt deposits to dissolve the salt, creating a brine solution.
  2. Pump the brine solution to the surface.
  3. Evaporate the water from the brine, leaving behind solid sodium chloride.
- **Electrolysis:**
  1. In industrial settings, sodium chloride can be used to produce sodium metal and chlorine gas through electrolysis.
  2. Molten sodium chloride serves as an electrolyte in this process.

4. Recrystallization:

- **Purification from Impure Sources:**
  1. Dissolve impure sodium chloride in hot water to form a solution.
  2. Allow the solution to cool slowly, promoting the formation of larger, purer crystals.
  3. Filter or decant the solution to separate the purified sodium chloride crystals.

5. Chemical Reaction:

- **Synthesis from Sodium Carbonate and Hydrochloric Acid:**
  1. React sodium carbonate (Na_2CO_3) with hydrochloric acid (HCl).
  2. The resulting reaction is: $2Na_2CO_3+2HCl \rightarrow 2NaCl+H_2O+CO_2$

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Safety Considerations:

- When working with concentrated acids or bases, appropriate safety precautions, including gloves, goggles, and a well-ventilated area, should be taken.
- Follow established laboratory or industrial safety protocols for handling chemicals.

It's important to note that the method chosen will depend on the scale of production, available resources, and the purity requirements for the sodium chloride. The methods described here are general and may be adapted based on specific needs and conditions.

Sodium Hydroxide (NaOH):

Sodium hydroxide (NaOH), commonly known as caustic soda or lye, is a strong base with a wide range of applications in various industries, including chemical manufacturing, water treatment, and soap production. This discussion will cover the properties, uses, and methods of synthesis of sodium hydroxide.

Properties of Sodium Hydroxide:

1. **Chemical Formula:**
    - Sodium hydroxide has the chemical formula NaOH, indicating one sodium (Na) atom, one oxygen (O) atom, and one hydrogen (H) atom.
2. **Physical State:**
    - At room temperature, sodium hydroxide is a white, solid substance.
    - It is highly hygroscopic, meaning it readily absorbs water from the air.
3. **Solubility:**
    - Sodium hydroxide is highly soluble in water, and this dissolution is exothermic, releasing heat.
    - The resulting solution is strongly alkaline.
4. **Reactivity:**

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- NaOH is a strong base and reacts vigorously with acids, forming water and a corresponding salt.
- It can also react with certain metals, producing hydrogen gas and forming metal hydroxides.

5. **Corrosiveness:**
    - Sodium hydroxide is corrosive to organic materials, including skin and certain metals, and should be handled with care.

Uses of Sodium Hydroxide:

1. **Chemical Manufacturing:**
    - NaOH is a key ingredient in the production of various chemicals, including detergents, paper, textiles, and pharmaceuticals.
2. **Water Treatment:**
    - It is used for pH adjustment in water treatment processes.
    - Sodium hydroxide can be added to water to neutralize acidic substances and control alkalinity.
3. **Soap and Detergent Production:**
    - NaOH is employed in the saponification process, converting fats and oils into soap.
    - It is also used to adjust the pH of detergent formulations.
4. **Alumina Production:**
    - In the Bayer process, sodium hydroxide is used to extract alumina from bauxite ore in the production of aluminum.
5. **Food Processing:**
    - NaOH is used in food processing for various purposes, such as peeling fruits and vegetables, curing olives, and processing cocoa.

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Synthesis of Sodium Hydroxide:

1. **Chlor-Alkali Process:**
    - The most common industrial method for producing sodium hydroxide is the chlor-alkali process.
    - In this process, sodium chloride (NaCl) is electrolyzed in a diaphragm cell or a membrane cell, leading to the formation of chlorine gas (Cl_2) at the anode and sodium hydroxide at the cathode.
    - The overall reaction is: $2NaCl+2H_2O \rightarrow Cl_2+H_2+2NaOH$
2. **Mercury Cell Process:**
    - An older method involves using a mercury cell, where sodium is produced by the reduction of sodium ions at the cathode.
    - The sodium reacts with water to produce sodium hydroxide and hydrogen gas.
3. **Direct Reaction with Sodium:**
    - Sodium hydroxide can also be produced by the direct reaction of sodium with water, although this method is less common due to the highly reactive nature of sodium.
4. **Laboratory Synthesis:**
    - In a laboratory setting, sodium hydroxide can be prepared by reacting sodium metal with water, or by neutralizing a solution of sodium carbonate with hydrochloric acid or sulfuric acid.

Safety Considerations:

- Sodium hydroxide is caustic and can cause severe burns. Protective equipment, including gloves and goggles, should be worn when handling NaOH.
- Proper ventilation and caution are necessary to avoid exposure to fumes when using sodium hydroxide.

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In summary, sodium hydroxide is a versatile compound with numerous industrial applications. Its synthesis methods are well-established, with the chlor-alkali process being the predominant method for large-scale production. When working with sodium hydroxide, safety precautions should be rigorously observed due to its corrosive nature.

9.3.8 Important Term: Diagonal relationship

Diagonal relationship refers to the relationship between certain pairs of elements in the periodic table that are located diagonally from each other. The most well-known diagonal relationship exists between lithium (Li) in Group 1 and magnesium (Mg) in Group 2 of the periodic table.



Elements in diagonal relationships often share similar chemical and physical properties despite being in different groups. Here's a more detailed explanation:

Diagonal Relationship Example: Lithium (Li) and Magnesium (Mg)

1. **Atomic Size:**
    - Lithium and magnesium have similar atomic sizes due to the diagonal relationship. Lithium is a small alkali metal, while magnesium is a larger alkaline earth metal. The diagonal relationship mitigates the expected increase in size as you move from left to right across a period.
2. **Ionic Radii:**
    - The ionic radii of Li^+ and Mg^{2+} ions are comparable, further emphasizing their diagonal relationship. Both ions have a similar effective nuclear charge, contributing to their similar sizes.
3. **Similarities in Solubility:**

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- Lithium compounds, like lithium carbonate (Li_2CO_3), and magnesium compounds, like magnesium carbonate ($MgCO_3$), exhibit similarities in solubility and behavior in solution. Both form sparingly soluble carbonates.

4. **Hydration Energy:**
   - Both lithium ions (Li^+) and magnesium ions (Mg^{2+}) have high hydration energies. This is due to the high charge density of these ions, making them attract water molecules strongly.
5. **Similarities in Chemistry:**
   - Lithium and magnesium both have unique properties compared to other elements in their respective groups. For example, lithium is the only alkali metal that forms a stable nitride (Li_3N), and magnesium is the only alkaline earth metal that forms a stable nitride (Mg_3N_2).
6. **Formation of Nitrides:**
   - Both lithium and magnesium form nitrides (Li_3N and Mg_3N_2), showcasing their similarities in reactivity.
7. **Complex Formation:**
   - Both Li^+ and Mg^{2+} ions form stable complexes with ligands in coordination chemistry, further highlighting their similarities.
8. **Diagonal Relationship Limitations:**
   - While lithium and magnesium exhibit a diagonal relationship, it is not always a perfect match. Other factors, such as electronegativity and ionization energy trends, also play roles in determining the overall behavior of elements.

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The diagonal relationship phenomenon is not limited to lithium and magnesium; similar relationships can be observed between other pairs of elements in different areas of the periodic table. These relationships provide interesting insights into the periodic trends and chemical behavior of elements, showcasing the interconnected nature of the periodic table.

9.3.9 Anomalous Behaviours of Li, Na & K

Lithium (Li), sodium (Na), and potassium (K) exhibit some anomalous characteristics compared to the rest of their respective groups in the periodic table. Here are some of the anomalous features for each element:

Lithium (Li):

1. **Smaller Size:**
    - Lithium is smaller in size compared to other alkali metals. This is partly due to the significant increase in atomic size from helium to lithium.
2. **High Ionization Energy:**
    - Lithium has a higher ionization energy compared to the other alkali metals in Group 1. This is because it has a stable, filled $1s^2$ configuration with a helium-like electron arrangement.
3. **Formation of Covalent Compounds:**
    - Lithium has a tendency to form some covalent compounds, especially with elements like oxygen and nitrogen. For example, lithium nitride (Li_3N) has some covalent character.

Sodium (Na):

1. **Lower Ionization Energy:**
    - Sodium has a lower ionization energy compared to the other alkali metals in Group 1. This makes it more reactive and enhances its ability to lose an electron easily.

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2. **Distinct Flame Colour:**
    - Sodium produces a distinctive yellow flame colour (sodium yellow) when burned, which is different from the characteristic flame colours of the other alkali metals.

Potassium (K):

1. **Lower Ionization Energy:**
    - Similar to sodium, potassium has a lower ionization energy compared to the other alkali metals in Group 1. This contributes to its high reactivity.
2. **Distinct Flame Colour:**
    - Potassium produces a lilac or violet flame colour when burned, which is unique among the alkali metals.
3. **Greater Reactivity:**
    - Potassium is more reactive than the other alkali metals. It can react vigorously with water, releasing more heat and hydrogen gas compared to lithium and sodium.
4. **Formation of Peroxides:**

Potassium has a higher tendency to form peroxides (K_2O_2) when exposed to oxygen, which is not as common for the other alkali metals.

These anomalous characteristics can be attributed to factors such as atomic size, ionization energy, and electronic configuration. As you move down a group, the size of the atoms increases, leading to variations in properties. Additionally, electronic configurations play a crucial role in determining the reactivity and chemical behavior of these alkali metals.

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9.4 Be-Mg-Ca-Sr-Ba: Alkaline Earth Metals

9.4.1 Introduction

Alkaline earth metals are a fascinating group of elements that reside in Group 2 of the periodic table. Comprising beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra), these metals showcase distinct properties and play crucial roles in various aspects of our daily lives. Known for their shiny appearance, relatively low density, and reactivity, alkaline earth metals share common characteristics, yet each element brings its unique flavour to the chemical symphony. Let's dive into the world of alkaline earth metals to uncover the intriguing chemistry and applications that make them essential components of the elemental ensemble.

9.4.2 Physical Properties

Atomic Size: Size of these elements are small as compared to alkali metals and it increases on going downwards in the group. Order of size: Be < Mg < Ca < Sr < Ba.

Oxidation State: These metals exhibt + 2 oxidation state, difference of their second and first ionisation potentials is 11 eV. Therefore, their + 2 oxidation state of these metals is more stable.

Density: Atomic weight increase from Be to Ba in a group and volume also increases, but increase in atomic weight is more as compared to volume. Therefore, density increases from Be to Ba.

Exception: Density of Mg is more as compared to Ca. Density: Ca < Mg < Be < Sr < Ba

Tendency of forming ionic Bond: There are two electrons in the outermost shell of these metal, which are donated to form ionic compounds. For example, $BaCl_2$, $CaCl_2$, $MgCl_2$, etc. Due to small size of cations of Be and Mg, their compounds have covalent character.

Standard Electrode Potential or Standard Oxidation Potential: Size of these metals is smaller than that of alkali metals. Therefore, their ionisation potential will be higher than

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those of alkali metals, i.e. they have low tendency of donating electron as compared to alkali metals. Their standard electrode potentials (oxidation potentials) are lower than those of alkali metals and increases in the group with the increases in atomic size from Be to Ba. Be < Mg < Ca < Sr < Ba

Colourless and Diamagnetic ions: These metals form diapositive ions (M^{+2}). These diapositive ions have noble gas configuration and their compounds are colourless, because all the electrons are paired. Their ions are diamagnetic due to the presence of paired electrons. For example, $BeCl_2$, $CaCl_2$, $CaCO_3$, $BaSO_4$, etc., are colourless compounds.

Flame Test: Size of Be and Mg is very small and their electrons are strongly bonded to the nucleus. These electrons cannot be excited to higher energy level by the flame of the burner. Thus, Be and Mg do not impart any colour to the flame. Elements and their respective colour imparted to the flame are given below:

Element	Be	Mg	Ca	Sr	Ba
Flame	-	-	Brick red	Blood red	Apple green

Photoelectric effect: Due to small size of these metals as compared to alkali metals, their ionisation potential is high. Thus, electrons can be released only by high energy radiations.

Solubility in Liquefied Ammonia: Due to small size of Be and Mg. Their ionisation potential is high. Therefore, they do not dissolve in liquefied ammonia. Ca, Sr and Ba give ammoniated electron by getting dissolved in liquefied ammonia due to large size, due to which the solution turns blue. Ca + nNH3 → Ca+2 + 2e– $(NH_3)n$ The solution is a good conductor of electricity and a strong reducing agent.

Hydration Energy: Hydration energy of the metal ions (M+2) is higher than that of the elements of IA group, because the size of these cations is small and charge is high. Hydration energy decreases on going downwards in the group, due to increase in the size of cations. Be > Mg > Ca > Sr > Ba

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Reactivity: Due to small size of these metals as compared to alkali metals, the alkaline earth metals are less reactive than the alkali metals. Their reactivity increases from Be to Ba with increase in the size of the metal. (i) Beryllium does not react with hot water, Mg reacts with hot water, whereas Ca, Sr and Ba react even with cold water. (ii) All these metals react with oxygen to form MO type oxides (M = Be, Mg, Ca, Sr and Ba), but due to low ionisation potential and high reactivity, Ca, Sr and Ba form peroxides also at low temperature. (iii) Be and Mg are less reactive due to their high ionisation potential and they form normal oxides because of breaking of O = O bond.

Lustrous Surface: Lustre is due to mobile electron in the metallic lattice. Valence electrons generated vibration in the electrical field of the light waves. The vibrating electrons emit electromagnetic energy in the form of light, and thus the surface of these metals starts shining.

Tendency of Forming Complex compounds: These metals have weak tendency of forming complex compounds due to large size, low charge density and absence of vacant orbitals. But these metals have higher tendency of forming complex compounds as compared to alkali metals, due to their relatively smaller size. This tendency decreases from Be to Ba.

Strength of metallic Bonds (Softness): There are two electrons in the outermost shell of these metals, which participate in bond formation. Therefore, metallic bond is weak, but a little bit stronger than the elements of IA group. Their atomic size is smaller as compared to elements of IA group. Therefore, these metals from strong metallic bonds as compared to metals of IA group. Thus, these metals are harder than the metals of IA group. Order of their hardness is Be > Mg > Ca > Sr > Ba They have BCC, HCP and FCC structures, i.e., packing efficiency is more than that of the elements of IA group.

Melting point and Boiling Point:

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Melting and boiling points of these metals are low, but these metals are harder as compared to metals of IA group. Thus, their melting and boiling points are higher as compared to metals of IA group.

Hardness decreases from Be to Ba, due to which melting and boiling points decrease.

Be > Ca > Sr > Ba > Mg

Higher melting and boiling points of Ca than Mg are due to the presence of d-orbitals in its outermost shell, which starts from Ca. The d-orbital forms strong metallic point.

Metal	Be	Mg	Ca	Sr	Ba
Melting Point, °C	1280	647	850	770	710
Boiling Point, °C	1500	1135	1490	1360	1535

Reducing Nature (a) The alkaline earth metals have the tendency to loose electrons and change into bivalent cation. $M \rightarrow M^{2+} + 2^{e-}$ Hence they act as strong reducing agents. (b) The reducing nature increases as the atomic number increases.

Electronic Configuration	IP (eV)	At. Vol.	At. Radii 'Å'	Ionic radii 'Å'	m.pt. °C	b.pt. °C	Standard electrode potential (volt)	Electronegativity
$[He]2s^2$	9.3	5.0	0.9	0.31	1277	2970	–1.80	1.5
$[Ne]\ 3s^2$	7.6	14.0	1.36	0.65	650	1100	–2.37	1.2
$[Ar]\ 4s^2$	6.1	29.9	1.74	0.99	838	1440	–2.87	1.0
$[Kr]\ 5s^2$	5.7	33.7	1.91	1.13	768	1380	–2.89	1.0
$[Xe]\ 6s^2$	5.2	39.0	1.98	1.35	714	1640	–2.90	0.9

9.4.3 Chemical Properties

Reaction with Oxygen

(a) Except Ba and Ra, all other metals when burnt in oxygen form oxide of type MO.

$$2M + O_2 \longrightarrow 2MO$$

$$Ba \xrightarrow{O_2} BaO \xrightarrow[\text{high temp.}]{O_2} BaO_2$$

(b) BeO is amphoteric in nature while other oxides are basic in nature.

$$MO + H_2O \longrightarrow M(OH)_2 + \text{heat.}$$

(c) Basic nature of oxide increases from Be to Ba.

Action of Water

(a) Mg decomposes boiling water.

(b) Be is not attacked by water at any temperature.

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(c) Ca, Sr, Ba, Ra decomposes cold water with evolution of H_2 gas.

$M + 2H_2O \rightarrow M(OH)_2 + H_2$.

(d) $Be(OH)_2$ is amphoteric, but other hydroxides are basic. The basic strength increase from Be to Ba.

(e) Solubility of hydroxides also increases from $Be(OH)_2$ to $Ba(OH)_2$.

Hydride formation

(a) Except Be, all other metals directly combines with hydrogen to form hydrides of the type MH_2.

(b) BeH_2 and MgH_2 are covalent hydride while other hydrides are ionic in nature.

(c) Ionic hydrides are violently decomposed by water evolving hydrogen.

$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$

Halides

(a) Metals directly combines with X_2 to form halides

$M + X_2 \longrightarrow MX_2$.

(b) BeX_2 is covalent in nature, whereas other metal halides are ionic solids.

(c) These halides are hygroscopic in nature and readily form hydrates *e.g.*, $MgCl_2.6H_2O$, $BaCl_2.2H_2O$ etc.

Carbonates and Bicarbonates

(a) Carbonates of metals are insoluble in water, they dissolve in presence of CO_2 only.

$MCO_3 + H_2O + CO_2 \longrightarrow M(HCO_3)_2$.

(b) Solubility of carbonates decreases on moving down the group, while stability increases.

Sulphates

$MO + H_2SO_4 \longrightarrow MSO_4 + H_2O$.

(a) Solubility of sulphates decreases on moving down the group.

$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$.

(b) Solubility depends upon hydration energy of cation which is maximum in Be^{2+}.

Complex Formation

Be^{2+} and Mg^{2+} due to their small size show some tendency of complex formation.

Ex. $[BeF_3]^-$, $[BeF_4]^{2-}$ and $[Be(H_2O)_4]^{2+}$, chlorophyll (Complex of Mg^{2+})

Organometallic Compounds

Be and Mg forms a number of compounds with M – C bonds.

e.g., Grignard reagent.

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9.4.3 Behaviour of Beryllium Different from Other Alkaline Earth Metals

Beryllium exhibits different behaviour due to small size as compared to other elements of its group.

(1) Ionisation potential and electronegativity of Be are higher than those of other metals.

(2) $BeCl_2$ is insoluble in water, due to its covalent nature, but soluble in organic solvents. Other chlorides ($CaCl_2$, $SrCl_2$ and $BaCl_2$) get dissolved in water.

(3) $BeCl_2$ gets hydrolysed due to its covalent nature. Chlorides of Ca, Sr and Ba get dissociated.

(4) BeO and $Be(OH)_2$ are amphoteric in nature. Therefore they react with acids as well as bases. Other oxides react only with acids due to their alkaline nature

$$BeO + 2NaOH + H_2O \rightarrow Na_2[Be(OH)_4]$$

Sodium berylate

$$BeO + 2HCl \rightarrow BeCl_2 + H_2O$$

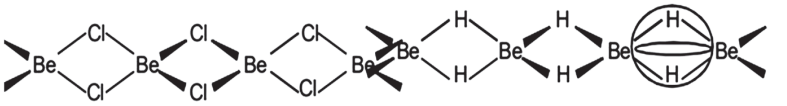
(5) Beryllium forms single type of oxide (MO), Ca Sr and Ba form peroxides also.

(6) Hydration energy of Be is higher than that of other metals.

(7) Beryllium does not give flame test, Ca, Sr and Ba impart characteristic colours to the flame.

(8) Due to small size, Be forms complex compounds, Ca, Sr and Ba are insoluble in water.

(9) Hydrides and halides of Be get polymerizes.



Polymerized BeH_2 in which tricentric forces are present.

(10) Beryllium does not react with water even at high temperatures. Others (Ca, Sr and Ba) react even with cold water.

9.4.5 Important Compounds

Compounds of Be

Beryllium forms a variety of compounds due to its versatile chemical properties. Some notable compounds of beryllium include:

Beryllium Oxide (BeO): Also known as beryllia, beryllium oxide is a white, crystalline solid with high thermal conductivity and excellent electrical insulating properties. It is commonly used in ceramics, electronics, and as a neutron moderator in nuclear reactors.

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Beryllium Chloride ($BeCl_2$): Beryllium chloride exists as a white, hygroscopic solid at room temperature. It is primarily used as a catalyst in organic synthesis, particularly in Friedel-Crafts reactions. However, it is highly toxic and poses significant health hazards if mishandled.

Beryllium Hydroxide ($Be(OH)_2$): Beryllium hydroxide is a white, amorphous solid that can be obtained by treating beryllium salts with alkali hydroxides. It is used in the production of beryllium metal, as well as in the manufacturing of beryllium-containing ceramics.

Beryllium Fluoride (BeF_2): Beryllium fluoride is a white, crystalline solid that is highly soluble in water. It is commonly used in the production of beryllium metal by the electrolysis of beryllium chloride, as well as in the manufacturing of optical glasses and as a component in dental materials.

Beryllium Sulfate ($BeSO_4$): Beryllium sulfate is a white, crystalline solid that is sparingly soluble in water. It is primarily used in the production of beryllium metal, as well as in analytical chemistry as a reagent for the detection of sulfates.

These are just a few examples of the many compounds that beryllium can form. Beryllium compounds are valued for their unique properties and find applications in various industries, including aerospace, electronics, and healthcare. However, it's important to handle them with care due to the toxicity of beryllium and its compounds.

Compounds of Mg

Magnesium compounds are a diverse group of chemical substances that contain the element magnesium, which is a vital component in many biological processes and industrial applications. Magnesium itself is a light, silvery metal that is highly reactive, making it rare to find in its pure form in nature. However, it forms numerous compounds with other elements, resulting in a wide range of useful and interesting substances.

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One of the most well-known magnesium compounds is magnesium oxide (MgO), also known as magnesia. Magnesium oxide is a white, powdery substance that occurs naturally as the mineral periclase. It is commonly used in a variety of applications, including as a refractory material in the production of bricks and ceramics, in the manufacture of electrical insulators, and as a component in some antacids and laxatives due to its alkaline properties.

Another important magnesium compound is magnesium sulfate (MgSO4), also known as Epsom salt. This compound is hydrated magnesium sulfate and is commonly used in bath salts for its purported muscle-relaxing and stress-reducing properties. In addition to its use in personal care products, magnesium sulfate is also used in agriculture as a fertilizer, in medicine as a component of intravenous solutions, and in various industrial processes.

Magnesium carbonate (MgCO3) is another significant magnesium compound that is often used as a drying agent, an antacid, and a bulking agent in the production of tablets and capsules. It is also used in the manufacturing of cement, rubber, and plastics.

Other notable magnesium compounds include magnesium hydroxide (Mg(OH)2), which is used as an antacid and a laxative, and magnesium chloride (MgCl2), which is used in the production of magnesium metal and as a deicing agent for roads and sidewalks.

In addition to their industrial and commercial applications, magnesium compounds also play essential roles in biological systems. Magnesium ions (Mg^{2+}) are crucial for many enzymatic reactions and are involved in processes such as muscle contraction, nerve function, and DNA replication.

Epsom Salt ($MgSO_4$)

Preparation:

In a laboratory setting, Epsom salt can be synthesized through two methods. Firstly, by introducing magnesium ribbon to dilute sulfuric acid. Alternatively, Epsom salt can be produced by combining magnesium carbonate with sulfuric acid. To accomplish this, start by pouring 20 milliliters of sulfuric

E-copy

acid into a pristine beaker. Next, gradually introduce small quantities of magnesium carbonate into the beaker while stirring the solution gently after each addition.

Chemical Composition: Epsom salt, scientifically known as magnesium sulfate ($MgSO_4$), is a crystalline compound consisting of magnesium, sulfur, and oxygen ions.

Origins: The name "Epsom salt" derives from the town of Epsom in Surrey, England, where natural deposits of magnesium sulfate were first discovered in mineral springs. However, it is now produced synthetically as well.

Physical Properties: Epsom salt typically appears as colorless, odourless, and crystalline granules or powder. It is highly soluble in water, with its solubility increasing with higher temperatures.

Uses:

Personal Care: Epsom salt is popularly used in bath salts for its purported therapeutic properties. It is believed to help relax muscles, soothe soreness, and alleviate stress when dissolved in warm bathwater.

Gardening and Agriculture: Epsom salt is used as a supplement for magnesium and sulfur in gardening and agriculture. It is often applied to soil or foliage to correct nutrient deficiencies, promote plant growth, and improve the quality of crops.

Health and Wellness: Some people use Epsom salt as a home remedy for various conditions, including constipation (when taken orally), minor skin irritations, and as a natural exfoliant in skincare products.

Medical Applications: In the medical field, Epsom salt is used in certain medical procedures, such as a component of intravenous solutions for the treatment of magnesium deficiency or to induce relaxation in pregnant women during preterm labour.

Precautions: While generally considered safe for external use and oral consumption in moderate amounts, excessive ingestion of Epsom salt can lead to adverse effects such as diarrhea and dehydration. It is essential to follow recommended usage guidelines and consult a healthcare professional if unsure about its suitability for specific conditions.

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Availability: Epsom salt is widely available over-the-counter at pharmacies, grocery stores, and online retailers in various forms, including bulk bags, pre-packaged bath salts, and topical creams or lotions.

9.5 Summary

Beryllium (Be), magnesium (Mg), calcium (Ca), and strontium (Sr) are elements belonging to the alkaline earth metals group. Each element exhibits unique chemical properties and forms a variety of compounds with diverse applications.

Beryllium compounds, such as beryllium oxide and beryllium chloride, are utilized in ceramics and organic synthesis. Despite their usefulness, they pose significant health hazards due to beryllium's toxicity.

Magnesium compounds, including magnesium oxide (MgO) and magnesium sulfate ($MgSO_4$), find widespread applications in industries ranging from refractory materials to pharmaceuticals. Epsom salt, a magnesium sulfate compound, is particularly renowned for its therapeutic properties in personal care and gardening.

Calcium compounds play essential roles in various fields. Calcium carbonate ($CaCO_3$) is widely used in industries like construction and agriculture, while calcium hydroxide ($Ca(OH)_2$) serves as a key ingredient in cement and as a chemical reagent.

Strontium compounds, such as strontium carbonate ($SrCO_3$) and strontium chloride ($SrCl_2$), are employed in pyrotechnics, luminescent materials, and medicinal applications. Strontium ranelate is a notable pharmaceutical compound used in the treatment of osteoporosis.

In summary, compounds of beryllium, magnesium, calcium, and strontium exhibit diverse properties and find applications across various industries, though careful handling and consideration of their toxicity are necessary in certain cases

9.6 Model Questions

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A. Some Multiple-Choice Questions

1. Which group of elements do the s-block elements represent in the periodic table?

a) Group 1 and Group 2

b) Group 2 and Group 3

c) Group 17 and Group 18

d) Group 1 and Group 17

2. Which of the following statements about alkali metals is true?

a) They have two electrons in their outermost s orbital.

b) They are less reactive compared to alkaline earth metals.

c) They tend to form covalent compounds with other elements.

d) They include elements like beryllium and magnesium.

3. What is the general electron configuration of Group 1 alkali metals?

a) [He] ns^1

b) [Ne] ns^1

c) [He] np^1

d) [Ne] np^1

4. Which alkali metal is the least dense and lightest in its group?

a) Sodium

b) Potassium

c) Lithium

d) Rubidium

5. What is the characteristic flame color produced by potassium when burned?

a) Red

b) Yellow

c) Blue

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d) Violet

6. What compound is formed when lithium reacts with water?

a) LiOH

b) Li_2O

c) Li_2O_2

d) Li_3N

7. Which of the following alkali metals reacts the most vigorously with water?

a) Lithium

b) Sodium

c) Potassium

d) Rubidium

8. What is the primary application of lithium-ion batteries?

a) Transportation

b) Agriculture

c) Construction

d) Telecommunication

9. Which alkali metal forms the least soluble fluoride compound in water?

a) Lithium

b) Sodium

c) Potassium

d) Rubidium

10. Which property increases down the group for alkali metals?

a) Ionization energy

b) Density

c) Atomic radius

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d) Melting point

11. Which group of elements in the periodic table do beryllium, magnesium, calcium, strontium, barium, and radium belong to?

A) Group 1

B) Group 2

C) Group 17

D) Transition metals

12. What is the order of atomic size from smallest to largest among the alkaline earth metals?

A) Ba < Sr < Ca < Mg < Be

B) Be < Mg < Ca < Sr < Ba

C) Mg < Be < Ca < Sr < Ba

D) Be < Ca < Mg < Sr < Ba

13. Which of the following statements about the oxidation state of alkaline earth metals is correct?

A) They exhibit a +1 oxidation state.

B) Their +2 oxidation state is less stable due to low ionization potential.

C) The difference in their second and first ionization potentials is 10 eV.

D) Their +2 oxidation state is more stable due to a difference of 11 eV in ionization potentials.

14. Why do beryllium and magnesium compounds have covalent character?

A) Due to their high ionization potential

B) Because of their low reactivity

C) Because they readily donate electrons

D) Due to the large size of their cations

15. Which alkaline earth metal does not impart any color to a flame test?

A) Beryllium

B) Magnesium

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C) Calcium

D) Strontium

16. What is the reason behind the high hydration energy of alkaline earth metal ions?

A) Small size and low charge

B) Large size and high charge

C) Large size and low charge

D) Small size and high charge

17. Which alkaline earth metal is least reactive?

A) Beryllium

B) Magnesium

C) Calcium

D) Barium

18. What is the primary use of beryllium chloride?

A) As a catalyst in organic synthesis

B) In the production of nuclear reactors

C) As a component in dental materials

D) In the manufacturing of optical glasses

19. Which magnesium compound is commonly used as a drying agent and antacid?

A) Magnesium oxide

B) Magnesium sulfate

C) Magnesium carbonate

D) Magnesium hydroxide

20. Where are natural deposits of Epsom salt first discovered?

A) France

B) Germany

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C) England

D) United States

B. Short Type Questions

3. What is the general electron configuration for alkali metals?
4. Describe the reactivity trend of alkali metals as you move down Group 1 of the periodic table.
5. Which alkali metal is the least dense and lightest in Group 1?
6. Write the balanced chemical equation for the reaction of lithium with water.
7. Which alkali metal forms lithium oxide as the main product on combustion in air?
8. Name two important compounds of lithium used in the production of lithium chemicals and pharmaceuticals.
9. What is the significance of sodium in biological systems?
10. Explain how sodium chloride is prepared industrially.
11. Describe the properties and uses of sodium hydroxide.
12. What is the diagonal relationship, and give an example of elements that exhibit this phenomenon?
13. Name two alkaline earth metals that react with water even at cold temperatures.
14. What is the colour imparted to the flame by strontium?
15. Why do beryllium and magnesium compounds exhibit covalent character?
16. Which alkaline earth metal has the highest hydration energy?
17. Describe the reactivity trend observed among alkaline earth metals from beryllium to barium.
18. What is the primary use of beryllium oxide in industrial applications?
19. Name one notable compound of beryllium and its application.
20. Briefly explain why magnesium is rarely found in its pure form in nature.
21. What is the common name for magnesium sulfate, and what are its uses?
22. Where were natural deposits of Epsom salt first discovered?

C. Assay Types Questions

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1. How can the presence of alkali metals in a compound be confirmed using a flame test? Describe the characteristic flame colors observed for lithium, sodium, and potassium.
2. Discuss the method of atomic absorption spectroscopy for quantifying the concentration of alkali metals in a sample. Highlight its sensitivity and potential interferences.
3. Explain the principle behind the precipitation titration method for determining the concentration of alkali metals in a solution. Provide an example of a suitable precipitating agent.
4. Describe the process of extracting alkali metals from their respective salts using ion exchange chromatography. Discuss the selectivity of this method.
5. Discuss the significance of alkali metals in flame photometry and how this technique can be utilized for their quantitative analysis.
6. Explain the concept of ion-selective electrodes and their application in determining the concentration of alkali metal ions in aqueous solutions.
7. Describe the principle of coulometric titration and its use in quantifying alkali metal ions in a sample. Highlight its advantages over other titration methods.
8. Discuss the role of complexometric titration in determining the concentration of alkali metal ions in the presence of interfering ions. Provide an example of a suitable complexing agent.
9. Explain the procedure for conducting a gravimetric analysis to determine the concentration of alkali metal ions in a sample. Discuss the potential sources of error in this method.
10. Discuss the applications of atomic emission spectroscopy in analyzing alkali metals in various samples. Highlight its sensitivity and detection limits for these elements.

11. Define alkaline earth metals and briefly explain their significance in chemistry.

12. Compare the reactivity of alkaline earth metals with alkali metals, highlighting their similarities and differences.

13. Classify the alkaline earth metals based on their flame test colors and provide an explanation for the observed variations.

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14. Explain the cause behind the covalent character of beryllium and magnesium compounds and its effect on their chemical behavior.

15. Describe one industrial application each of beryllium oxide, magnesium oxide, calcium carbonate, and strontium carbonate.

16. Analyze the trend in the hydration energy of alkaline earth metal ions and its relationship with their atomic properties.

17. Interpret the implications of the standard electrode potentials of alkaline earth metals compared to alkali metals in terms of their reactivity and chemical behavior.

18. Evaluate the importance of handling beryllium and its compounds with care in industrial and research settings, considering their toxicity and potential hazards.

19. Predict the effect of increasing atomic number on the reducing nature of alkaline earth metals and justify your prediction based on their electronic configurations.

20. Discuss the role of Epsom salt (magnesium sulfate) in agriculture, healthcare, and personal care, highlighting its diverse applications and benefits.

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Unit 10: Chemistry of p-block elements:

Contents

10.1 Objectives
10.2 Brief Introduction on B-Al-Ga-In-Tl
10.3 Chemistry of Boron (B)
- 10.3.1 Boranes
- 10.3.2 Borazine
- 10.3.3 Borane Nitride
- 10.3.4 Boric Acid
- 10.3.5 Borax

10.4 C-Si-Ge-Sn-Pb
- 10.4.1 Introduction
- 10.4.2 Inert Pair effect
- 10.4.3 Chemical Properties of Group 14 elements
- 10.4.4 Physical Properties of Group 14 elements
- 10.4.5 Allotropy in Carbon
- 10.4.6 Allotropes of Carbon
- 10.4.7 Silicon and Compounds

10.5 O-S-Se-Te
- 10.5.1 Introduction
- 10.5.2 Chemistry and Compounds of Oxygen
- 10.5.1 1 Introduction to Oxygen
- 10.5.1 2. Atomic and Molecular Properties
- 10.5.1 3. Allotropes of Oxygen
- 10.5.1 4. Oxides of Oxygen
- 10.5.1 5. Peroxides and Superoxides
- 10.5.1 6. Oxygen-Containing Acids
- 10.5.1 7. Organic Compounds Containing Oxygen
- 10.5.1 8. Industrial and Biological Importance

10.6 Sulphur
10.7 Compounds of Selenium
10.8 Compounds of Tellurium (Te)
10.9 F-Cl-Br-I
- 10.9.1 Brief Introduction on F-Cl-Br-I
- 10.9.2 Chemistry of Fluorine
- 10.9.3 Chemistry of Chlorine
- 10.9.4 Chemistry of Bromine
- 10.9.5 Chemistry of Iodine

10.10 He-Ne-Ar-Kr-Xe
- 10.10.1 Brief Introduction on He-Ne-Ar-Kr-Xe

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10.10.2 Xenon fluoride
10.10.3 Xenon Oxides

10.11 Summary

10.12 Model Questions

10.13 Further Reading

10.1 Objectives

The p-block elements are found in groups 13 to 18 of the periodic table. Here are some objectives you might consider when studying these elements:

- To comprehend the electronic configurations of p-block elements and how they relate to their properties.
- To explore the existence of allotropes and isotopes within the p-block elements and understand their significance in various applications.
- To recognize and explain any anomalous behavior exhibited by specific p-block elements and understand the underlying reasons for such deviations from general trends.
- To explore the practical applications and industrial uses of p-block elements, including their role in materials science, electronics, medicine, and other fields.
- To assess the environmental impact of certain p-block elements and their compounds, including pollutants and their potential remediation strategies.
- To delve into the coordination chemistry of p-block elements, especially in the formation of complexes and their importance in catalysis and biological systems.

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10.2 Brief introduction on: B-Al-Ga-In-Tl

Boron (B), Aluminum (Al), Gallium (Ga), Indium (In), and Thallium (Tl). These elements are part of the boron group, also known as Group 13, in the periodic table. Let's discuss each element briefly:

Boron (B):

Symbol: B

Atomic Number: 5

Boron is a metalloid and is often found in compounds with oxygen. It has some unique properties and is used in various industries, such as in the production of boron fibers and certain types of glasses.

Aluminum (Al):

Symbol: Al

Atomic Number: 13

Aluminum is a lightweight metal with excellent corrosion resistance. It is widely used in construction, aerospace, and packaging industries. Aluminum alloys are also common in the manufacturing of various products.

Gallium (Ga):

Symbol: Ga

Atomic Number: 31

Gallium is a soft metal that has a low melting point, just above room temperature. It is used in the electronics industry, particularly in the production of certain types of semiconductors.

Indium (In):

Symbol: In

Atomic Number: 49

Indium is a metal often used in the production of electronics, such as in the manufacturing of indium tin oxide (ITO), a transparent conducting material used in electronic devices like touchscreens.

Thallium (Tl):

Symbol: Tl

Atomic Number: 81

Thallium is a heavy metal and is toxic. It has limited uses due to its toxicity, but it has been used in some medical imaging procedures and in certain electronic devices.

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These elements share some common characteristics due to their placement in the same group in the periodic table. They exhibit a progression in properties from nonmetals (boron) to metals (aluminum, gallium, indium) and then a post-transition metal (thallium). Their properties and applications can vary widely due to their individual characteristics.

10.3 Chemistry of Boron (B)

10.3.1 Boranes

Boron is second (only after carbon) in the number of hydrides that it forms. Over 50 neutral boranes, (B_nH_m) and an even larger number of borane anions, ($B_nH_m^{x-}$), are known. There are three reasons why the chemistry of boranes is important.

i. The shapes of borane molecules are different from those of other hydrides.
ii. The bonding in boranes has required the expansion of molecular orbital theory.
iii. The reaction chemistry of the boranes has interesting and parallels to organic chemistry.

❑ ***Structures of Boranes*** :

The simplest borane is B_2H_6 (Figure 3). As can be seen from the figure, one of the most unique aspects of borane chemistry is that hydrogen atoms often act as bridges between neighboring boron atoms. Also, the boron atoms often form triangular units. Any polyhedron containing triangular faces (such as an octahedron) is generically known as a deltahedron. There are three common classes of boranes and borane anions:

i. The *closo*-cluster, where the boron atoms form a closed deltahedral cage. The generic formula is $[B_nH_n]^{2-}$, for example, $[B_6H_6]^{2-}$ (Figure 3).

ii. The *nido*-cluster, an open cage cluster derived from a closed deltahedron with one boron atom missing. The common generic formulas are B_nH_{n+4} or $[B_nH_{n+3}]^-$, for example, B_2H_6, B_5H_9 (Figure 3). and $[B_5H_8]^-$

iii. The *arachno*-cluster, an open cage cluster derived from a closed deltahedron with two boron atoms missing. The common generic formulas are for example B_nH_{n+6} or $[B_nH_{n+5}]^-$, B_4H_{10} (Figure 3) and. $[B_4H_9]^-$.

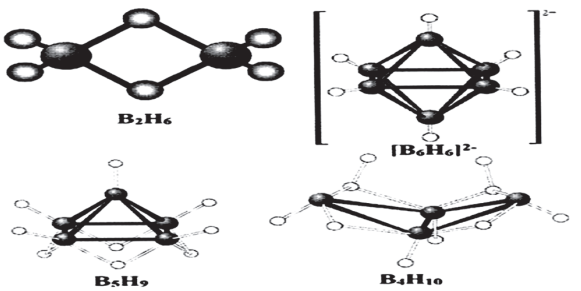


Fig. 3. Structure of different Borames

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All of the Boranes are thermodynamically unstable with respect to decomposition into their constituent elements. To name a borane, the numbers of boron atoms are indicated by the normal prefixes, while the numbers of hydrogen atoms are denoted by Arabic numbers in parentheses. Hence, B_4H_{10} is called tetraborane and B_5H_9 is pentaborane. The discovery that the simplest borane had the molecular formula B_2H_6 (not BH_3) proved to be a major headache for inorganic chemists. Traditionally, a hydrogen atom was believed to form only one covalent bond. In fact, as can be seen from the structure in Figure 3, two hydrogen atoms link, or bridge, the pair of boron atoms. The utilization of hydrogen atoms as bridges means that one electron pair can satisfy the bonding requirements of two boron atoms. Each terminal hydrogen atom forms a normal two-electron bond with a boron atom. Each boron atom then has one electron left, and this is paired with the electron of one of the bridging hydrogen atoms (Figure 4A). The shape of the molecule can be described as approximately tetrahedral around each boron atom, with the bridging hydrogen atoms in what are sometimes called "banana bonds." The hydridic bonds behave like weak covalent bonds (Figure 4B). The bonding in a diborane molecule can be described in terms of hybridization concepts. According to these concepts, the four bonds, separated by almost equal angles, would correspond to sp^3 hybridization. Three of the four hybrid orbitals will contain single electrons from the boron atom. Two of these half-filled orbitals would then be involved in bonding with the terminal hydrogen atoms. This arrangement would leave one empty and one half-filled hybrid orbital. To explain how we make up the eight electrons in the sp^3 orbital set, we consider that the single half-filled hybrid sp^3 orbitals of the two borons overlap with each other and with the Is orbital of a bridging hydrogen atom at the same time. This arrangement will result in a single orbital that encompasses all three atoms (a *three-center bond*). This orbital is capable of containing two electrons (Figure 4C). An identical arrangement forms the other B-H-B bridge. The bonding electron distribution of diborane is shown in Figure 4D. Alternatively, we can consider the molecular orbital explanation. The detailed molecular orbital diagram for this eight-atom molecule is complex. Although molecular orbitals relate to the molecule as a whole, it is sometimes possible to identify molecular orbitals that are involved primarily in one particular bond. In this case, we find that the mixing of the orbital wave functions of the atoms in each bridge bond results in the formation of three molecular orbitals. When we compare the energies of the atomic orbitals with those of the molecular orbitals, we find that one molecular orbital is lower in energy (s bonding), one is higher in energy (s antibonding), and the third has an energy level equivalent to the mean energy of the three component atomic orbitals (s nonbonding). The bridging hydrogen atom contributes one electron, and each boron atom contributes one-half electron. This arrangement fills the bonding orbital between the three atoms (Figure 4E). Because

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there is one bonding orbital shared between two pairs of atoms, the bond order for each *B-H* component must be 1/2. The same arguments apply to the other bridge. From bond energy measurements, we do indeed find each *B-H* bridging bond to be about half the strength of a terminal *B-H* bond, although it is still in the energy range of a true covalent bond, unlike the much weaker protonic bridges in hydrogen bonded molecules. Of equal importance, the set of molecular orbitals shows that the structure makes maximum use of the few boron electrons. The presence of more electrons would not strengthen the bond because these electrons would enter nonbonding molecular orbitals.

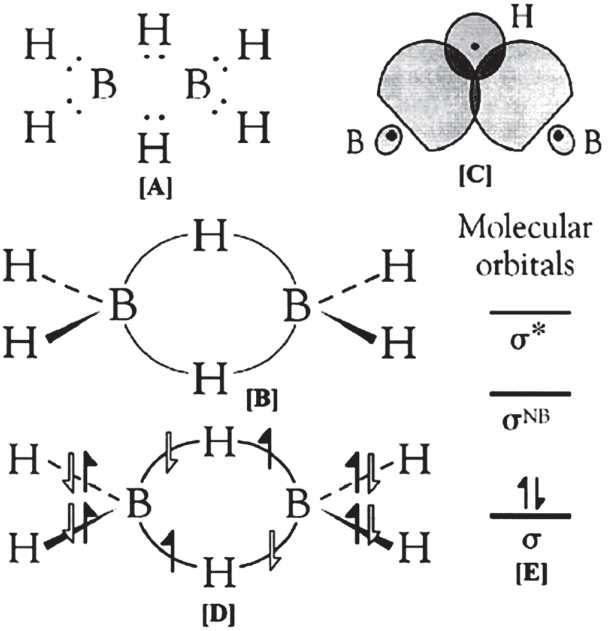


Fig. 4 [A] : Electron-pair arrangement in diborane, B_2H_6[*B*] : Geometry of the diborane molecule. [*C*]: Overlap of the sp^3 hybrid orbitals of the two boron atoms with Is orbital of the bridging hydrogen atom. [*D*]: The electron pairing that is consistent with sp^3 hybridization for each boron atom and with the two-electron, three-atom *B-H-B* bridging bonds. The electrons contributed by the hydrogen atoms are the open half-headed arrows.[*E*]: The molecular orbitals that are involved in the hydride bridge.

❑ ***Synthesis and Reactions of Boranes*** **:**

About 200 tonnes of diborane are produced each year. The industrial synthesis is accomplished by the reaction of boron trifluoride with sodium hydride to produce toxic, colorless diborane :

$$2\ BF_3\,(g) + 6NaH\ (s) \rightarrow B_2H_6\,(g) + 6NaF\ (s)$$

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The boranes possess partially negatively charged hydrogen atoms because of the low electronegativity of boron. This reversed polarity of the bond results in a high chemical reactivity for these compounds. For example, diborane, like most of the neutral boranes, catches fire in air and explodes when mixed with pure dioxygen. The extremely exothermic reaction produces diboron trioxide and steam :

$$B_2H_6(g) + 30_2(g) \rightarrow B_20_3 + 3H_20(g)$$

Reaction with water to give boric acid (sometimes written as $[B(OH)_3]$ and hydrogen is also very exothermic :

$$B_2H_6(g) + 6\ H_2O\ (l) \rightarrow 2\ H_3BO_3\ (aq) + 3\ H_2O\ (l).$$

Most of the other boranes are synthesized from diborane. For example, tetraborane is formed from the condensation of two diborane molecules, then pentaborane is formed by reaction with another molecule of diborane :

$$2B_2H_6(g) \xrightarrow{high\ pressure} B_4H_{10}(g) + H_2(g)$$

$$B_4H_{10}(g) + B_2H_6(g) \rightarrow B_5H_{11}(g) + 2H_2(g)$$

Diborane is an important reagent in organic chemistry. The gas reacts with unsaturated hydrocarbons (those containing double or triple carbon-carbon bonds) to form alkylboranes. For example, diborane reacts with propene :

$$B_2H_6(g) + 6\ CH_2{=}\ CHCH_3(g) \rightarrow 2\ B\ (CH_2\ CH_2\ CH_3)_3\ (1)$$

The product of this *hydrobomtion* reaction can be reacted with a carboxylic acid to give a saturated hydrocarbon, with hydrogen peroxide to give an alcohol, or with chromic acid to give a ketone or a carboxylic acid. Hydroboration is a favored route of organic synthesis for two reasons: the initial hydride addition is accomplished under very mild conditions, and a wide variety of final products is possible (depending on the other reagent used).

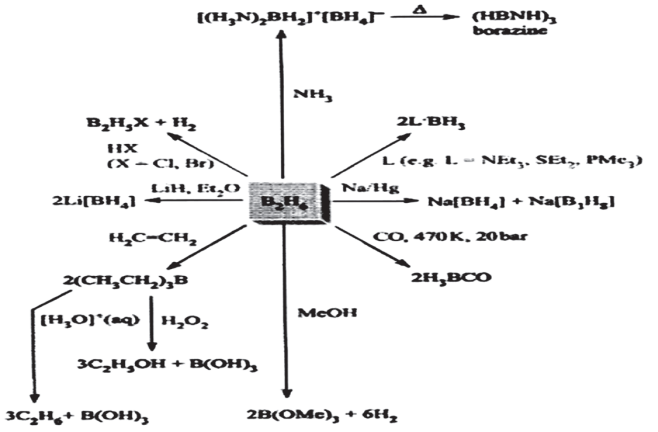


Fig. 5 Selected reactions of B_2H_6

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10.3.2 Borazine

BH_3 forms adducts with a wide range of donor ligands, such as $Me_3N.BH_3$. When the donor is also a hydride, loss of hydrogen can also occur. For example, B_2H_6 and NH_3 initially form the expected $H_3N.BH_3$ which gives the compound borazine, $B_3N_3H_6$ '(Fig.6)' on warming to room temperature. Borazine is isoelectronic with benzene (C_6H_6) and also has a delocalized structure, with all *B-N* bond lengths identical (144 pm). However, in borazine the electronegative N atoms are polarized δ- and the electropositive B atoms δ +, so the reactivity of borazine is rather different to that of benzene, and the sometimes-used term 'inorganic benzene' is not a good description of borazine.

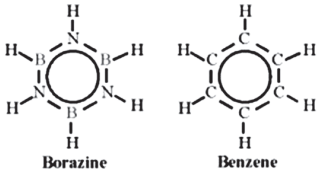


Fig. 6 : Borazene & Benzene

The reaction between diborane, B_2H_6, and ammonia gives borazine, $B_3N_3H_6$,

$$3B_2H_6(g) + 6NH_3(g) \rightarrow 2B_3N_3H_6(l) + 12\ H_2(g).$$

There are many other derivatives of this type, involving different substituents on *B* and/or *N*. The eaction of NH_4C1 with BCl_3 gives *B,B,B* trichloroborazine, $B_3N_3H_3Cl_3$

$$3NH_4C1 + 3BC1_3 \rightarrow B_3N_3H_3C1_3 + 9HC1$$

Despite similarities in boiling points, densities, and surface tensions, the polarity of the boron nitrogen bond means that borazine exhibits less aromaticity than benzene. Hence, borazine is much more prone to chemical attack than is the homogeneous ring of carbon atoms in benzene. For example, hydrogen chloride reacts with borazine to give $B_3N_3H_9C1_3$, in which the chlorine atoms bond to the more electropositive boron atoms :

$$B_3N_3H_6(l) + 3\ HCl\ (g) \rightarrow B_3N_3H_9Cl_3(s)$$

Chemical reactions wit Borazine

$$B_3H_6N_3 = 3BN + 3H_2(300^{\circ}C\ or\ in\ the\ light).$$

$$B_3H_6N_3 + 9H_2O(hot) = 3B(OH)_3 \downarrow + 3NH_3 \uparrow + 3H_2 \uparrow.$$

$$B_3H_6N_3 + 3NaOH(cone.) + 12H_2O(cold) = 3Na[B(OH)_4] + 3H_2 \uparrow + 3(NH_3.H_20)$$

$$4B_3H_6N_3 + 21O_2 = 6B_2O_3 + 12NO + 12H_2O(electrie\ disch\arg e).$$

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10.3.3 Borane Nitride

Just as, borazine is isoelectronic with benzene, the material boron nitride (*BN*) is isoelectronic with carbon. Both carbon and *BN* form diamond and graphite-like structures. The graphite-like structure of *BN* (Figure 7) has layers consisting of planar, hexagonal B_3N_3 rings (with BN distances similar to those in borazine). These layers stack on top of each other such that the $B^{\delta+}$ and $N^{\delta-}$ atoms lie on top of each other.

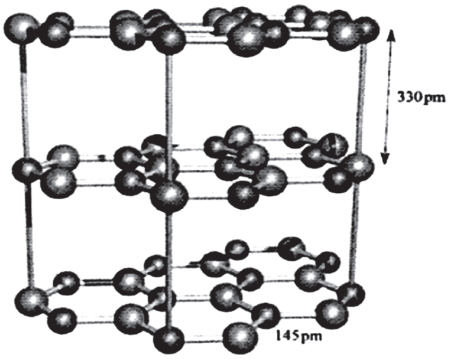


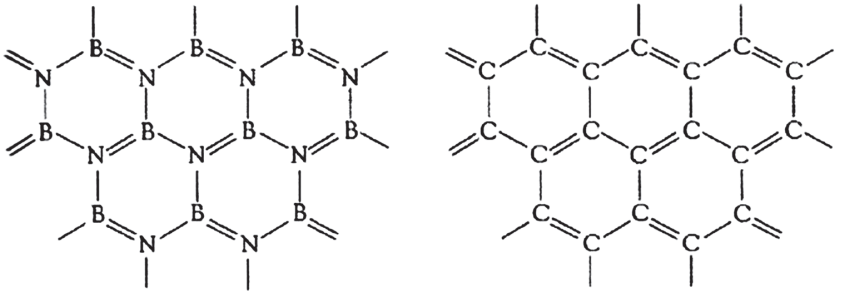
Fig.7: Part of the layer structure of the common polymorph of boron nitride, *BN*. Hexagonal rings in adjacent layers lie over one another so that *B* and *N* atoms are eclipsed.

Unfortunately, both carbon allotropes burn when heated to give carbon dioxide gas, thus precluding the use of either of these substances in high temperature applications. Boron nitride, BN, however, is the ideal substitute. The simplest method of synthesis involves heating diboron uioxide with ammonia at about 1000°C:

$$B_2O_3(s) + 2\ NH_3(g) \rightarrow 2BN(s) + 3H_2O\ (g)$$

The product has a graphite-like structure (Figure 8) and is an excellent high temperature, chemically resistant lubricant. Unlike graphite, boron nitride is a white solid that does not conduct electricity. This difference is possibly due to differences in the way the layers in the two crystals are stacked. The layers in the graphite-like form of boron nitride are almost exactly the same distance apart as those in graphite, but the boron nitride layers are organized so that the nitrogen atoms in one layer are situated directly over boron atoms in the layers above and below, and vice versa. This arrangement is logical, because the partially positive boron atoms and partially negative nitrogen atoms are likely to be electrostatically attracted to each other. By contrast, the carbon atoms in one layer of graphite are directly over the center of the carbon rings in the layers above and below. An alternative reason for the lack of electrical conductivity is the weaker aomaticity in the layers due to the differing electronegativities of boron an nitrogen.

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Boron nitride Graphite

Fig. 8. Comparative layer structures of boron nitride and araphite.

Chemical reactions with boron nitride :

$2BN + 3H_2O\ (vapor) = B_2O_3 + 2NH_3\ (800^\circ C)$.

$4BN + 3O_2 = 2B_2O_3 + 2N_2\ (above\ 700^\circ C)$.

$2BN + 3F_2 = 2BF_3 + N_2\ (normal\ temp.)$.

$BN + 4HF\ (cone.) = NH_4[BF_4]\ (normal\ temp.)$.

$BN + NaOH\ (come.) + 3H_2O = Na[B(OH)_4] + NH_3\ (boiling)$.

10.3.4 Boric Acid

The chemica formula of boric acid is H_3BO_3 [or $B(OH)_3$]. The chemical structure of boric acid is shown below :

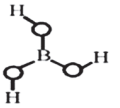


Fig. 9. Structure of Boric acid.

The central boron atom is connected to three hydroxyl (-OH) groups, which are capable of strong hydrogen bonding. Its solid crystalline structure consists of parallel layers of boric acid held together in place by hydrogen bonds. Boric acid is prepared by reacting minerals such as borax ($Na_2B_4O_7.10\ H_2O$), with strong acids like HCl:

$$Na_2B_4O_7 - 10H_2O + 2\ HCl \rightarrow 4\ H_3BO_3 + 2\ NaCl + 5\ H_2O$$

It can also be prepared by the hydrolysis of boron trihalides (such as BBr_3) or diborane (B_2H_6) :

$$BBr_3 + 3\ H_2O \rightarrow B(OH)_3 + 3\ HBr$$

$$B_2H_6 + 6\ H_2O \rightarrow 2\ B(OH)_3 + 6H_2$$

Boric acid is a weak monobasic acid, and is considered a Lewis acid. It dissolves in boiling water and in anhydrous sulfuric acid. When heated to high temperatures (over 170°C), it undergoes dehydration to form metaboric acid (HBO_2) :

$$H_3BO_3 \rightarrow HBO_2 + H_2O$$

Boric acid is non-toxic with antibacterial properties, and it is mainly used as an antiseptic agent, acne treatment, preservative, insecticide, pH buffer, swimming pool chemical, flame retardant, and a precursor to many useful chemicals. It is used industrially for the manufacture of fiberglass, household glass products and the glass used in LCD displays.

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Chemical reaction with boric acid:

$$B(OH)_3 = HBO_2 + H_2O \ (70 - 160^\circ C),$$

$$2B(OH)_3 = B_2O_3 + 3H_2O \ (235^\circ C).$$

$$B(OH)_3 (diluted) + H_2O = [B(H_2O)(OH)_3],$$

$$[B(H_2O)(OH)_3] + H_2O = [B(OH)_4]^{(-)} + H_3O^{(+)}$$

$$4B(OH)_3 + 2NaOH (\text{diluted}) = Na_2B_4O_7 + 7H_2O,$$

$$B(OH)_3 + NaOH (\text{saturated}) = Na[B(OH)_4].$$

$$B(OH)_3 + NaOH = NaBO_2 + 2H_2O (350 - 400^\circ C).$$

$$2B(OH)_3 + Na_2CO_3 = 2NaBO_2 + CO_2 + 3H_2O (\text{above } 850^\circ C).$$

$$B(OH)_3 + 4HF (\text{conc.}) = H[BF_4] + 3H_2O.$$

10.3.5 Borax

Sodium tetraborate decahydrate ($Na_2B_4O_7, 10H_2O$)

Salts of boric acids are called borates, Borax is sodium salt of tetraboric acid and is an important borate. Borax is obtained when boric acid is boiled with soda ash(Na_2CO_3)

$$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2 + 6H_2O$$

It is also obtained by boiling finely powdered colemanite [$Ca_2B_6O_{11}, 5H_2O$] with measured amount of Na_2CO_3 solution. On cooling it crystallizes out from the solution.

$$2Ca_2B_6O_{11} + 3Na_2CO_3 + H_2O = 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$$

Borax is now represented as $Na_2[B_4O_5(OH)_4], 8H_2O$

Th aqueous solution of borax is alkaline

$$Na_2[B_4O_5(OH)_4] + H_2O \rightarrow 2NaBO_2 + 2H_3BO_3$$

On heating it first swells losing water molecules. On further heating gives $NaBO_2$ and B_2O_3. A glossy bead is formed. When this glossy bead is heated strongly with coloured metal salts, specific colour beads are obtained. This offers a means of identifying certain metal ions like Cu, Co, Cr, Ni, Fe, etc.

$$CuSO_4 (\text{with heat}) \rightarrow CuO + SO_3$$

$$CuO + B_2O_3 \rightarrow Cu(BO_2)_2 \ (\text{green in oxidisisng flame})$$

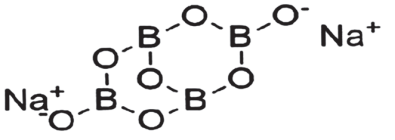


Fig. 10. structure of Borax

Chemical reactions with sodium tetraborate :

$$Na_2B_4O_7 \cdot 10H_2O = Na_2B_4O_7 + 10H_2O(380°C).$$

$$Na_2B_4O_7(diluted) + 8H_2O = 2[Na(H_2O)_4]^{(+)} + B_4O_7^{2-}$$

$$B_4O_7^{2-} + 11H_2O = 4[B(H_2O)(OH)_3] + 2OH^-$$

$$Na_2B_4O_7 + 2HCl(diluted) + 9H_2O = 2NaCl + 4[B(H_2O)(OH)_3],$$

$$Na_2B_4O_7 + 2H_2SO_4(conc.) + 5H_2O = 4B(OH)_3 \downarrow + 2NaHSO_4(40-50°C).$$

$$Na_2B_4O_7 + 7H_2O + 2NaoH(saturated) = 4Na[B(OH)_4],$$

$$Na\ B_4O_7 + 2NaOH = 4NaBO_2 + H_2O(700-750°C).$$

$$Na_2B_4O_7 + 3B_2O_3 = 2NaB_5O_8(650-700°C).$$

$$Na_2B_4O_7 + CoO = 2NaBO_2 + Co(BO_2)_2(blue)[750-800°C].$$

$$Na\ B_4O_7 + 2H_2SO_4(conc.) + 12C_2H_5OH = 4B(C_2H_5O)_3 \uparrow$$
$$+ 2NaHSO_4 + 7H_2O \text{ (normal temp.)},$$

10.4 C-Si-Ge-Sn-Pb

10.4.1 Introduction

The group 14 elements are the second group in the periodic table's p-block. It is also known as the carbon group. Carbon (C), Silicon (Si), Germanium (Ge), Tin (Sn), Lead (Pb) are members of this group.

The general electronic configuration of the group 14 elements is $ns^2\ np^2$.

The outermost p orbitals of these elements contain two electrons. Because all of the elements in group 14 have four electrons in their outermost shell, their valency is four. They use these electrons in bond formation to achieve an octet configuration.

10.4.2 Oxidation States and Inert pair Effect

The general oxidation states of group 14 elements are +4, and +2. The tendency to form +2 ions increases as we move down the group. This is because of the inert pair effect. P-block elements exhibit this effect. This is explained by the inert pair effect. It is the absence of the s-orbital during bonding due to insufficient shielding of the intervening electrons.

Electrons fill the d and f orbitals of elements such as Sn and Pb. Because the d and f orbitals have poor shielding abilities, the nuclear charge that seeps through attracts the s orbital closer to the nucleus. As a result, the s-orbital is reluctant to bond, and only the p electrons are involved in bonding. As a result, Pb^{+4} is an excellent oxidizing agent.

10.4.3 Chemical Properties of Group 14 elements

- **Covalent Radii:** The radii of group 14 elements are smaller than those of group 13. The increase in the effective nuclear charge can explain this. The increase in radii from C to Si is significant, followe by a smaller increase in radii. This is due to poor shielding of the d and f orbitals, which increases th effective nuclear charge, causing the radii to be small.
- **Ionization Enthalpy:** Group 14 elements have higher ionization energy than group 13 elements. Th can be attributed to physical size. The Ionization Enthalpy decreases as one moves down the group From C to Si, there is a sharp decrease, followed by a nominal decrease. The following is the order: **> Si > Ge > Pb >Sn.** Due to ineffective shielding of the d and f orbitals, Pb has a higher Ionization Enthalpy than Sn in this case.
- **Electronegativity:** Because of their small size, the elements in this group have slightly more electronegativity than the elements in group 13. The electronegativity values of elements ranging from Si to Pb are nearly identical.

10.4.4 Physical Properties of Group 14 elements

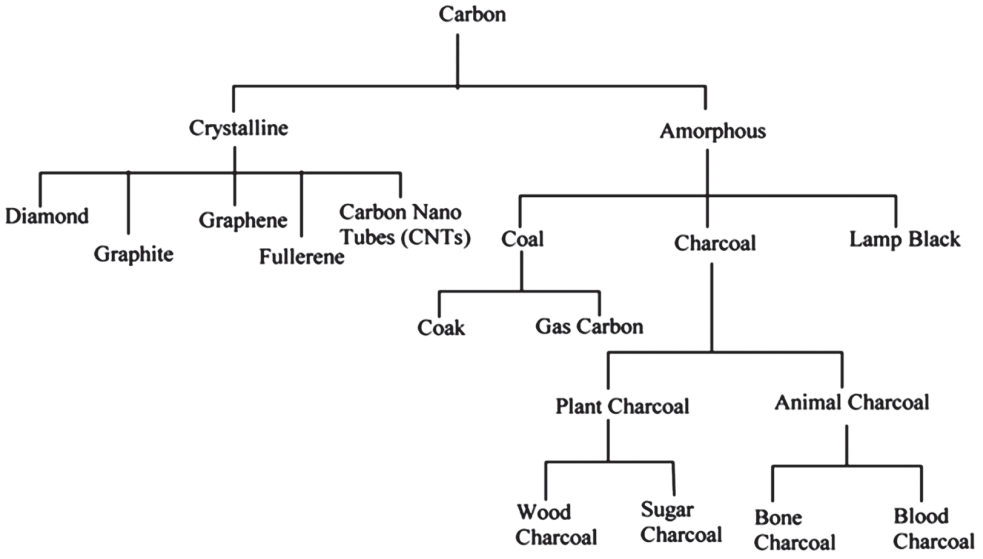
- **Metallic Character:** Due to their small size and high ionization enthalpy, group 14 elements are less electropositive than group 13. The metallic character grows stronger as you progress through the group. Sn and Pb are soft metals with low melting points, while C and Si are nonmetals and Ge is a metalloid.
- **Melting and Boiling Points:** Carbon, silicon, and germanium have extremely high melting and boiling points due to their extremely stable solid structures. Because of the inert pair effect, Sn and Pb have a lower melting point because only two bonds are formed instead of four. Carbon has a very high melting point. All of the elements in group-14 have a diamond-like lattice structure that is extremely stable in nature. These highly stable lattice structures are broken as a result of the melting process. As the size of the atoms increases, the melting point decreases down the group as the M-M bonds are reduced. Because tin and lead are metals, their melting points are significantly lower.
- **Four Covalent Compounds:** Four covalent compounds are those in which the four electrons in the valence shell actively participate in bonding. This property is shared by the majority of the elements in Group 14.
- **Density:** Density rises as the atomic number rises due to an increase in mass per unit volume down the group.

10.4.5 Allotropy in Carbon

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The allotropes of carbon exist in the nature are classified broadly into two categories (1) crystalline carbon and (2) amorphous carbon.

There are five types of crystalline forms of carbon is available; they are (1) Diamond (2) Graphite (3) Graphene (4) Fullerene and (5) Carbon Nano Tubes (CNTs)



Diamond: Diamond is transparent and extremely shining. It is the hardest form of carbon not only the hardest among the all allotropes but also it is the hardest usable substance in the earth. It is 150 times harder than the carborundum (silicon carbide). Its density is 3.52 g/cc and refractive index is 2.42. Its heat of combustion is 7.873 k cal/g. It is non-conductor of heat and electricity. Its reactivity is low, under normal condition it does not react with acid and bases but if it is melted with Na_2CO_3 then diamond is converted into carbon monoxide and sodium oxide. If it is combusted with oxygen and fluorine around 700-800^{0}C then it forms CO_2 and CF_4 respectively.

$Na_2CO_3 + C = Na_2O + 2CO$ $\qquad$ $2C + O_2 + 2F_2 = CO_2 + CF_4$

Structure of diamond: Structural information of the diamond was obtained from the X-ray diffraction studies of its single crystal. It forms a cubic crystal where each carbon atom is sp^3 hybridized and is attached to four other carbon atoms with a single bond to form the entire three dimensional networks. C-C bond distance is 1.54Å.

The melting point and boiling point of diamond is very high because of this sigma bonding network. Melting and boiling requires breaking of these strong sigma bonds which require huge energy.

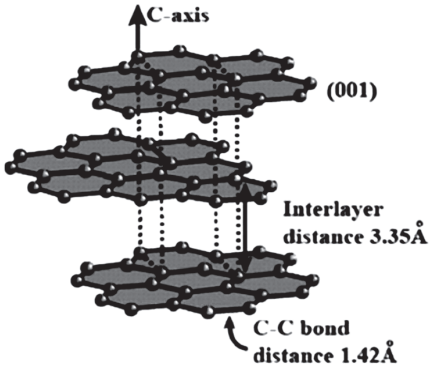
Each valence electron of carbon atom is strongly bonded with the other carbon atoms with strong sigma bonds. There is no π-bond present in diamond. As there are no free or loosely held electrons present in the diamond it cannot conduct heat or electricity.

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Graphite: It is another form for carbon which is opaque, soft and greasy to touch. It has metallic lustre and it conducts heat and electricity. Its density is 2.26g/cc, which is lesser than diamond.

In graphite each carbon atom is attached with three other carbon atoms through covalent bonds to form a planer hexagonal arrangement. Graphite is made up of layers of planer hexagonal sheets and the distance between the two consecutive layers is 3.35Å. Each layer is held with the other by weak van der Waal's forces. Each carbon of graphite is sp^2 hybridised has loosely held ð-electrons which is responsible for its electrical conductivity.





Graphene: Graphene is a super thin, super strong and transparent crystalline allotrope of carbon with. Its carbon atoms are densely packed in a regular hexagonal honeycomb pattern like graphite. It is conductive and self-repairing material. Each atom has four bonds, one σ-bond with each of its three neighbours and one π-bond that is oriented out of plane.

Fullerene: This is the spherical shaped allotrope of carbon characterized first in 1985. The molecular formula of the first reported fullerene is C_{60}, where 60 carbon atoms are arranged in 20 six-memebered and 12 five-memebered rings to from a football or a bucky ball like shape. Buckminster used this shape in his architecture that is why it is known as buckmister fullerene. 1996 Nobel Prize in chemistry was awarded to Richard Smalley and Harry Kroto for the discovery of fullerene.

Thin films of C_{60} are mustard-coloured but in bulk it appears dark brown. Films of C_{70} are red-brown and grey-black in bulk. Solution of C_{60} is magenta coloured where as the C_{70} solution is dull-red. Both the solids have very high melting points they dissolve slowly in organic solvent only. Each carbon atom of the fullerene molecule may be supposed to be sp^2 hybridized and attached with three other carbon atoms with covalent bonds. Two different C-C bond distances 1.40 and 1.50 Å were observed in its structure.

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10.4.6 Allotropes of Carbon

Carbon Nano Tubes (CNTs): When a layer of graphene is wrapped in shape of cylinder and bonded together to form a tube then it is called carbon nano tubes. In 1991 a Japanese scientist Sumio Iijima first discovered the carbon nanotubes. The outer radius of the carbon nanotubes may vary from 1-30 nm.



10.4.7 Silicon and Compounds

"Si" is the chemical symbol for **silicon**, a non-metallic element with atomic number **14** in the periodic table. It is one of the most abundant elements in the Earth's crust, primarily found in the form of silicon dioxide (**SiO_2**, also known as quartz) and silicate minerals.

Compounds of Silicon

Silicon forms a variety of compounds, primarily with oxygen and other elements. These compounds are widely used in industries such as electronics, construction, and medicine. Here are some of the most important **compounds of silicon**:

1. Silicon Dioxide (SiO_2) – Silica

- **Occurrence:** Found naturally as quartz, sand, and various minerals.
- **Structure:** A three-dimensional network of Si and O atoms.
- **Uses:**
  - Manufacturing of **glass, ceramics, and cement**.
  - Used as an **abrasive** in toothpaste and polishes.
  - Present in **optical fibers** for telecommunications.

2. Silicones:

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Silicones, more correctly called polysiloxanes, constitute an enormous family of polymers, and they all contain a chain of alternating silicon and oxygen atoms. Attached to the silicon atoms are pairs of organic goups, such as the methyl goup, $-CH_3$. The structure of this simplest silicone is shown in Fig. 27, where the number of repeating units, n, is very large. To synthesize this compound, chloromethane, CH_3Cl, is passed over a coper-silicon alloy at 300°C. A mixture of compounds is produced, including $(CH_3)_2SiCl_2$:

$$2CH_3Cl(g) + Si(s) \xrightarrow{\Delta} (CH_3)_2SiCl_2(l)$$

Water is added, causing hydrolysis :

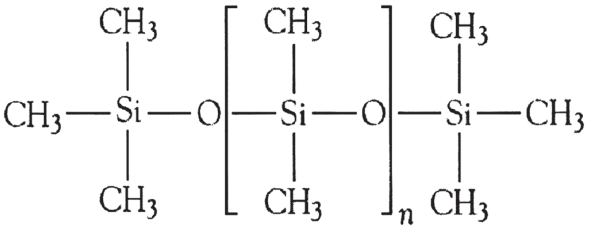
$$(CH_3)_2SiCl_2(l) + 2H_2O(l) \rightarrow (CH_3)_2Si(OH)_2(l) + 2HCl(g)$$

The hydroxo compound then polymerizes, with loss of water :

$$n(CH_3)_2Si(OH)_2(l) \rightarrow [-O - Si(CH_3)_2-]n(l) + H_2O(l)$$

Silicones are used for a wide variety of purposes. The liquid silicones are more stable than hydrocarbon oils. In addition, their viscosity changes little with temperature, whereas the viscosity of hydrocarbon oils changes dramatically with temperature. Thus, silicones are used as lubricants and wherever inert fluids are needed, for example, in hydraulic braking systems. Silicones are very hydrophobic, hence, they are used in water-repellent sprays for shoes and other items. By the cross-linking of chains, silicone rubbers can be produced. Like the silicone oils, the rubbers show great stability to high temperature and to chemical attack. Their multitudious uses include the face-fitting edges for snorkel adn scuba masks. The rubbers also are very useful in medical applications, such as transfusion tubes. However, silicone gels have attained notoriety in their role as a breast implant material. While sealed in a polymer sack, they are believed to be harmless. The major problem arises when the container walls leak or break. The silicone gel can then diffuse into surrounding tisues. The chemical inertness of silicones turns from a benefit to problem, because the body has no mechanism for breaking down the polymer molecules. Many medical personnel believe that these alien gel fragments trigger the immune system, thereby causing a number of medical problems. The advantages of the silicone polymers over carbon-based polymers result from several factors. First, the silicon-oxygen bond in the backbone of the molecule is stronger than the carbon-carbon bond in the organic polymers (452 *kJ/mol*, compared to about 346 *kJ/mol*), making the silicon-based polymers more resistant to oxidation at high temperatures. It is for this reason that high-temperature oil baths always utilize silicone oils, not hydrocarbon oils. The absence of substituent on the oxygen atoms in the chain and the wider bond angle (*Si–O–Si* is 143° compared with 109° for *C–C–C*) results in the greater flexibility of a silicone polymer.

E-copy



It is interesting to note that Silicones are water repellent while alkyl substituent chlorisilanes readily undergo hydrolysis. It is believed that in silicones '*Si-O*' bonds have some double bond character. The π bonds are formed between filled *p* orbitals of '*O*' and empty d orbitals of Si. These π bonds make the *d* orbitals unavailable for nucleophilic attack by H_2O

Silicates:

About 95 percent of the rocks of the Earth's crust are silicates, and there is a tremendous variety of silicate minerals. The simplest silicate ion has the formula SiO_4^{4-}; zirconium silicate, $SrSiO_4$, the gemstone zircon, being one of the few minerals to contain this ion. Silicates ar generally very insoluble, as one might expect of rocks that have resisted rain for millions of years. The one common exception is sodium silicate, which can be prepared by reacting solid silicon dioxide with molten sodium carbonate :

$$SiO_2(s) + 2Na_2CO_3(l) \xrightarrow{\Delta} Na_4SiO_4(s) + 2CO_2(g)$$

A concentrated solution of sodium (ortho) silicate is called water glass, and it is extermely basic as a result of hydrolysis reactions of the silicate antion. Before modern refrigeration became available, the water glass solution was used to preserve eggs, the soft porous shell of calcium carbonate being replaced by a tough, impervious layer of calcium silicate that seals in the egg contents :

$$2CaCO_3(s) + SiO_4^{4-}(aq) \rightarrow Ca_2SiO_4(s) + CO_3^{2-}(aq)$$

The silicates are classified on the basis of the way by which the $(SiO_4)^{4-}$ tetrahedral units are linked together.

❑ **Orthosilicates :** These contain discrete tetrahedral SiO_4^{4-} unit. Example : Phenacite [Be_2SiO_4], Zircon [$ZrSiO_4$]

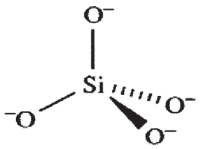


Fig. 30. Orthosilicate

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❑ **Pyrosilicates :** These contain $(Si_2O_7)^{6-}$ units formed by joining two tetrahedral units through one oxygen atom. Ex. Thortveitite $(Sc_2Si_2O_7)$

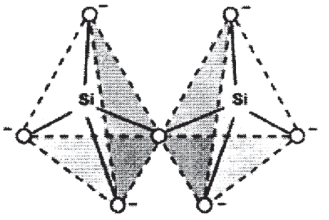


Fig. 31. Pyrosilicates

❑ **Cyclic Silicates :** Tetrahedra sharing two '*O*' atoms to form a ring structures with either $[Si_3O_9]^{6-}$ or $[Si_6O_{18}]^{12-}$ anions. Ex. Wollastonite, $Ca_3[Si_3O_9]$

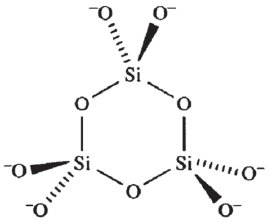


Fig. 32. Cyclic silicates

❑ **Chain Silicates :** An open chain linear polymeric structure is possible if the tetrahedra share two '*o*' atoms. This contains $(SiO_3)_n^{2n-}$. Example : Pyroxenes $(MgSiO_3)$

❑ **Three dimensional Silicates :** Sharing all four corners of tetrahedral gives an infinite three dimensional frame work. Example : Silica $[(SiO_2)_n]$

❑ **Sheet Silicates :** An infinite two dimensional structure with empirical formula $(Si_2O_5)_n^{2n-}$ is obtained when SiO_4 tetrahydra share three cornrrs. Example : Mica Sheet.

10.5 O-S-Se-Te

10.5.1 Introduction

O-S-Se-Te refers to a quaternary chalcogenide system composed of oxygen (O), sulfur (S), selenium (Se), and tellurium (Te). These elements belong to Group 16 of the periodic table and exhibit a wide range of chemical and physical properties. Their combination in various ratios can lead to the formation of novel materials with tunable electronic, optical, and catalytic characteristics.

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Chalcogenide materials containing oxygen, sulfur, selenium, and tellurium are of significant interest due to their applications in semiconductors, photovoltaics, thermoelectrics, and optoelectronic devices. The gradual substitution of lighter chalcogens (O, S) with heavier ones (Se, Te) alters properties such as bandgap energy, electrical conductivity, and thermal stability. These materials are also explored for their role in energy storage, sensors, and phase-change memory applications.

10.5.2 Chemistry and Compounds of Oxygen

10.5.1 1 Introduction to Oxygen

Oxygen (O) is a chemical element with atomic number 8, belonging to Group 16 (chalcogens) of the periodic table. It is a highly reactive nonmetal and the most abundant element in the Earth's crust, second most abundant in the atmosphere (after nitrogen), and essential for life.

10.5.1 2. Atomic and Molecular Properties

- **Atomic Number**: 8
- **Atomic Mass**: 15.999 u
- **Electron Configuration**: $1s^2\ 2s^2\ 2p^4$
- **Oxidation States**: -2 (most common), -1 (in peroxides), +1, +2 (in rare cases)
- **Electronegativity**: 3.44 (Pauling scale)
- **Ionization Energy**: 1313.9 kJ/mol
- **Bonding**: Forms covalent and ionic bonds

10.5.1 3. Allotropes of Oxygen

(a) Dioxygen (O_2)

- The most common form of elemental oxygen.
- A colorless, odorless gas essential for respiration and combustion.
- Exists as a diatomic molecule with a double bond.

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- **Uses**: Industrial oxidation, medical applications, welding.

(b) Ozone (O_3)

- A triatomic molecule of oxygen.
- Forms in the upper atmosphere and absorbs harmful UV radiation.
- Highly reactive and used as an oxidizing agent.
- **Uses**: Disinfection, water treatment, bleaching.

(c) Singlet Oxygen ($^1O_2$)

- A high-energy, excited state of O_2.
- Involved in photochemical reactions and biological oxidative stress.

10.5.1 4. Oxides of Oxygen

Oxygen forms oxides with nearly all elements. The types of oxides include:

(a) Basic Oxides

- Formed with metals (e.g., Na_2O, CaO).
- React with water to form hydroxides.
- **Example**:
  - $Na_2O + H_2O \rightarrow 2NaOH$
  - $CaO + H_2O \rightarrow Ca(OH)_2$

(b) Acidic Oxides

- Formed with nonmetals (e.g., CO_2, SO_3, NO_2).
- React with water to form acids.
- **Example**:
  - $CO_2 + H_2O \rightarrow H_2CO_3$
  - $SO_3 + H_2O \rightarrow H_2SO_4$

(c) Amphoteric Oxides

- Exhibit both acidic and basic behavior (e.g., Al_2O_3, ZnO).
- **Example**:
  - $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ (acidic reaction)
  - $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$ (basic reaction)

(d) Neutral Oxides

- Do not react with acids or bases (e.g., CO, N_2O).

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- **Example**: Carbon monoxide (CO), which is a product of incomplete combustion.

10.5.1 5. Peroxides and Superoxides

(a) Peroxides (O_2^{2-})

- Contain an O–O single bond.
- Highly reactive oxidizing agents.
- **Examples**:
  - Hydrogen peroxide (H_2O_2)
  - Sodium peroxide (Na_2O_2)
  - Barium peroxide (BaO_2)

(b) Superoxides (O_2^-)

- Contain the superoxide ion.
- More reactive than peroxides.
- **Examples**:
  - Potassium superoxide (KO_2)
  - Rubidium superoxide (RbO_2)

10.5.1 6. Oxygen-Containing Acids

Oxygen forms several important oxyacids:

- **Sulfuric Acid (H_2SO_4)**
  - Strong acid, widely used in industries.
  - $H_2SO_4 \rightarrow H^+ + HSO_4^-$
- **Nitric Acid (HNO_3)**
  - Strong acid, used in fertilizers and explosives.
  - $HNO_3 \rightarrow H^+ + NO_3^-$
- **Carbonic Acid (H_2CO_3)**
  - Weak acid, important in buffering blood pH.
  - $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
- **Phosphoric Acid (H_3PO_4)**
  - Used in fertilizers and food industry.
  - $H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$

10.5.1 7. Organic Compounds Containing Oxygen

(a) Alcohols (R-OH)

- Contain hydroxyl (-OH) groups.
- Example: Ethanol (C_2H_5OH)

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(b) Ethers (R-O-R')

- Oxygen bonded to two alkyl groups.
- Example: Dimethyl ether (CH_3OCH_3)

(c) Aldehydes and Ketones

- Contain carbonyl (C=O) groups.
- Examples:
  - Aldehyde: Formaldehyde (HCHO)
  - Ketone: Acetone (CH_3COCH_3)

(d) Carboxylic Acids (R-COOH)

- Contain carboxyl (-COOH) groups.
- Example: Acetic acid (CH_3COOH)

(e) Esters (R-COO-R')

- Derived from carboxylic acids and alcohols.
- Example: Methyl acetate (CH_3COOCH_3)

10.5.1 8. Industrial and Biological Importance

(a) Industrial Uses

- Steelmaking (oxygen blowing in blast furnaces).
- Combustion and rocket propulsion.
- Chemical manufacturing (e.g., H_2O_2 production).
- Water treatment (ozonation).

(b) Biological Role

- Essential for cellular respiration (O_2 in mitochondria).
- Present in hemoglobin for oxygen transport.
- Key component of DNA, proteins, and enzymes.

10.6 Sulphur

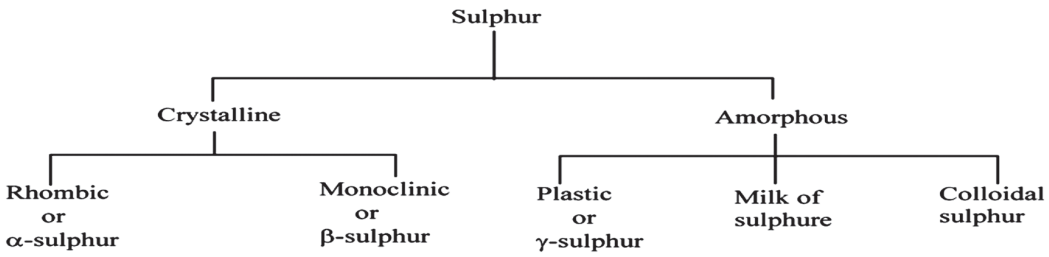
Sulphur (S) is a non-metal element belonging to Group 16 (chalcogens) of the periodic table.

It is an essential element for life and is widely found in nature in elemental form, minerals, and

biological compounds.

Allotropes of Sulphur

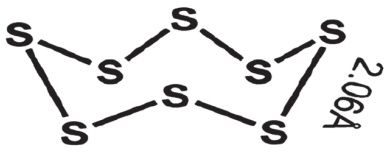
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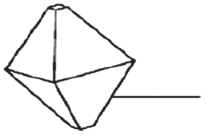


Rhombic sulphur: It is the most stable form of sulphur with melting point 112.8°C. Its density is 2.06 g/cc and it is highly soluble in CS_2.

It is prepared by the slow evaporation of the solution of roll sulphur in CS_2. It forms transparent lemon yellow crystals. Its molecular formula is S8. X-ray diffraction study with the crystals has shown that eight membered ring is formed by the sulphur atoms with S-S bond distance 2.06Å and SSS bond angles 102-108^0.

Monoclinic sulphur: It is unstable at ordinary temperature but stable above 95.5°C. It is prepared by the evaporation of solution of sulphur in CS_2. Its melting pint is 118.8°C. Its formula is S_8 and forms 8-membered ring like rhombic sulphur.







Compounds of Sulphur

Sulphur Containing Acids

Sulfoxilic acid

It is prepared as a cobalt salt of it by the reaction of sodium hyposulfite and cobalt acetate and by passing ammonia gas through it.

$$Na_2S_2O_4 + Co(CH_3COO)_2 = CoS_2O_4 + 2CH_3COONa$$

$$CoS_2O_4 + 2NH_3 + 2H_2O = CoSO_2 + (NH_4)_2SO_3$$

Sulfoxilic acid is not available in free state it only exists as its salt. It is a dibasic acid. in aqueous solution its salt exhibit reducing properties.

Sulfurous acid

E-copy

It is prepared by passing sufur di-oxide (SO_2) gas into cold water.

$$SO_2 + H_2O = H_2SO_3$$

Pure sulfurous acid could not be prepared. It is a strong di-basic acid. With the reaction of base it forms both acidic and neutral type of salts. Its aqueous solution is reducing in nature.

Hypo-sulfurous acid

It is also known as di-thionous acid. It is prepared by the reduction of sulfurous acid with zinc-amalgum (Zn-Hg).

$$H_2SO_3 + Zn/Hg \longrightarrow H_2S_2O_4 + ZnO + H_2O.$$

Free acid is not available it is available only in aqueous solution. It is a di-basic acid and a very strong reducing agent.

Pyrosulfurous acid

It is only available as its salt. Its salt is prepared by the reaction of sodium or potassium bisulfite with sulfur di-oxide.

$$Na_2SO_3 + SO_2 = Na_2S_2O_5$$

Sulfuric acid

E-copy

It is prepared in two steps. In the first step, sulfur di-oxide is oxidized to sulfur tri-oxide by the atmospheric oxygen using platinum or V_2O_5 as catalyst at 450°C.

In second step, SO_3 is absorbed in 98% sulfuric acid to produce pure H_2SO_4. Actually it reacts with the water present in the 98% H_2SO_4. This method is known as *contact process*.

$$SO_2 + O_2\,(air) \xrightarrow[Pt\ or\ V_2O_5]{450^\circ C} SO_3$$

$$SO_2 + H_2O = H_2SO_4$$

There is another popular method of preparation of H_2SO_4 known as *chamber process*. In this process oxidation of SO_2 is done by NO_2. Then sulfuric acid is prepared by absorbing SO_3 in dilute H_2SO_4.

10.7 Compounds of Selenium (Se)

Selenium (Se) is a Group 16 (chalcogen) element with an atomic number of **34**. It exhibits oxidation states of **-2, 0, +2, +4, and +6**, forming a variety of compounds, including oxides, acids, halides, and organoselenium compounds.

Oxides of Selenium

E-copy

Selenium forms two primary oxides:

(a) Selenium Dioxide (SeO_2)

- **Oxidation State:** +4
- **Physical Properties:** White solid, soluble in water to form selenous acid (H_2SeO_3).
- **Preparation:**

$$Se + O_2 \rightarrow SeO_2$$

- **Chemical Properties:**
  - Dissolves in water:

$$SeO_2 + H_2O \rightarrow H_2SeO_3$$

  - Acts as an oxidizing agent.

(b) Selenium Trioxide (SeO_3)

- **Oxidation State:** +6
- **Physical Properties:** White crystalline solid, strong oxidizing agent.
- **Preparation:**

$$SeO_2 + O_2 \rightarrow SeO_3$$

- **Chemical Properties:**
  - Dissolves in water to form selenic acid:

$$SeO_3 + H_2O \rightarrow H_2SeO_4$$

Selenium Acids

E-copy

Selenium forms oxyacids similar to sulfuric and sulfurous acids.

(a) Selenous Acid (H_2SeO_3)

- **Oxidation State:** +4
- **Weak acid, acts as an oxidizing agent.**
- **Preparation:**

$$SeO_2 + H_2O \rightarrow H_2SeO_3$$

- **Reactions:**
  - Reduction to elemental selenium:

$$H_2SeO_3 + 2SO_2 + H_2O \rightarrow Se + 2H_2SO_4$$

(b) Selenic Acid (H_2SeO_4)

- **Oxidation State:** +6
- **Strong acid, similar to sulfuric acid (H_2SO_4).**
- **Preparation:**

$$SeO_3 + H_2O \rightarrow H_2SeO_4$$

- **Reactions:**
  - Strong oxidizing properties:

$$H_2SeO_4 + HCl \rightarrow Cl_2 + Se + H_2O$$

Selenium Halides

Selenium reacts with halogens to form **selenium halides (SeX_2, SeX_4, SeX_6)**.

(a) Selenium Dichloride ($SeCl_2$)

- **Oxidation State:** +2
- **Prepared by reaction of selenium with chlorine gas.**
- **Preparation:**

$$Se + Cl_2 \rightarrow SeCl_2$$

E-copy

(b) Selenium Tetrachloride ($SeCl_4$)

- Oxidation State: +4
- Pale yellow solid, hydrolyzes in water.
- Preparation:

$$Se + 2Cl_2 \rightarrow SeCl_4$$

(c) Selenium Hexafluoride (SeF_6)

- Oxidation State: +6
- Colorless gas, non-polar molecule.
- Preparation:

$$Se + 3F_2 \rightarrow SeF_6$$

Selenides (Selenium in Oxidation State -2)

Selenium forms **selenides (M_2Se or MSe_2)** with metals.

(a) Hydrogen Selenide (H_2Se)

- Analogous to H_2S, toxic gas with a rotten egg smell.
- Preparation:

$$Se^{2-} + 2H^+ \rightarrow H_2Se$$

- Reaction with oxygen:

$$2H_2Se + O_2 \rightarrow 2Se + 2H_2O$$

(b) Metal Selenides

- **Examples:** ZnSe, CdSe, PbSe.
- **Applications:** Semiconductors, optoelectronics.

6. Organic Selenium Compounds

Selenium forms organoselenium compounds similar to organosulfur compounds.

(a) Selenols (R-SeH)

- Analogous to thiols (R-SH), but less stable.

(b) Selenides (R-Se-R')

- Analogous to sulfides (R-S-R').

(c) Selenoureas and Selenocyanates

- Used in pharmaceuticals and organic synthesis.

Industrial and Biological Importance

(a) Industrial Uses

- **Selenium dioxide (SeO_2)** → Used in glass manufacturing.
- **Metal selenides (CdSe, ZnSe)** → Used in semiconductors, solar cells.
- **Selenic acid (H_2SeO_4)** → Used in oxidizing reactions.

(b) Biological Role

- **Essential trace element:** Part of selenoproteins.
- **Antioxidant properties:** Component of glutathione peroxidase.
- **Deficiency:** Leads to Keshan disease (cardiomyopathy).

10.8 Compounds of Tellurium (Te)

Tellurium forms a variety of compounds with different elements, including oxygen, halogens, hydrogen, and metals. Some important categories of tellurium compounds include:

1. Oxides of Tellurium

- **Tellurium Dioxide (TeO_2)**: A white or yellowish solid, TeO_2 exists in two crystalline forms (α and β). It is amphoteric, meaning it reacts with both acids and bases. It is used in optical and electronic applications.

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- **Tellurium Trioxide (TeO_3)**: A less common compound, TeO_3 is an oxidizing agent and can react with water to form telluric acid.

2. Tellurium Halides

- **Tellurium Tetrachloride ($TeCl_4$)**: A yellow crystalline solid that hydrolyzes in water to form tellurous acid.
- **Tellurium Hexafluoride (TeF_6)**: A volatile, colorless gas used in some chemical applications.
- **Tellurium Diiodide (TeI_2) and Tellurium Tetraiodide (TeI_4)**: These are iodine-containing tellurium compounds with applications in organic synthesis.

3. Tellurium Hydrides

- **Hydrogen Telluride (H_2Te)**: A highly toxic and unstable gas with a foul odor. It is the tellurium analog of hydrogen sulfide (H_2S) and reacts with oxygen to form tellurium dioxide.

4. Tellurium Acids and Their Salts

- **Tellurous Acid (H_2TeO_3)**: Formed when tellurium dioxide dissolves in water. It is weakly acidic and forms tellurites (TeO_3^{2-}) as salts.
- **Telluric Acid (H_6TeO_6 or H_2TeO_4)**: A stronger acid than tellurous acid, it forms tellurates (TeO_6^{2-}) and is used as an oxidizing agent.

5. Tellurium Organometallic Compounds

- **Dimethyl Telluride ($(CH_3)_2Te$)**: A volatile organotellurium compound that has applications in semiconductor manufacturing.
- **Tellurophenes**: Analogous to thiophenes, these are aromatic compounds containing a tellurium atom in the ring.

6. Metal Tellurides

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- **Silver Telluride (Ag_2Te), Lead Telluride (PbTe), and Bismuth Telluride (Bi_2Te_3)**: These semiconducting materials are widely used in thermoelectric devices.
- **Cadmium Telluride (CdTe)**: A key material in solar cells and optoelectronic applications.

10.9 F-Cl-Br-I

10.9.1 Brief Introduction on F-Cl-Br-I

Fluorine (F), Chlorine (Cl), Bromine (Br), and Iodine (I) belong to the halogen group (Group 17) in the periodic table. These elements share similar chemical properties due to their high electronegativity and ability to form halide compounds. Fluorine is the most reactive and electronegative, followed by chlorine, bromine, and iodine, with reactivity decreasing down the group. They play crucial roles in various industrial, biological, and pharmaceutical applications, including disinfectants, flame retardants, and organic synthesis.

10.9.2 Chemistry of Fluorine

Fluorine (F) is a highly reactive, pale yellow gas at room temperature and is the most electronegative element on the periodic table (electronegativity: **3.98**). It belongs to the halogen group (**Group 17**) and has the atomic number **9**.

Chemical Properties of Fluorine

1. **High Reactivity**
    - Fluorine is the most reactive non-metal and can react with almost all elements, including noble gases like xenon and krypton.
    - Its strong oxidizing power allows it to form compounds with even the least reactive elements.
2. **Strong Bonding with Hydrogen**
    - Forms **hydrogen fluoride (HF)**, a weak acid in dilute form but a very strong acid in concentrated form (hydrofluoric acid).
    - HF forms strong hydrogen bonds, giving it unique properties compared to other hydrogen halides.
3. **Formation of Fluorides**

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- Fluorine forms stable **ionic fluorides** (e.g., NaF, CaF_2) and **covalent fluorides** (e.g., SF_6, BF_3).
- Fluorides are widely used in industrial and medical applications (e.g., toothpaste, Teflon, and pharmaceuticals).

4. **Oxidation States**
   - Fluorine always exhibits a **-1-oxidation state** in compounds.
   - It never shows positive oxidation states because it is the most electronegative element.
5. **Reactivity with Water**
   - Fluorine reacts violently with water, forming **oxygen and hydrogen fluoride**: $2F_2+2H_2O \rightarrow 4HF+O_2$
   - Unlike chlorine, it does not form oxoacids like HFO.
6. **Reaction with Metals and Nonmetals**
   - Reacts directly with most metals to form fluorides: $2Na+F_2 \rightarrow 2NaF_2$
   - Can also react with nonmetals, forming compounds like **carbon tetrafluoride (CF_4)** and **sulfur hexafluoride (SF_6)**.
7. **Interaction with Noble Gases**
   - Fluorine can form compounds with noble gases, such as **XeF_2, XeF_4, and XeF_6**, due to its extreme reactivity.

Uses of Fluorine and Fluorides

- **Teflon (Polytetrafluoroethylene, PTFE):** Used for non-stick cookware.
- **Fluorinated Pharmaceuticals:** Used in anesthetics (e.g., Sevoflurane) and antidepressants (e.g., Fluoxetine).
- **Nuclear Industry:** UF_6 is used in uranium enrichment.

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- **Toothpaste & Water Fluoridation:** Sodium fluoride (NaF) and stannous fluoride (SnF_2) help prevent dental cavities.

10.9.3 Chemistry of Chlorine

1. General Properties:

- Atomic number: **17**
- Electronic configuration: **[Ne] $3s^2$ $3p^5$**
- Oxidation states: **-1, +1, +3, +5, +7**
- Exists as a diatomic molecule **(Cl_2)** in nature
- Highly reactive non-metal and strong oxidizing agent

2. Reactivity and Compounds:
Chlorine is highly reactive due to its strong electronegativity (**3.16**) and tendency to gain one electron to achieve a stable octet.

(a) Reaction with Metals

- Forms metal chlorides: $2Na+Cl2 \rightarrow 2NaCll$
- Most metal chlorides are **ionic**, but some (like $AlCl_3$) show covalent character.

(b) Reaction with Non-Metals

- Forms covalent compounds like:
- $P4+6Cl_2 \rightarrow 4PCl_3$
- $P4+6Cl_2 \rightarrow 4PCl_3$
- $PCl_3+Cl2 \rightarrow PCl_5$

Oxyacids of Chlorine:

Chlorine forms four oxyacids in increasing oxidation states:

1. **Hypochlorous acid ($HClO$, +1)**
2. **Chlorous acid ($HClO_2$, +3)**
3. **Chloric acid ($HClO_3$, +5)**
4. **Perchloric acid ($HClO_4$, +7)**

4. Uses of Chlorine:

- **Disinfectant** (water purification, bleach)
- **Production of PVC** (polyvinyl chloride)
- **Chlorinated organic compounds** (solvents, pesticides)
- **Pharmaceuticals** (drugs, antiseptics)
- **Paper and textile industries** (bleaching agent)

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Chlorine oxides

Like nitrogen, there are chlorine oxides in which chlorine has every possible odd oxidation state. All of these oxides are thermodynamically unstable but kinetically stable. As a result of this and a low activation energy of decomposition, they are very unstable and have a tendency to explode. However, there are two oxides of importance, both of which have unpaired electrons; that is, they are free radicals. The first of these is chlorine monoxide, which is environmentally important even though it exists only in the upper atmosphere. The second is chlorine dioxide. Chlorine dioxide is a strong oxidizing agent, and it is becoming increasingly important as a disinfectant.

❑ Chlorine Monoxide :

Many species that are too unstabl to exist in significant concentrations at ambient temperature and pressure play important roles in atmospheric chemistry. Another important atmospheric molecule is chlorine monoxide, *ClO*. Chlorine monoxide is a key stratospheric species responsible for causing the "ozone hole," a decrease in *UV*-filtering ozone concentration over the south and, to a lesser extent, north polar regions during their respective spring seasons. The saga is believed to begin with the buildup of chlorine molecules, predominantly from the breakdown of *CFCs* during the dark winter in the isolated air mass over the Antarctic. With the arrival of spring, sunlight causes the weakly bonded chlorine molecules (bond energy 242 *Kj/mol*) to dissociate into chlorine atoms :

$$Cl_2(g) \xrightarrow{h\upsilon} 2Cl(g)$$

The chlorine atoms react with ozone (trioxygen) to give chlorine monoxide and dioxygen :

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$$

If the reaction terminated here, the damage to the oxone layer would be minimal. However, the chlorine monoxide takes part in a reaction cycle that regenerates the chlorine atoms, causing this process to be catalytic. That is, the chlorine atom acts as a catalyst for the conversion of ozone to dioxygen. The first step in this process is the combination of two chlorine monoxide radicals to form the *ClOOCl* dimer molecule. However, dissociation would immediately occur unless the to radicals simultaneously collide with a third body, *M*. It is the role of the species *M* to remove the excess energy. The identity of *M* is any molecule that can remove the energy—usually dinitrogen, N_2, or dixygen, O_2, as these are the most common atmospheric molecules.

$$2ClO(g) + M(g) \rightarrow Cl_2O_2(g) + M^*(g)$$

Sunlight again becomes involved, this time to fission the Cl_2O_2 molecule asymmetrically :

$$Cl_2O_2(g) \xrightarrow{h\upsilon} ClOO(g) + Cl(g)$$

The *ClOO* species is very unstable and rapidly breaks down to give a chlorine atom and a dioxygen molecule :

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$$ClOO(g) \rightarrow Cl(g) + O_2(g)$$

Then the chlorine atmos are again available to react with ozone molecules. It is this catalytic cycle that results in the severe polar ozone depletion.

❑ Chlorine Dioxide

Chlorine dioxide, ClO_2, is a yellow gas that condnses to a deep red liquid at 11°C. The compound is quite soluble in water, giving a fairly stable, green solution. Being a free radical species, chlorine dioxide is paramagnetic, like nitrogen dioxide. Yet unlike nitrogen dioxide, it shows no tendency to dimerize. The chlorine-oxygen bond length is only 140 pm, much shorter than the 170 pm that is typical for a single bond length, and it is very close to that of a typical chlorine-oxygen double bond. Chlorine dioxide, usually diluted with dinitrogen or carbon dioxide for safety, is a very powerful oxidizing agent. For example, to bleach flour to make white bread, chlorine dioxide is 30 times more effective than dichlorine. Large quantities of chlorine dioxide also are used as dilute aqueous solutions for bleaching wood pulp to make white paper. In this role, it is preferred over dichlorine, because chlorine dioxide bleaches without significant formation of hazardous chlorinated wastes. Another advantage of chlorine dioxide is that, unlike dichlorine, it does not attack the cellulose structure, so it preserves the mechanical strength of paper. Similarly, chlorine dioxide is being used increasingly for domestic water treatment, because, in this context too, it does not chlorinate hydrocarbon pollutants that are present in the water to any measurable extent. Chlorine dioxide was used to destroy any anthrax spores contaminating congressional offices during the anthrax-letter scare in 2001. Thus, even though pure chlorine dioxide is explosive, it is of major industrial importance. About 106 tonnes are produced every year worldwide. It is difficult to determine the exact production total, because the gas is so hazardous that it is generally produced in comparatively small quantities at the sites where it is to be used. The synthetic reaction involves the reduction of chlorine in the +5 (ClO_3^-) oxidation state by chlorine in the –1(Cl^-) oxidatin state in very acid conditions to give chlorine in the +4(ClO_2) and 0(Cl_2) oxidation states :

$$2ClO_3^{2-}(aq) + 4H^+(aq) + 2Cl^-(aq) \rightarrow 2ClO_2(g) + Cl_2(g) + 2H_2O(l)$$

Sulfur dioxide is added to reduce (and remove) the dichlorine gas to chloride ion, the sulfur dioxide being simultaneously oxidized to sulfate :

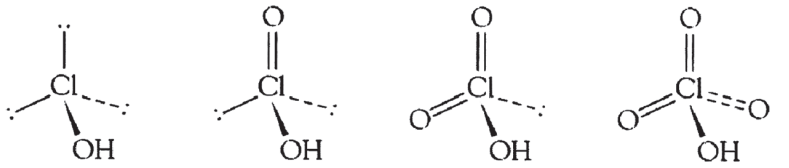
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$

$$SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

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Chlorine oxyacids

Chlorine forms a series of oxyacids and oxyanions for each of its positive odd oxidation states from 11 to 17. The shapes of the ions (and related acids) are based on a tetrahedral arrangement around the chlorine atom (Figure 25). The short chlorine-oxygen bonds in each of the ions indicate that multiple bonding must be present, possibly involving some contribution to the π bonding by the full *p* orbitals on the oxygen atoms and empty *d* orbitals on the chlorine atom.



(*a*) (*b*) (*c*) (*d*)

Fig. 25. A possible representation of the bonding in (*a*) hypochlorous acid, (*b*) chlorous acid, (*c*) chloric acid, and (*d*) perchloric acid.

Acid strength increases as the numebr of oxygen atoms increases. Thus, hypochlorous acid is very weak; chlorous acid, weak; chloric acid, strong; and perhloric acid, very strong.

Hypochlorous acid:

Preparation: It is prepared by the reaction of freshly precipitated HgO with chlorine water and refluxing the filtrate.

$$2HgO + 2Cl_2 + H_2O = 2HOCl + HgO.HgCl_2$$

Pure HOCl is highly unstable in nature. It is stable in cold aqueous solution to be kept in dark. In presence of light it dissociates to produce several products.

$2HOCl = 2HCl + O_2\uparrow$; $HCl + HOCl = H_2O + Cl_2$; $3HOCl = HClO_3 + 2HCl$

It is a monobasic weak acid and can easily produce hypchlorite salt on reaction with a base. It acts as oxidizing agent and its oxidizing power is higher than free chlorine gas.

Cl—OH

E-copy

❑ **Hypochlorous acid and the hypochlorite ion :**

Hypochlorous acid and hydrochloric acid are formed when dichlorine is dissolved in cold water :

$$Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl_2(aq) + HClO(aq)$$

Hypochlorous acid is a very weak acid; thus, solutions of hypochlorites are very basic as a result of the hydrolysis reaction :

$$ClO_2(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$$

Hypochlorous acid is a strong oxidizing agent and, in the process, is reduced to chlorine gas ;

$$2HClO(aq) + 2H^+(aq) + 2e \rightarrow Cl_2(g) + 2H_2O(l) \quad E^\circ = +1.64V$$

The hypochlorite ion, however, is a weaker oxidizing agent that is usually reduced to the chloride ion :

$$ClO^-(aq) + H_2O(l) + 2e \rightarrow Cl^-(aq) + 2OH^-(aq) \quad E^\circ = +0.89V$$

It is this oxidizing (bleaching and bactericidal) power that renders the hypochlorite ion useful. The two compounds of industrial importance are sodium hypochlorite and calcium hypochlorite. Sodium hypochlorite is only stable in solution, not in the solid phase; thus, calcium hypochlorite is used as a solid source of hypochlorite ion. Sodium hypochlorite solution is used in commercial bleach solutions, and for bleaching and decolorization of wood pulp and textiles. Both sodium and calcium hypochlorites are used in disinfection. Calcium hypochlorite is also used as a disinfectant in dairies, breweries, food processing, and bottling plants and in domestic mildew removers.

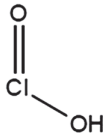
Chlorous acid:

Chlorous acid is prepared by the reaction of barium chlorite with dil. H_2SO_4.

$$Ba(ClO)_2 + H_2SO_4 = BaSO_4 + 2HClO_2$$

It is highly unstable acid and not available in free state. Even in aqueous solution it dissociates.

$$4HClO_2 = 2ClO_2 + ClO_3^- + Cl^- + 2H^+ + H_2O$$



Chloric acid:

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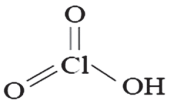
Chloric acid is prepared in similar way that of chlorous acid, barium chlorate is taken instead of barium chlorite.

$$Ba(ClO)_3 + H_2SO_4 = BaSO_4 + 2HClO_3$$

Its aqueous solution is colorless and odorless. Though free chloric acid it is not available but it is relatively more stable than chlorous acid.

Choric acid is a very strong oxidizing agent. It oxidizes sulfur dioxide SO_2 to sulfuric acid.

$$3SO_2 + HClO_3 + 3H_2O = 3H_2SO_4 + HCl$$

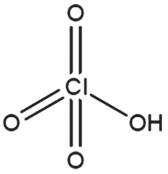


Perchloric acid:

Preparation: It is prepared by refluxing $KClO_4$ with conc. H_2SO_4 at very low pressure (10-20 mm of Hg).

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4$$

Anhydrous perchloric acid is a colourless fuming liquid at room temperature. It is highly explosive in nature. At 90°C it starts boiling but at 92°C it explodes.



❑ **Perchloric Acid :**

The strongest simple acid of all is perchloric acid. The pure acid is a colorless liquid that can explode unpredictably. As a result of its oxidizing nature and high oxygen content, contact with organic materials such as wood or paper causes an immediate fire. Concentrated perchloric acid, usually a 60 percent aqueous solution, is rarely used as an acid but is far more often used as a very powerful oxidizing agent, for example, to oxidize metal alloys to the metal ions so that they can be analyzed. Special perchloric acid fume hoods should be used when these oxidations are performed. Cold dilute solutions of perchloric acid are reasobably safe.

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10.9.4 Chemistry of Bromine

Bromine (Br) is a halogen element with atomic number 35 and belongs to Group 17 of the periodic table. It is a reddish-brown liquid at room temperature and has a strong, choking odor. It is highly reactive and forms compounds with many elements.

Inorganic Compounds of Bromine

(a) Hydrogen Bromide (HBr)

- A colorless gas that dissolves in water to form hydrobromic acid
- A strong acid, used in organic synthesis and industrial processes

(b) Bromine Water (Br_2 Solution)

- An aqueous solution of bromine, used as a test for alkenes (decolorizes due to an addition reaction)
- Acts as a mild oxidizing agent

(c) Metal Bromides (e.g., NaBr, KBr, $CaBr_2$)

- Formed when bromine reacts with metals
- Sodium bromide (NaBr) and potassium bromide (KBr) are widely used in medicine and photography
- Calcium bromide ($CaBr_2$) is used in drilling fluids for oil wells

(d) Silver Bromide (AgBr)

- Light-sensitive compound used in photographic films
- Precipitates as a pale yellow solid in reactions with $AgNO_3$

(e) Bromine Oxides

- Dibromine monoxide (Br_2O): A strong oxidizing agent
- Bromine dioxide (BrO_2) and bromine pentoxide (Br_2O_5): Less common but have strong oxidizing properties

(f) Bromates (BrO_3^-) and Hypobromites (BrO^-)

- Potassium bromate ($KBrO_3$): A powerful oxidizer, once used in baking but now restricted due to health concerns
- Sodium hypobromite (NaOBr): Used as a disinfectant and bleaching agent

2. Organic Compounds of Bromine

(a) Alkyl Bromides (R-Br, e.g., Methyl Bromide CH_3Br)

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- Methyl bromide (CH_3Br): A fumigant (banned in many countries due to ozone depletion)
- Ethyl bromide (C_2H_5Br): Used in organic synthesis

(b) Bromobenzene (C_6H_5Br)

- A precursor in the production of pharmaceuticals and agrochemicals
- Used in Grignard reagent synthesis (C_6H_5MgBr)

(c) Polybrominated Diphenyl Ethers (PBDEs)

- Used as flame retardants in electronics, textiles, and furniture
- Environmental concerns due to their persistence and toxicity

(d) Tetrabromobisphenol A (TBBPA)

- A major flame retardant in plastic and circuit boards

(e) Bromoform ($CHBr_3$)

- Used in chemical research and as a solvent

3. Biologically Important Bromine Compounds

(a) Bromotyrosine Compounds

- Found in marine organisms, have potential pharmaceutical applications

(b) Brominated Disinfectants (e.g., HOBr - Hypobromous Acid)

- Used in water purification and sanitation

10.9.5 Chemistry of Iodine

Iodine (I) is a halogen element with atomic number 53 and belongs to Group 17 of the periodic table. It exhibits a variety of oxidation states, including -1, 0, +1, +3, +5, and +7, allowing it to form several important chemical compounds. Below are some key chemical compounds of iodine:

1. Elemental Iodine (I_2)

- Molecular iodine exists as a diatomic molecule.
- It is a violet-black solid that sublimes into a purple vapor.
- Poorly soluble in water but dissolves well in organic solvents.

2. Iodides (I^-)

- Formed when iodine gains an electron.
- Common iodides:
    - Potassium iodide (KI) – Used in medical treatments and iodized salt.

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- Sodium iodide (NaI) – Used in thyroid medicine and scintillation detectors.
- Hydroiodic acid (HI) – A strong acid used in organic synthesis.

3. Iodates (IO_3^-)

- Contain iodine in the +5-oxidation state.
- Common iodates:
  - Potassium iodate (KIO_3) – Used in iodized salt and as an oxidizing agent.
  - Sodium iodate ($NaIO_3$) – Used in analytical chemistry.

4. Periodates (IO_4^- and IO_6^{5-})

- Contain iodine in the +7-oxidation state.
- Examples:
  - Sodium periodate ($NaIO_4$) – Used as an oxidizing agent in organic synthesis.
  - Potassium periodate (KIO_4) – Used in analytical chemistry.

5. Iodine Oxides

- Iodine forms several oxides, mainly as strong oxidizers:
  - Iodine pentoxide (I_2O_5) – Used for quantitative iodine determination.
  - Iodine trioxide (I_2O_3) – Less common, an unstable compound.

6. Interhalogen Compounds

- Formed between iodine and other halogens:
  - Iodine monochloride (ICl) – A red-brown compound used as a halogenation reagent.
  - Iodine trichloride (ICl_3) – A strong oxidizing agent.
  - Iodine pentafluoride (IF_5) and iodine heptafluoride (IF_7) – Used in fluorination reactions.

7. Organic Iodine Compounds

- Iodoform (CHI_3) – A yellow crystalline compound used as an antiseptic.
- Methyl iodide (CH_3I) – Used in organic synthesis as a methylating agent.
- Thyroxine (T_4) and Triiodothyronine (T_3) – Essential iodine-containing hormones in the thyroid gland.

8. Polyiodides

- Formed in the presence of excess iodine and iodide ions.
- Example: I_3^- (Triiodide ion) – Found in iodine-starch complexes.

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Basic properties of iodine

Iodine is a non-metallic, dark-gray/purple-black, lusturous, solid element. Iodine is the most electropositive halogen and the least reactive of the halogens even if it can still form compounds with many elements. Iodine sublime easily on heating to give a purple vapour. Iodin dissolves in some solvents, such as carbon tetrachloride and it is only slightly soluble in water.

❑ Environmental effects of iodine :

Iodine in ar can combine with water particles and precipitate into water or soils. Iodine in soils will combine with organic matter and remain in the same place for a long time. Plants that grow on these soils may absorb iodine. Cattle and other animals will absorb iodine when they eat these plants.

Iodine in surface water will vaporize and re-enter the air as a result. Humans also add iodine gas to the air, by burning coal or fuel oil for energy. But the amount of iodine that enters the air through human activity is fairly small compared to the amount that vaporize from the oceans. Iodine may be radioactive. The radioactive isotopes are formed naturally during chemical reaction in the atmosphere. Most radioactive isotopes of iodine have very short half-lives and will reshape into stable iodine compounds quickly. However, there is one radioactive form of iodine that has a half-live of millions of years and that is seriously harmful to the environment. This isotope enters the air from nuclear power plants, where it is formed during uranium and plutonium processing. Accidents in nuclear power plants have caused the release of large amounts of radioactive iodine into air.

Interhalogen compounds and polyhalide ions

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There is an enormous number of combinations of pairs of halogens form interhalogen compounds and polyhalide ions. The neutral compounds fit the formu XY, XY_3, XY_5, and XY_7, where X is the halogen of higher atomic mass and Y, that lower atomic mass. All permutations are known for XY and XY_3, but XY_5 is o known where Y is fluorine. Thus, once again, it is only with fluorine that the high oxidaton states are obtained. The formula XY_7, in which X would have the oxidat state of +7, is found only in IF_7. The common argument for the lack of chlorine a bromine analogs is simply that of size : only the iodine atom is large enough accommodate seven fluorine atoms. The interhalogen compounds are of particu interest to inorganic chemists because of their geometries. The shapes of compounds all follow the VSEPR rules, even iodine heptafluoride, IF_7, which has rare pentagonal bipyramidal shape of a seven-coordinate species. All of interhalogens can be prepared by combination reactions of th constituent elemer For example, heating iodine and fluorine in a 1:7 ratio gives iodine heptafluori IF_7 :

$$I_2(g) + 7F_2(g) \rightarrow 2IF_7(g)$$

Bubbling chlorine gas through an aqueous solution of iodide ion gives a brown-black solution of iodine, then dark brown iodine monochloride, and finally pale yellow iodine trichloride :

$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$

$$Cl_2(aq) + I_2(aq) \rightarrow 2ICl(aq)$$

$$Cl_2(aq) + ICI(aq) \rightarrow ICl_3(aq)$$

The simple interhalogens such as iodine monochloride have colors intermediate between those of the constituents. However, the melting points and boiling points of the interhalogens are slightly higher than the mean values of the constituents because the interhalogen molecules are polar. More important, the chemical reactivity of an interhalogen compound is usually similar to that of the more reactive parent halogen. To chlorinate an element or compound, it is often more convenient to use solid iodine monochloride than chlorine gas, although sometimes the nonhalogen atom in the two products has different oxidation states. This outcome can be illustrated for the chlorination of vanadium :

$$V(s) + 2Cl_2(g) \rightarrow VCl_4(l)$$

$$V(s) + 3ICl(s) \rightarrow VCl_3(s) + 3/2I_2(s)$$

When we add the brown solution of the interhalogen to the unsaturated fat, decolorization occurs as the halogens add across the double bond :

$$-CH = CH - + ICI \rightarrow -CH(I) - CH(Cl) -$$

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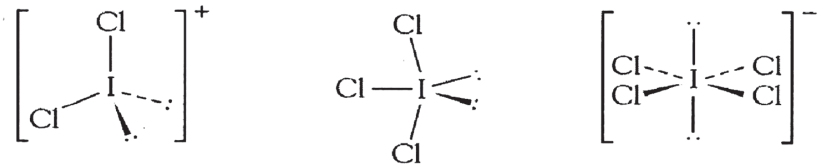
When a permanent brown color remains, the reaction has been completed. The only interhalogen compound produced on an industrial scale is chlorine trifluoride, a liquid that boils at 11°C. It is a convenient and extremely powerful fluorinating agent as a result of its high fluorine content and highbond polarity. It is particularly useful in the separatin of uranium from most of the fission products in used unclear fuel. In aqueous solution, interhalogen molecules are hydrolyzed to the hydrohalic acid of the more electronegative halogen and the hypohalous acid of the less electronegative halogen. For example :

$$BrCl(g) + H_2O(l) \rightarrow HCl(aq) + HBrO(aq)$$

The halogens also form polyatomic ions. Iodine is the only halogen to readily form polyhalide anions by itself. The triiodide ion, (I_3^-) is important becuase its formation provides a means of "dissolving" molecular iodine in water by using a solution of the iodide ion :

$$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

The ion is linear and has equal iodine-iodine bond lengths of about 293 pm; these bonds are slightly longer than the single bond in the diiodine molecule (272 pm). There are many other polyiodide ions, including I_5^- and I_7^- but these are less stable than the triiodide ion. There also are a wide variety of interhalogen cations and anions, for example, the dichloroiodine ion, ICI_2^+ and the tetrachloroiodate ion, ICI_4^- .



(*a*) (*b*) (*c*)

Fig. 26. (*a*) The dichloroidine ion, ICI_2^+ (*b*) the iodine trichloride olecule, ICI_3; and (*c*) the tetrachloroiodate ion, ICI_4^-

10.10 He-Ne-Ar-Kr-Xe

10.10.1 Brief Introduction on He-Ne-Ar-Kr-Xe

Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), and Xenon (Xe) are noble gases belonging to Group 18 of the periodic table. They are colorless, odorless, and chemically inert under normal conditions due to their full valence electron shells. Here's a brief introduction to each:

1. Helium (He)

E-copy

- Lightest noble gas and second-lightest element.
- Has the lowest boiling point of any element (-268.93°C).
- Used in cryogenics, as a coolant for superconducting magnets, and in helium-neon lasers.

2. Neon (Ne)

- Produces a bright red-orange glow in neon signs.
- Used in high-voltage indicators, vacuum tubes, and cryogenic applications.
- Inert and does not form stable compounds under normal conditions.

3. Argon (Ar)

- Third-most abundant gas in Earth's atmosphere (~0.93%).
- Used in welding, incandescent and fluorescent lighting, and as an inert atmosphere for chemical reactions.
- Forms some rare compounds, like argon fluorohydride (HArF).

4. Krypton (Kr)

- Used in high-performance lighting, such as flash lamps and fluorescent bulbs.
- Can form some weakly bound compounds like krypton difluoride (KrF_2).
- Used in ion propulsion systems in space applications.

5. Xenon (Xe)

- Heaviest stable noble gas.
- Used in high-intensity lamps, xenon flash tubes, and ion propulsion for spacecraft.
- Can form stable compounds like xenon hexafluoride (XeF_6) and xenon tetraoxide (XeO_4), showing its ability to participate in chemical bonding.

10.10.2 Xenon fluoride

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Xenon forms three fluorides :

$$Xe(g) + F_2(g) \rightarrow XeF_2(s)$$
$$Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$$
$$Xe(g) + 3F_2(g) \rightarrow XeF_6(s)$$

The product depends on the mole ratios of teh reactants and on the exact reaction conditions of temperature and pressure, although very high partial pressures of difluorine are needed to form the xenon hexafluoride. All three xenon fluorides are white solids and are stable with respect to dissociation into elements at ordinary temperatures; that is, they have negative free energies of formation at 25°C. As noted earlier, it is not necessary to invoke any novel concepts to explain the bonding; in fact, the three compounds are isoelectronic with well-established iodine polyfluoride anions. All the fluorides hydrolyze in water; for example, xenon difluoride is reduced to xenon gas :

$$2XeF_2(s) + 2H_2O(l) \rightarrow 2Xe(g) + O_2(g) + 4HF(l)$$

Xenon hexafluoride is first hydrolyzed to xenon oxide tetrafluoride, $XeOF_4$, which in turn is hydrolyzed to xenon trioxide :

$$XeF_6(s) + H_2O(l) \rightarrow XeOF_4(l) + 2HF(l)$$

$$XeOF_4(l) + 2H_2O(l) \rightarrow XeO_3(s) + 4HF(l)$$

The fluorides are strong fluorinating agents, For example, xenon difluoride can be used to fluorinate double bonds in organic compounds. It is a very “clean” fluorinating agent, in that the inert xenon gas can be easily separated from the required product :

$$XeF_2(s) + CH_2 = CH_2(g) \rightarrow CH_2F - CH_2F(g) + Xe(g)$$

Furthermore, a fluoride in which the other element is in its highest possible oxidation state can be produced by using xenon fluorides as reagents. Thus, xenon tetrafluoride will oxidize sulfur tetrafluoride to sulfur hexafluoride :

$$XeF_4(s) + 2SF_4(g) \rightarrow 2SF_6(g) + Xe(g)$$

10.10.3 Xenon Oxides

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Xenon forms two common oxides : xenon trioxide and xenon tetraoxide. Xenon trioxide is a colorless, deliquescent silid that is quite explosive. The oxide is an extremely strong oxidizing agent, although its rections are often kinetically slow. Because of its lone pair, it is a trigonal pyramidal molecule. Xenon trioxide reacts with dilute base to give the hydrogen xenate ion, $HXeO_4^-$. However, this ion is not stable, and disproportionation to xenon gas and the perxenate ion, XeO_6^{4-} occurs.

$$XeO_3(s) + OH^-(aq) \rightarrow HXeO_4^-(aq)$$

$$2HXeO_4^-(aq) + 2OH^-(aq) \rightarrow XeO_6^{4-}(aq) + Xe(g) + O_2(g) + 2H_2O(l)$$

Perxenates are among the most powerful oxidizing agents known, which is not really surprising considering that the xenon is in the formal oxidation state of +8. For example, they rapidly oxidize manganese(II) ion to permanganate, themselves being reduced to the hydrogen xenate ion :

$$XeO_6^{4-}(aq) + 5H^+(aq) + 2e^- \rightarrow HXeO_4^-(aq) + 2H_2O(l)$$

$$4H_2O(l) + Mn^{2+}(aq) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^-$$

Xenon tetroxide is prepared by adding concentrated sulfuric acid to solid barium perxenate :

$$Ba_2XeO_6(s) + 2H_2SO_4(aq) \rightarrow 2BaSO_4(s) + XeO_4(g) + 2H_2O(l)$$

10.11 Summary

Boron (B) and Its Compounds

Boron, a Group 13 element, forms various important compounds:

- Boranes (B_nH_n) are boron-hydrogen compounds with unique cage-like structures.
- Borazine ($B_3N_3H_6$) is a boron-nitrogen analog of benzene with similar aromatic properties.
- Boron Nitride (BN) exists in structures analogous to graphite and diamond, exhibiting high thermal and chemical stability.
- Boric Acid (H_3BO_3) is a weak monobasic acid used in antiseptics and glass production.
- Borax ($Na_2B_4O_7 \cdot 10H_2O$) is a boron mineral widely used in cleaning agents and ceramics.

Group 14 Elements: C, Si, Ge, Sn, Pb

- The inert pair effect leads to stabilization of lower oxidation states in heavier elements.
- Chemical properties vary, with carbon forming strong covalent bonds, while heavier elements exhibit metallic character.
- Physical properties show increasing density and decreasing electronegativity down the group.

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- Allotropy in Carbon includes diamond, graphite, graphene, fullerenes, and carbon nanotubes.
- Silicon and Its Compounds are essential in semiconductors, ceramics, and silicates.

Group 16: O, S, Se, Te

- Oxygen Chemistry includes molecular oxygen (O_2), ozone (O_3), and oxides.
- Peroxides and Superoxides contain O_2^{2-} and O_2^- ions, respectively.
- Oxygen-containing acids include H_2SO_4 and HNO_3, crucial in industry.
- Organic oxygen compounds include alcohols, ketones, and ethers.
- Sulfur Compounds include sulfides, sulfates, and sulfuric acid.
- Selenium and Tellurium Compounds have applications in electronics and metallurgy.

Group 17: Halogens (F, Cl, Br, I)

- Fluorine is the most reactive, forming strong bonds with metals and nonmetals.
- Chlorine is widely used in disinfectants and PVC production.
- Bromine is a liquid at room temperature, used in flame retardants.
- Iodine is essential for thyroid function and has antiseptic properties.

Group 18: Noble Gases (He, Ne, Ar, Kr, Xe)

- Xenon Fluorides (XeF_2, XeF_4, XeF_6) are stable noble gas compounds.
- Xenon Oxides (XeO_3, XeO_4) have strong oxidizing properties.

10.12 Model Questions

A. Multiple Choice Type Questions

1. Which of the following boron compounds is known as inorganic benzene?

A) Borax
B) Borazine
C) Boric Acid
D) Diborane

Answer: B) Borazine

2. What is the oxidation state of boron in boric acid (H_3BO_3)?

A) +1
B) +2
C) +3
D) 0

Answer: C) +3

3. The inert pair effect is most prominent in which of the following elements?

A) Carbon
B) Silicon
C) Tin
D) Lead

Answer: D) Lead

4. Which of the following allotropes of carbon is the hardest?

A) Graphene
B) Fullerene
C) Diamond
D) Graphite

Answer: C) Diamond

5. What is the molecular formula of ozone?
A) O_2
B) O_3
C) O_4
D) O_2^-
Answer: B) O_3

6. Which of the following is a peroxide?
A) H_2O
B) H_2O_2
C) CO_2
D) $HClO_4$

Answer: B) H_2O_2

7. Which of the following halogens is a liquid at room temperature?
A) Fluorine
B) Chlorine
C) Bromine
D) Iodine

Answer: C) Bromine

8. Which noble gas forms stable compounds with fluorine and oxygen?

A) Helium
B) Neon
C) Krypton
D) Xenon

Answer: D) Xenon

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9. Which of the following compounds contains a B-N bond?

A) Borax
B) Borazine
C) Boric Acid
D) Diborane

Answer: B) Borazine

10. What is the primary industrial use of borax?

A) As a fertilizer
B) As a cleaning agent
C) As an oxidizing agent
D) As a reducing agent

Answer: B) As a cleaning agent

B. **Short Type Questions 10**

1. What is the general formula of boranes?
2. Why is borazine called "inorganic benzene"?
3. What is the inert pair effect?
4. Name two crystalline allotropes of carbon.
5. Write the molecular formula of boric acid.
6. What are the two main allotropes of oxygen?
7. Which halogen is the most reactive and why?
8. Name a noble gas that forms stable compounds.
9. Write a use of borax in daily life.
10. What is the oxidation state of sulfur in sulfuric acid (H_2SO_4)?

C. Assay Type Questions

1. Describe the structure, bonding, and properties of boranes.
2. Explain the similarities and differences between borazine and benzene.
3. Discuss the inert pair effect in Group 14 elements with suitable examples.

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4. Explain the allotropy of carbon and describe the properties of its different allotropes.
5. Discuss the chemical properties and industrial applications of boric acid and borax.
6. Describe the different oxides of oxygen and their significance.
7. Explain the chemistry of fluorine and compare it with other halogens.
8. Discuss the compounds of xenon, including xenon fluorides and oxides, highlighting their structures and bonding.
9. Explain the role of sulfur in industrial and biological systems.
10. Compare the physical and chemical properties of Group 16 elements (O, S, Se, Te).

- **10.13 Further Reading**

1. J.D. Lee – Concise Inorganic Chemistry (Best for understanding Group chemistry)
2. F.A. Cotton, G. Wilkinson, and P.L. Gaus – Basic Inorganic Chemistry
3. Gary Miessler, Paul Fischer, Donald Tarr – Inorganic Chemistry
4. Shriver & Atkins – Inorganic Chemistry

Module IV: Redox & Acid Base

Unit-11: Redox Reactions and precipitation reactions

Contents

11.0 Objectives

11.1 Introduction

11.2 Qualitative idea about complimentary, noncomplimentary, disproportionation and comproportionation reactions

11.3 Standard redox potentials with sign conventions

11.4 Electrochemical series and its application to explore the feasibility of reactions and equilibrium constants

11.5 Applications of electrochemical series

11.6 Comparison of Reactivities of Metals

11.7 Calculation of the EMF of the Cell

11.8 Predicting the Liberation of Hydrogen Gas from Acids by Metals

11.9 Predicting Feasibility of a Redox Reaction

11.10 The Relationship between Cell Potential & the Equilibrium Constant

11.11 Nernst equation, Effect of pH, Complexation and Precipitation on Redox Potential, Formal Potential

- 11.11.1 Formal Potential
- 11.11.2 Formal Potential Depending on the pH of the Medium
- 11.11.3 Formal Potential Depending on the Complexation of the Medium
- 11.11.4 Effects of Precipitation on Electrode Potentials

11.12 Basis of Redox Titration and Redox Indicators

- 11.12.1 Titration
- 11.12.2 Redox Indicator

11.13 Summary

11.14 Model Questions

11.15 Further Reading

11.0 Objectives

- Understand the fundamental differences between these reaction types.
- Identify examples of each reaction type in electrochemical systems.
- Explain the meaning of standard redox potentials (E°) and their determination.
- Interpret the sign conventions used in redox reactions (positive for spontaneous
- Define the electrochemical series and understand its derivation.
- Derive and apply the Nernst equation to non-standard conditions.
- Examine the effect of pH on redox potentials.
- Analyze how complexation and precipitation influence redox equilibria.
- Define formal potential and differentiate it from standard redox potential.
- Understand how it accounts for solution conditions like pH and complexation.

11.1 Introduction

Oxidation-reduction reactions are some of the most important chemical reactions. Redox reactions, as they are called, are the energy-producing reactions in industry as well as in the body. The core of a redox reaction is the passing of one or more electrons from one species to another. The species that loses electrons is said to be oxidized, and the species gaining electrons is reduced. These are old terms, but they are still used today. Oxidation and reductin occur simultaneously. Oxidation numbers are assigned to each element in a chemical reaction to help us learn which element is oxidized and which element is reduced. If, in a reaction, the oxidation number of an element increases (becomes more positive), the element is being oxidized. On the other hand, if the oxidation number of an element decreases, the element is being reduced. The changes in oxidation numbers are also used to balance redox equations. The goal is to keep

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the total number of electrons lost in the oxidation equal to the total number gained in the reduction. Clearly, the study of oxidationreduction reactions should begin by learning about oxidation numbers. In chemistry, the word precipitation has a different meaning: instead of something that falls out of the sky, a precipitate is something that falls out of a solution. One of the ways a prcipitate can be formed is when two soluble compounds interact. A soluble compound is one that will dissolve in water. Insoluble compounds do not dissolve in water.

11.2 Qualitative idea about complimentary, noncomplimentary, disproportionation and comproportionation reactions

Complementary Reaction

The change in oxidation state of the reducing agent is the same as the change in oxidation state of the oxidizing agent. Some examples are

$$Cr^{+2} + Ag^{+} \rightarrow Ag^{0} + Cr^{+3}$$

$$Zn^{0} + Cu^{+2} \rightarrow Zn^{+2} + Cu^{0}$$

Noncomplementary Reaction

The oxidizing agent and reducing agent undergo different net changes in oxidation state. Some examples are

$$2Cr^{+2} + Tl^{+3} \rightarrow Cr^{+3} + Tl^{+}$$

$$Zn^{0} + 2Fe^{+3} \rightarrow Zn^{+2} + 2Fe^{+2}$$

The complementary reactions are generally faster than the noncomplementary reactions. The noncomplementary and multiple electron transfer reactions cannot occur in a single step electron transfer and it takes place multistep. If any one step of such reaction is slow then the overall reaction becomes slow, or if any such step is thermodynamically disfavored then it leads to the low concentratin of an essential intermediate and consequently the overall reactions become slow.

Disproportionation Reaction

A particular species act as a reducing agent as well as oxidizing agent. Thus a fraction of the species is brought to higher oxidatin state and at the same time, an equivalent fraction is brought down to a lower oxidatin state.

$$3Au^{+} \rightleftharpoons Au^{+3} + 2Au$$

$$2Cu^{+} \rightleftharpoons Cu + Cu^{+2}$$

Comproportionation Reaction

The reverse of disproportionation reaction is called a comproportionatin reaction in which two species of a particular substance with different oxidation state combine to form a product having an intermediate oxidation state.

$$Ag^{+2} + Ag \rightleftharpoons 2Ag^{+}$$

11.3 Standard redox potentials with sign conventions

For the process, $Ox + ne \rightleftharpoons$ Red, the electrode potential (more correctly, the reductin potential) is given by the Nernst equation as follows :

$$E = E^0 + RT/nF In^a_{Ox}/^a_{Red} = E^0 + 0.059/n\ In^a_{Ox}/^a_{Red,} \text{ at } 25°C$$

Where n is the number of electrons getting transferred, F = 96,500 coulombs per mole of electron, R = 8.3 joules/degree/mole, T = temperature in Kelvin scale, E = electrode potential in volt, $E°$ = Standared potential in volt. Thus, it is evident that when both the oxidant and reductant are at unit activity, the electrode potential becomes the standard electrode potential.

There are two different sign conventions which are apparently confusing but each one is justified in its own argument. These are European convention and American convention.

According to European convention, sign of the electrode potential is the experimentally observed electrostatic potential with respect to the standard hydrogen electrode (*SHE*). It is obtained from the emf of a cell in which the negative electrode is *SHE* (for which a potential of 0 V has been arbitrarily assigned) and the positive electrode is made up of the electrode whose potential is to be determined. Thus, in this convention, the sign of the electrode potential is the same as that of the electrostatic charge of the electrode in forming the electrical double layer. On the other hand, the American convention takes care of the thermodynamic property of the electrode reaction.

In the European convention, the $Zn - Zn^{2+}$ electrode has the potential – 0.76 volt, because on dipping a *Zn*-rod in a solution containing Zn^{2+} ions, the *Zn*-rod becomes negatively charged electrostatically. It happens so due to the higher tendency (compared to the tendency of hydrogen in SHE, i.e. $H \rightarrow 2H^+ + 2e$) of Zn-metal to pass into the solution as Zn^{2+} ions (i.e. $Zn \rightarrow Zn^{2+} + 2e$). According to the American convention, the electrode potential for the above process is + 0.76 volt. The reason is that, if the potential is taken as –ve then the corresponding Gibbs free energy change (i.e. $\Delta G = -nFE'$) becomes positive and the process cannot be spontaneous; but if it is taken as + *ve*, then ΔG becomes –ve which is in conformity with the thermodynamic criterion of spontaneity of the electrode process, $Zn + 2H^+ \rightleftharpoons Zn^{2+} + H_2$, $\Delta G < 0$.

To overcome this aparent confusion, IUPAC has recommended the electrostatic potential as the electrode potential designated by V (a sign invariant quantity) and the thermodynamic quantity (i.e. *emf*) designated by E should be related as proper

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sign in the relation, $\Delta G = -nFE$. Thus, when a standard Zn/Zn^{2+} ($a = 1$) electrode is coupled with a *SHE*, the experimental potential is – 0.76 *V* and it is actually the standard electrode potential (*V*) of Zn/Zn^{2+}. When this electrode is used as negative electrode in some cell, the electrod potential will still be taken as – 0.76 *V* (i.e. a sign invariant). But, here we shall follow the thermodynamic convention. Thus – 0.76 volt is regarded as standard reduction potential of th couple, $Zn - Zn^{2+}$, while + 0.76 volt can be taken as the standard oxidation potential. Thus, so-called European convention refers to actually to the reduction potential.

11.4 Electrochemical Series and its Application to Explore the Feasibility of Reactions and Equilibrium Constants

If the standard reduction potentials of the electrode process, $M^{n+}_{(aq)} + ne \rightleftharpoons M_{(s)}$ for different metals are placed in a series in order of increasing value, we get the table 1 which gives the electrochemical series.

Here the potential values are given as per the thermodynamic convention. The Gibbs free energy change for the reduction electrode process is given by, $\Delta G^\circ = -nFE^\circ_{red}$. Thus, for the system of higher positive value of $E^0_{red.}$ the reduction process gets more favoured. In fact for the systems having negative E^0_{red} value, the reverse process, i.e. oxidation is favoured. In the table 1, the metals residing at the top are highly electropositive. With the increase of $E^0_{red.}$ the oxidizing power increases and the reducing power runs in the opposite direction.

Table 1. The electrochemical series (standard reduction potentials, at 25°C)

Element	***Electrode couple***	$E^o(V)$
Li	Li^+/Li	– 3.05
K	K^+/K	– 2.93
Ca	Ca^{2+}/Ca	– 2.84
Na	Na^+/Na	– 2.71
Mg	Mg^{2+}/Mg	– 2.36
Al	Al^{3+}/Al	– 1.66
Mn	Mn^{2+}/Mn	– 1.08
Zn	Zn^{2+}/Zn	– 0.76
Fe	Fe^{3+}/Fe	– 0.44
Cd	Cd^{2+}/Cd	– 0.40
Co	Co^{2+}/Co	– 0.27
Ni	Ni^{2+}/Ni	–0.23
Sn	Sn^{2+}/Sn	– 0.14
Pb	Pb^{2+}/Pb	– 0.13
H	H^+/H	0.00*
Cu^2	Cu^{2+}/Cu^2	+ 0.35
Ag	Ag^+/Ag	+ 0.80
Au	Au^{3+}/Au	+ 1.38

*Standard Hydrogen Electrode (SHE)

This difference in the reduction tendencies of the two electrodes in a cell finds many applications in chemistry.

11.5 Applications of electrochemical series

The main applications of the electrochemical series are:

Oxidizing and Reducing Strengths

The electrochemical series helps to pick out substances that are good oxidizing agents and those which are good reducing agents. For example, a very high negative reduction potential of lithium electrode indicates that it is very difficult to reduce A/ ions to *Li* atoms. Therefore, *Li* cannot accept electrons easily and so loses electrons to behave as a reducing agent. As the reduction potential increases (negative value decreases), the tendency of the electrode to behave as reducing agent decreases.

Thus, all the substances appearing on the top of the series behave as good reducing agents. For example, *Li* and *K* are good reducing agents while *Ag* and *Au* are the poorest reducing agents. Similarly, substances at the bottom of the table have high reduction potential and they can be easily reduced. Therefore, they act as strong oxidizing agents. From the table we ca conclude that H+ is a better oxidizing agent than *Z/r* while *Cir+* is a better oxidizing agent than H+; *Fe3+* is a better oxidizing agent than *AP* and so on.

All the substances appearing at the bottom of the table are good oxidizing agents.

11.6 Comparison of Reactivities of Metals

The relative ease with which the various species of metals and ions may be oxidized or reduced is indicated by the reduction potential values. The metals with lower reduction potential is not reduced easily but are easily oxidized to their ions losing electrons. These electrons would reduce the other metals having higher reduction potentials. In other words, a metal having smaller reduction potential can displace metals having larger reduction potentials from the solution of their salt. For example, copper lies above silver in the electrochemical series, therefore, if copper metal is added to $AgNO_3$ solution, silver is displaced from the solution. In

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general, a metal occupying higher position in the series can displace the metals lying below it from the solutions of their salts and so are more reactive in displacing the other metals. Thus, *Li* is the most electropositive element in solutions and fluorine is the most electronegative element.

11.7 Calculation of the EMF of the Cell

The following steps determine the reduction potential of the cathode and anode:

Step I

The two half-cell reactions are written in such a way that the reaction taking place at the left-hand electrode is written as an oxidation reaction and that taking place at the right electrode is written as reduction reaction.

Step II

The number of electrons in the two equations are made equal by multiplying one of the equations if necessary, by a suitable number. However, electrode potential values *(E°)* are not multiplied.

Step III

The electrode potentials of both the electrodes are taken to be reduction potentials and so the EMF of the cell is equal to the difference between the standard potential of the right-hand side and the left-hand side electrode.

$$E_{cell} = E_R - E_L$$

Step IV

If the *EMF* of the cell is +ve, the reaction is feasible in the given direction and the cell is correctly represented, i.e., oxidation occurs at left electrode (anode) and reduction occurs at the right electrode (cathode). If it is -ve, the cell reaction is not feasible in the given direction and the cell is wrongly represented. Thus, to get positive value for the E*MF* the electrodes must be reversed.

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11.8 Predicting the Liberation of Hydrogen Gas from Acids by Metals

All metals having negative electrode potentials (negative $E°$ values) show greater tendency of losing electrons as compared to hydrogen. So, when such a metal is placed in an acid solution, the metal gets oxidized, and H^+ (hydrogen) ions get reduced to form hydrogen gas. Thus, the metals heving negative $E°$ values liberate hydrogen from acids.

$$M_{(s)} \rightleftharpoons M^{n+}(aq) + ne^-$$

metal having negative $E°$ value

$$nH^+(aq) + ne^- \rightleftharpoons n/2\ H_2(g)$$

Thus, $M + nH^+(aq) \rightleftharpoons M^{n+}(aq) + n/2\ H_2(g)$

For example, metals such as Mg ($E°(Mg^{2+} + \rightarrow Mg) = -\ 2.37\ V$),

Zn ($E°(Zn^{2+}/Zn) = -\ 0.76V$), Iron ($E°(Fe^{2+}/Fe) = -\ 0.44\ V$) etc., can displace hydrogen from acids such as HCl and H_2SO_4. But metals such as Copper, ($E°(Cu^{2+}/Cu) = +\ 0.34V$), silver ($E°(Ag^+/Ag) = +\ 0.80V$) and gold ($E°(Au^{3+}/Au) = +1.42V$) cannot displace hydrogen from acids because of their positive reduction potential value.

11.9 Predicting Feasibility of a Redox Reaction

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From the E° values of the two electrodes one can find out whether a given redox reaction is feasible or not. A redox reaction is feasible only if the species which has higher potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidized i.e., loses electrons.

The electrochemical series gives the increasing order of electrode potentials (reduction) of different electrodes on moving down the table. This means that the species, which accept the electrons (reduced) must be lower in the electrochemical series as compared to the other which is to lose electrons. (oxidized). For example,

$$2Ag(s)+Cu^{2+}(aq)\rightarrow 2Ag^{+}(aq)+Cu(s)$$

From the electrochemical series E° value of Cu = + 0.34V and that of Ag = + 0.80 V since the reduction potential of Ag is more than that of Cu, this means that silver has greater tendency to get reduced in comparison to copper. Thus, the reaction

$$Ag^{+}(aq)+e^{-}\rightarrow Ag(s)$$

occurs more readily than the reaction

$$Cu^{2+}(aq)+2e^{-}\rightarrow Cu(s)$$

The reduction potential of copper is less than that of Ag, this means that copper will be oxidized or will go into solution as ions in comparison to Ag. Thus, the reaction,

$$Cu(s)\rightarrow Cu^{2+}(aq)+2e^{-}$$

occurs more readily than

$$Ag(s)\rightarrow Ag^{+}(aq)+e^{-}$$

Therefore, silver will be reduced and copper will be oxidized and the above reaction is not feasible. Rather the reverse reaction,

$$2Ag^{+}(aq)+Cu(s)\rightarrow 2Ag(s)+Cu^{2+}(aq)$$

can occur. Thus a metal will displace, any other metal, which occurs below it in the electrochemical series from its salt solution. When a metal having lower E° value is placed in a solution, containing ions of another metal having higher E° value, then the metal having lower E° value gets dissolved and the ions of the metal having higher E° value get precipitated.

11.10 The Relationship between Cell Potential & the Equilibrium Constant

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We can use the relationship between $\Delta G°$ and the equilibrium constant K, to obtain a relationship between $E°_{cell}$ and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation :

$\Delta G° = -RTlnK$

Given the relationship between the standard free-energy change and the standard cell potential $-nFE°_{cell} = -RTlnK$

Rearranging this equation,

$E°_{cell} = (RT/nF)lnK$

For $T = 298\ K$,

$E°_{cell} = [[8.314J/(mol{\cdot}K)(298K)]/n[96,486J/(V.mol)]]2.303\log K = (0.0591\ V/n)\log K$

$\log K = nE°_{cell}/0.0591V$

Thus $E°_{cell}$ is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of $E°_{cell}$ and vice versa.

11.11 Nernst equation, Effect of pH, Complexation and Precipitation on Redox Potential, Formal Potential

11.11.1 Formal Potential

In the process, Ox + ne $\rightleftharpoons$ Red, the potential is given by :

$E = E^0 + RT/nF\ ln^a_{Ox}/^a_{Red} = E^0 + 0.059/n\ ln^a_{Ox}/^a_{Red,}$ at 25°C

Where n is the number of moles of electrons getting transferred, F = 96,500 coulombs per mole of electron, R = 8.3 joules/degree/mole, T = temperature in Kelvin scale, E = electrode potential in volt, $E°$ = Standard potential in volt.

$E = E° + 0.059/n\ ln\ [Ox]/[Red]$ (in dilute solution)

Here it is believed that all the involved species will remain in their simple forms and the activity equals the concentration. Such a situation may only exist n a very dilute condition. In practice, the solution is sufficiently concentrated to disallow the condition, activity = concentration. But in reality, we deal with the concentration terms instead of the activity term. Beside this, the ions may not exist as in simple forms in presence of other electrolytes. In such cases, the concept of standard potential is of no practical use and it requires another parameter called formal potential or conditional potential which takes care of the actual situation existing in solution.

The formal potential of a system is the experimentally observed potential of the system in solution where the formal concentration of the oxidized and reduced forms is same. The formal potentials cover the effect of the concentration of the species, pH of the solution, the possibility of complexation and other factors.

11.11.2 Formal Potential Depending on the pH of the Medium

Nernst equation describes potential of electrochemical cell as a function of concentrations of ions taking part in the reaction :

$$E = E_0 - \frac{RT}{nF} In(Q)$$

Where Q is a **reaction quotient** and n is number of electrons exchanged. For constant temperature expression RT/F has constant value. To simplify the calculation, it is often combined with conversion factor between natural logarithm (denoted here by In) and decimal logarithm (denoted here by log) to form value of 0.0591 (for 25°C). Thus, for example for half reactin of MnO_4^- in acidic media :

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad E^0_{MnO4^-/Mn^{2+}} = +1.51 \text{ volt}$$

potential is given by

$$E = 1.51 - \frac{0.0591}{5} \log\left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right)$$

To be precise we should use not concentrations, but thermodynamic activities of the ions present in the solution.

$$E = 1.51 - 8/5(0.059)pH + 0.059/5 \log[MnO_4^-]/[Mn^{2+}]$$

$$E = E^0_f + 0.059/5 \log[MnO_4^-]/[Mn^{2+}] \qquad [\text{Where } E^0_f = 1.51 - 8/5(0.059)pH]$$

To express E^0_f the pH term is to be included with in the E^0 term. Thus, we can write :

$$E = E^0_f = E^0 - 8/5(0.059)pH = E^0 - 0.0944pH \text{ when } [MnO_4^-] = [Mn^{2+}] = 1M;$$

activity coefficients are taken to be unity.

Thus the Nernst equation in terms of E^0_f (formal potential) of the couple is given by :

$$E = E^0_f + 0.0118 \log[MnO_4^-]/[Mn^{2+}]$$

11.11.3 Formal Potential Depending on the Complexation of the Medium

Potential (in aqueous solution) of the involved couples are : $E^0_{Cu^{2+}/Cu} = 0.34V > E^0_{Zn^{2+}/Zn} = -0.76V$. Hence, on the electrolysis of a solution containing both Cu^{2+} and Zn^{2+}, copper deposition should start earlier. But in presence of excess CN^-, Zn^{2+} forms $Zn(CN)_4^{2-}$ complex while Cu^{2+} oxidises CN^- to CN_2 gas and itself reduced to $Cu(CN)_4^{2-}$ which is more stable than zinc complex. In fact the stability constants are so widely different that the deposition potentials of the couples becomes comparable, i.e. $E^0_{Cu(CN)_4^{2-}/Cu} \approx E^0_{Zn(CN)_4^{2-}/Zn^-}$ Thus the simultaneous deposition of both Cu and Zn can be achieved by the complexation with excess cyanide in the medium.

$$Cu^+ + e \rightleftharpoons Cu \qquad E^0 = 0.52V$$

$$Cu^+ + 4CN^- \rightleftharpoons Cu(CN)_4^{3-}\ ,\ \log K \approx 30.0$$

$$K = [Cu(CN)_4^{3-}]/[Cu^+][CN^-]^4$$

$$E = E^0 = 0.059\log[Cu^+] = E^0 = 0.059\ \log[Cu(CN)_4{}^{3-}]/[CN^-]^4$$

$$= (0.52 - 0.059\times 30) + 0.059[Cu(CN)_4{}^{3-}]/[CN^-]^4 = -1.25 + [Cu(CN)_4{}^{3-}]/[CN^-]^4$$

$$E = -1.25 - 0.059\times 4\log[CN^-] + 0.059\log[Cu(CN)_4{}^{3}]$$

$$E = -1.25 + 0.236\log[CN^-] \text{ when } [Cu(CN)_4{}^{3-}] = 1M$$

Thus the standard potential of the following couple is

$$-1.25V (= E^0{}_f \text{ for } [CN^-] = 1M)$$

$$[Cu(CN)_4{}^{3-}] + e \rightleftharpoons Cu + 4CN^-,$$

We can calculate the change of potential of the system Zn^{2+}/Zn couple in the presence of CN^- in the same way.

$$Zn^{2+} + 2e \rightleftharpoons Zn \qquad E^0 = -\ 0.76V$$

$$Zn^{2+} + 4CN^- \leftrightarrow Zn(CN)_4{}^{2-},\ \log K \approx 20.0$$

$$K = [Zn(CN)_4{}^{2-}]/[Zn^{2+}][CN^-]^4$$

$$E = E^0 + 0.059\log[Zn^{2+}] = E^0 + 0.059\log[Zn(CN)_4{}^{2-}]/K[CN^-]^4$$

$$E = E^0 + (0.059/2)\log(1/K) + (0.059/2)\log[Zn(CN)_4{}^{2-}]/[CN^-]^4$$

$$= -1.35 + (0.059/2)\log[Zn(CN)_4{}^{2-}]/[CN^-]^4$$

i.e. for the couple, $Zn(CN)_4{}^{2-} + 2e \rightleftharpoons Zn + 4CN^-$ the standard potential is –1.35V.

11.11.4 Effects of Precipitation on Electrode Potentials

Iodometric determination of copper is based on the oxidation of iodides to iodine by copper (II) ions, which get redced to Cu^{+}.

Comparison of standard potentials for both half reactions ($Cu^{2+}/Cu^{+} E^{0} = 0.15V$, $I_2/I^{-} E^{0} = 0.54V$) suggests that it is iodine that should be acting as oxidizer. However, that's not the case, as copper (I) iodide CuI is very weakly soluble ($K_{sp} = 10^{-12}$). That means concentration of Cu^{+} in the solution is very low and the standard potential of the half reaction Cu^{2+}/Cu^{+} in the presence of iodides is much higher (arround $0.85V$).

$Cu^{2} + e \rightleftharpoons Cu^{+} E^{0} = 0.15V$; $E = E^{0} + 0.059\log[Cu^{2+}]/[Cu^{+}]$, (in dilute solution)

In presence of I^{-}, Cu^{+} is precipitated as CuI, having the solubility product 10^{-12}, i.e.

$Cu^{+} + I^{-} \rightleftharpoons CuI(\downarrow)$, $K_{sp} = 10^{-12}$.

Now we get;

$E = E^{0} + 0.059\log([Cu^{2+}][1^{-}]/K_{sp})$

$E = E^{0} - 0.059\log K_{sp} + 0.059\log([Cu^{2+}][I^{-}]$

$E = 0.85 + 0.059\log([Cu^{2+}][I^{-}]$

$E = 0.85 + 0.059\log[I^{-}]$ when $[Cu^{2+}] = 1M$

We can express E^{0}_{f} as follows :

$E^{0}_{f} = E = E^{0} - 0.059\log K_{sp} + 0.059\log[I^{-}] = 0.85 + 0.059\log[I^{-}]$

Thus formal potential of the system depends on the concentration of the iodide. Under the condition, $[I^{-}] >> [Cu^{2+}]$, the formal potential becomes : $E^{0}_{f} = 0.85 + 0.059\log[I^{-}]$

It explains the oxidation of iodide by Cu(II) in presence of excess iodide. The reaction is $2Cu^{2+} + 4I^{-} \rightarrow 2CuI(s) + I_2$

11.12 Basis of Redox Titration and Redox Indicators

All of us know that wine is made from the fermentation of grape juice using specific yeast cells. However, do you know wine requires a particular amount of fruit acid? So how is this acid content measured in industries? The determination of acid content is done by titration. Yes, the lab technique we all have done as well as read about. Moreover, a specialized titration technique

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known as redox titration is used for analysis of wines for sulfur dioxide. This is just one example.similarly, many other industrial processes require titration with respect to redox reactions. So let us know more about redox reactions as the basis of titration.

11.12.1 Titration

It is a very common laboratory technique. Titration helps in the quantitative chemical analysis. It helps in the determination of an unknown concentration of an already known analyte. Moreover, titration also helps in volumetric analysis or measurement of volume. There are different types of titration techniques which is applicable according to the goals and methods.

Types of Methods

- **Acid-base Titrations**
- **Redox Titrations**
- **Precipitation titrations**
- **Complexometric Titrations**

The most common titration methods that are commonly in use for "quantitative chemical analysis" are Redox and Acid-Base Titration. In the acid-base system, a titration method helps in finding out the strength of one solution against another solution by the use of the pH-sensitive indicator.

Similarly, in redox system, a titration method helps in determination of the strength of a particular oxidant or a reductant with the help redox-sensitive indicator. We will now discuss the definition of redox titration and how to use indicators in this technique.

Redox Titrations

When the oxidation-reduction reactions happen in a titration method, it is known as a redox titration. In this technique, transfer of electrons occurs in the reacting ions present in the aqueous solutions during the chemical reaction. This is further classified on the basis of regent used in the redox titration.

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Sub-Divisions of Redox Titrations

- Permanganate Titrations
- Dichromate Titrations
- Iodometric Titrations

Permanganate Titrations

Potassium Permanganate is the oxidizing agent in this type of redox titration method. Maintenance of the solution is done with the help of dilute sulphuric acid. Moreover, the addition of Sulphuric acid also helps to increase the hydrogen ions present in the solution. In this technique, the reagent has intense colour due to the permanganate ion MnO~ In the case, the permanganate ion acts as a self-indicator in this method. The solution remains colourless prior to the endpoint. The equation of redox reaction:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 3H_2 + 5[O]$$

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$$

The result of the end point is noticeable when oxidation of the last of the reductant such as Fe^{2+} or $C_2O_4^{2-}$ occurs. At this point, the solution retains the first lasting tinge of the MnO_4^- (pink colour) appears. The concentration can be minimum of 10^{-6} mol L^{-1}. This assures the minimal "overshoot" of the pink colour after the equivalence point.

The equivalence point is where reductant and oxidant are equal with respct to the mole stoichiomety or the total number of electrons lost and electron gained in oxidation and reduction reaction will be equal. The postassium permanganate titration helps in the estimation of oxalic acid, hydrogen peroxide, ferrous salts, oxalates and more. However, it is very important to always standardize the solution prior to use.

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Iodimetric Titrations

This is an interesting but common method. In this case, free iodine reduction to iodide ions occurs as well as iodide ion oxidation to free iodine occurs. The oxidation and reduction reactions are

$I_2 + 2e \rightarrow 2I^-$ Reduction

$2I^- \rightarrow I_2 + 2e$ Oxidation

The solution acts as an indicator. The use of this method is limited to the reagents capable of oxidizing I^- ions. One of the examples of such reaction is of *Cu(II)*

Dichromate Titrations

In this method, potassium dichromate acts as the oxidant in the acidic medium. It is necessary to maintain the acidity of the medium by addition of dilute sulphuric acid. The equation of the reaction is

$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2Cr_2(SO_4) + 4H_2O + 3[O]$

$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$

In this situation, there is no substantial auto colour change as seen in the MnO_4^- titration. $Cr_2O_7^{2-}$ is not a self-indicator, However, $Cr_2O_7^{2-}$ oxidizes the indicator substance diphenylamine soon after achieving the equivalence point thereby producing an intense blue colour. The change in signals the end point of the titration. We can use the potassium dichromate solution in titrations directly. This method helps in the estimation of ferrous salts and iodides.

$2Cu^{2+}(aq) + 4I^- (aq) \rightarrow Cu_2I_2 (S) + I_2(aq)$

The ability of iodine to produce intense blue colour with starch as the substance and its capacity to react with thiosulphate ions ($S_2O_3^{2-}$) forms the basis of this method. The specific reaction with ($S_2O_3^{2-}$) is also a redox reaction.

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

In this case, I_2 is insoluble in nature with water but it remains in the solution in the form of KI_3 that contains *KI*. After the addition of starch, the iodine in the reaction liberates as iodide ions producing intense blue colour. However, the colour disappears on the consumption of iodine by the thiosulphate ions. The end point of the reaction is easily noticeable. Thus, it is easy to determine the concentration of the unknown solution by stoichiometric calculation.

11.12.2 Redox Indicator

Redox indicators are the chemicals used during the redox titration in order to detect the end point. In acid-base titrations, the indicators used were weak acids or bases which had two forms:

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dissociated (ionized) or non-ionized and both of these forms have a different color. Some common redox indicators with characteristic properties are listed in table 2.

Similarly, the redox indicators have two forms: oxidized form and reduced form. In both the forms, the color is different. Both the form has got a specific standard reduction potential.

$$E = E^0_{In} - 0.059 \log 10$$

$$E = E^0_{In} - 0.059$$

$$E_{tp} = E^0_{In} \pm 0.059/n$$

The change in the potential of the indicator which is required during the redox titration for the indicator to impart a color change is called transition potential.

The transition potential should coincide with the potential of the solution at the equivalence point (E_{ep}) for getting a better end point. $E_{ep} = E_t$

$$In_{ox} + ne \rightarrow In_{red}$$

Here we apply the same concept.

Let us suppose an indicator (In), and represent its oxidized form as (In_{ox}) and reduced form as (In_{red}).

Applying Nernst equation,

Thus, the electrode potential of the indicator when the ratio of (In_{ox}) to (In_{red}) is 10:1 would be :

$$E = E^0_{In} - 0.059 \log[In_{red}]/[In_{ox}]$$

n = transfer of electrons = 1.

$$E = E^0_{In} - 0.059 \log(1/10)$$

$$E = E^0_{In} + 0.059$$

Thus, the electrode potential of the indicator when the ratio of (In_{ox}) to (In_{red}) is 1:10 would be :

$$E = E^0_{In} - 0.059 \log 10$$

$$E = E^0_{In} - 0.059$$

$$E_{tp} = E^0_{In} \pm 0.059/n$$

The change in the potential of the indicator which is required during the redox titration for the indicator to impart a color change is called transition potential.

The transition potential should coincide with the potential of the solution at the equivalence point (E_{ep}) for getting a better end point. $E_{ep} = E_t$

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Some common redox indicators with characteristic properties

Indicators	colour		$E^0_{Ind}[H+] = 1.0$
	Ind_{ox}	Ind_{Red}	mol dm^{-3}
Methylene blue	Blue	Colourless	0.53
Diphenylamine	Blue-violet	Colourless	0.76
Diphenylamine-sulphonic acid	Red-violet	Colourless	0.85
N-Phenylanthranilic acid	Red-violet	Colourless	1.08
Ferroin, (Fe(II)-phenanthroline complex)	Paleblue	Red	1.14

11.13 Summary

Qualitative Idea about Complementary, Non-Complementary, Disproportionation, and Comproportionation Reactions

Redox reactions can be classified into complementary and non-complementary types. In complementary reactions, electron transfer occurs directly between reactants, while in non-complementary reactions, intermediate steps are involved. Disproportionation reactions involve a single species undergoing simultaneous oxidation and reduction, whereas comproportionation reactions occur when two species of the same element in different oxidation states combine to form a single species with an intermediate oxidation state.

Standard Redox Potentials and Electrochemical Series

The standard redox potential (E°) is a measure of a species' tendency to gain or lose electrons. The electrochemical series ranks elements based on their E° values, helping predict reaction feasibility, equilibrium constants, and reactivity trends among metals. This series determines which metals can displace others in redox reactions and whether a metal can liberate hydrogen from acids.

Electrochemical Cell EMF and Feasibility of Redox Reactions

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The electromotive force (EMF) of a cell is calculated using standard electrode potentials. The sign and magnitude of EMF indicate whether a redox reaction is spontaneous. A positive EMF means a feasible reaction, while a negative EMF suggests non-spontaneity. The relationship between EMF and the equilibrium constant (K) is given by the Nernst equation, which also accounts for pH, complexation, and precipitation effects on redox potential.

Redox Titrations and Indicators

Redox titrations determine the concentration of an unknown solution using oxidation-reduction reactions. Redox indicators signal the endpoint by undergoing a color change at a specific electrode potential. These titrations play a crucial role in analytical chemistry, particularly in determining the presence of oxidizing or reducing agents.

11.14 Model Questions

A. Multiple Choice Type Questions

1. Which of the following best describes a disproportionation reaction?

A) A reaction where one species is both oxidized and reduced
B) A reaction where two species of different oxidation states form a common oxidation state
C) A reaction where an oxidizing agent donates electrons to a reducing agent
D) A reaction where an element gains electrons only

Answer: A

2. What is the significance of the electrochemical series?

A) It helps predict the spontaneity of redox reactions
B) It determines the color of redox indicators
C) It is used to measure temperature variations in electrochemical cells
D) It is used for calculating atomic masses of elements

Answer: A

3. The standard reduction potential (E°) of an element is measured under which conditions?

A) 1 M concentration, 298 K, and 1 atm pressure
B) 0.1 M concentration, 273 K, and 2 atm pressure
C) 1 M concentration, 300 K, and 1 atm pressure
D) 0.01 M concentration, 310 K, and 1 atm pressure

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Answer: A

4. What will happen if a metal with a higher reduction potential is placed in a solution containing ions of a metal with a lower reduction potential?

A) No reaction will occur
B) The metal with a lower reduction potential will get reduced
C) The metal with a higher reduction potential will get oxidized
D) The solution will evaporate

Answer: C

5. The feasibility of a redox reaction can be predicted using which of the following?

A) Gibbs free energy (ΔG)
B) Nernst equation
C) EMF of the cell
D) All of the above

Answer: D

6. What is the relationship between the equilibrium constant (K) and the cell potential (E°cell)?

A) $E^\circ_{cell} = \frac{RT}{nF} \ln K$
B) $E^\circ_{cell} = -\frac{RT}{nF} \ln K$
C) $E^\circ_{cell} = \frac{nF}{RT} \ln K$
D) $E^\circ_{cell} = -\frac{nF}{RT} \ln K$

Answer: A

7. What is the effect of pH on redox potential?

A) Redox potential remains constant with pH change
B) Redox potential decreases with increasing pH if H^+ ions are involved in the reaction
C) Redox potential increases with increasing pH
D) Redox potential is independent of pH

Answer: B

8. Which metal is most likely to liberate hydrogen gas from acid, based on the electrochemical series?

A) Copper (Cu)
B) Silver (Ag)
C) Zinc (Zn)
D) Gold (Au)

Answer: C

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9. The formal potential of a redox reaction is affected by which of the following?

A) pH of the medium
B) Complexation of the metal ions
C) Precipitation of the reaction products
D) All of the above

Answer: D

10. Which of the following is true about redox indicators?

A) They change color at a specific electrode potential
B) They function by forming a complex with metal ions
C) They are only used in acid-base titrations
D) They work independently of redox potential

Answer: A

B. Short Type Questions

1. What is the difference between complementary and non-complementary redox reactions?
2. Define disproportionation and give an example.
3. What does a positive EMF value indicate about a redox reaction?
4. How does the electrochemical series help predict the feasibility of a reaction?
5. What is the relationship between the equilibrium constant (K) and cell potential (E°cell)?
6. How does pH affect the redox potential of a reaction?
7. What is the Nernst equation used for?
8. Why does zinc react with hydrochloric acid but copper does not?
9. What is a redox indicator, and how does it work in a titration?
10. How does complexation influence the formal potential of a redox reaction?

C. Assay Type Questions

1. Explain the concepts of complementary and non-complementary redox reactions with suitable examples.

2. Discuss disproportionation and comproportionation reactions in detail, providing chemical equations and real-world examples.
3. What are standard redox potentials? Explain their significance and the conventions used for sign assignment.
4. Describe the electrochemical series and its applications in predicting reaction feasibility, equilibrium constants, and metal reactivity.
5. How can the EMF of an electrochemical cell be calculated? Derive the expression and explain its significance.
6. Explain the factors affecting redox potential, including the effect of pH, complexation, and precipitation.
7. What is the Nernst equation? Derive its mathematical form and explain its applications in redox chemistry.
8. Discuss the role of redox indicators in titrations. How do they work, and how is the endpoint detected?
9. How does the relationship between cell potential and the equilibrium constant help predict the spontaneity of a redox reaction? Provide mathematical justification.
10. Compare and contrast the reactivities of metals based on their positions in the electrochemical series. How does this influence their ability to liberate hydrogen gas from acids?

11.15 Further Reading

1. **Atkins' Physical Chemistry** – Peter Atkins, Julio de Paula
2. **Electrochemical Methods: Fundamentals and Applications** – Allen J. Bard, Larry R. Faulkner
3. **Principles of Electrochemistry** – A. J. Bard, G. Inzelt, F. Scholz
4. **Modern Electrochemistry** (Volumes 1 & 2) – John O'M. Bockris, Amulya K. N. Reddy
5. **Physical Chemistry** – Ira N. Levine

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Unit 12: Basis of redox titration and redox indicators

Contents

12.0 Objectives
12.1 Introduction
12.2 Redox potential diagrams (Latimer and Frost) of common elements and their applications.
12.2.1 Latimer Diagram
12.12.2 Frost Diagrams

12.3 Solubility product principle
12.3.1 Solubility

12.3.2 Solubility Product Principle

12.3.3 Application of Solubility Product Principle

12.4 Ionic Product

12.5 Common Ion Effect

12.6 Applications of Common ion Effect in Chemistry

12.6.1 Purification of common salt

12.6.2 Precipitation of Sulphides of Group II.

12.6.3 Precipitation of Sulphides in Group III

12.6.4 Precipitation of Sulphides of Group IV

12.6.5 Softening of hard water

12.6.6 Manufacture of sodium bicarbonate: Solvay process

12.7 Summary

12.8 Model Questions

12.9 Further Reading

12.0 Objectives

- **Understand Redox Potential Diagrams**: Explain the construction and interpretation of Latimer and Frost diagrams for common elements, highlighting their significance in predicting redox stability and reaction feasibility.
- **Analyze Applications of Redox Diagrams**: Explore the practical applications of Latimer and Frost diagrams in electrochemistry, corrosion studies, environmental chemistry, and industrial processes.
- **Explain the Solubility Product Principle**: Define and illustrate the concept of the solubility product constant (Ksp), emphasizing its role in predicting the solubility of ionic compounds in aqueous solutions.
- **Investigate the Common Ion Effect**: Describe how the presence of a common ion influences the solubility of sparingly soluble salts, with examples from laboratory and industrial processes.
- **Apply Concepts to Precipitation and Separation**: Demonstrate the use of the solubility product and common ion effect in the selective precipitation and separation of metallic ions as hydroxides, sulfides, carbonates, sulfates, and halides in qualitative and quantitative chemical analysis.

12.1 Introduction

Redox potential diagrams, such as Latimer and Frost diagrams, are essential tools in electrochemistry for understanding the oxidation states and redox behavior of elements. These diagrams help predict reaction feasibility, stability, and possible redox transitions. Similarly, the solubility product principle (Ksp) and the common ion effect play a crucial role in determining the solubility and precipitation of ionic compounds. These concepts are widely applied in the selective precipitation and separation of metallic ions as hydroxides, sulfides,

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carbonates, sulfates, and halides. Understanding these principles is fundamental to various fields, including analytical chemistry, environmental science, and industrial applications.

12.2 Redox potential diagrams (Latimer and Frost) of common elements and their applications.

In addition to Pourbaix diagrams, there are two other kinds of redox stability diagrams known as Latimer and Frost diagrams. Each of these diagrams contains similar information, but one representation may be more useful in a given situation than the others. Latimer and Frost diagrams help predict stability relative to higher and lower oxidation states, usually at one fixed *pH*.

12.2.1 Latimer Diagram

Latimer diagrams are the oldest and most compact way to represent electrochemical equilibria for substances that have multiple oxidation states. Electrochemical potential values are written for successive redox reactions (from highest to lowest oxidation state), typically under standard conditions in either strong acid ($[H^+] = 1\ M$, pH 0) or strong base ($[OH^-] = 1\ M$, pH 14). The oxidation states of successive substances in a Latimer diagram can differ by one or more electrons. Oxidation states for the element undergoing redox are typically determined by

difference; we assign the oxygen atoms an oxidation state of –2 and the hydrogen atoms an oxidation state of +1.

The Latimer diagram for *Mn* illustrates its standard reduction potentials (in 1 *M* acid) in oxidation states from +7 to 0.

$$\underset{(+7)}{MnO_4^-} \xrightarrow{0.56} \underset{(+6)}{MnO_4^{2-}} \xrightarrow{+0.274} \underset{(+5)}{MnO_4^{3-}} \xrightarrow{4.27} \underset{(+4)}{MnO_2} \xrightarrow{0.95}$$

$$\underset{(+3)}{Mn^{3+}} \xrightarrow{1.51} \underset{(+2)}{Mn^{2+}} \xrightarrow{-1.18} \underset{(0)}{Mn}$$

The Latimer diagram compresses into shorthand notation all the standard potentials for redox reactions of the element *Mn*. For example, the entry that connects Mn^{2+} and Mn gives the potential for the half-cell reaction :

$$Mn^{2+}(aq) + 2e \rightarrow Mn(s) E^0_{1/2} = -1.18V$$

and the entry connecting Mn^{4+} and Mn^{3+} represents the reaction :

$$MnO_2(s) + 4H^+(aq) + e \rightarrow Mn^{3+}(aq) + 2H_2O(1) E^0_{1/2} = +0.95V$$

We can also calculate values for multi-electron reactions by first adding $\Delta G^0 (= -nFE^0)$ values and then dividing by the total number of electrons

For example, for the 5-electrons reduction of MnO_4^- to Mn^{2+}, we write

E^0 = [1(0.564) + 1(0.274) + 1(4.27) + 1(0.95) + 1(1.51)]/5 = + 1.51*V*

and for the three-electron reduction

E^0 = [1(0.564) + 1(0.274) + 1(4.27)]/3 = + 1.70*V*

Remember to divide by the number of electrons involved in the oxidation number change (5 and 3 for the above equations).

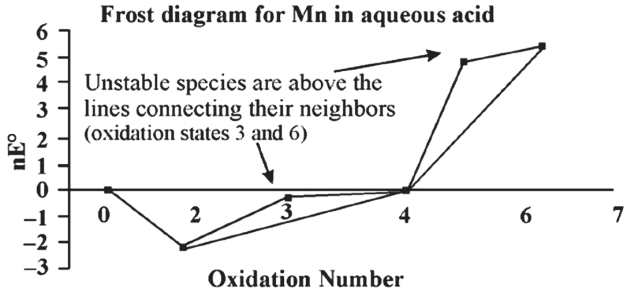
In general we can write :

$$E^0 = (n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + ...)/(n_1 + n_2 + n_3 + ...)$$

12.12.2 Frost Diagrams

Frost diagram or Frost-Ebsworth diagram is a type of graph to illustrate the relative stability of a number of different oxidation states of a particular substance. The graph illustrates the oxidation state vs free energy of a chemical species. This effect is dependent on pH, so this parameter also must be included. The free energy is determined by the oxidation–reduction half-reactions. The Frost diagram allows easier comprehension of these reduction potentials than the Latimer diagram, because the "lack of additivity of potentials" was confusing. In a Frost diagram, we plot ΔG^0/

F (= nE^0) *vs.* oxidation number. The zerooxidation state is assigned a nE^0 value of zero.



Stable and unstable oxidation states can be easily identified in the plot. Unstable compounds are higher on the plot than the line conecting their neighbors. Note that this is simply a graphical representation of what we did with the Latimer diagram to determine which oxidation states were stable and unstable.

The standard potential for any electrochemical reaction is given by the slope of the line connecting the two species on a Frost diagram. For example, the line connecting Mn^{3+} and MnO_2 on the Frost diaram has a slope of + 0.95, the standard potential of MnO_2 reduction to Mn^{3+}. This is the number that is written above the arrow in the Latimer diagram for *Mn*. Multielectron potentials can be calculated easily by connecting the dots in a Frost diagram.

- Thermodynamic stability is found at the bottom of the diagram. Thus, the lower a species is positioned on the diagram, the more thermodynamically stable it is (from a oxidationreduction perspective)

Mn (II) is the most stable species.

- A species located on a convex curve can undergo disproportionation MnO_4^{2-} and *Mn* (III) tends to disproportionate.
- Those species on a concave curve do not typically disproportionate.

MnO_2 does not disproportionate

- Any species located on the upper left side of the diagram will be a strong oxidizing agent.

MnO_4^- is a strong oxidizer.

- Any species located on the upper right side of the diagram will be a reducing agent. Manganese metal is a moderate reducing agent

- These diagrams describe the termodynamic stability of the various species.

Although a given species might be thermodynamically unstable toward reduction, the kinetics of such a reaction might be vey slow.

Although it is thermodynamically favorable for permanganate ion to be reduced to *Mn* (II) ion, the reaction is slow except in the presence of a catalyst. Thus, solutions of permanganate can be stored and used in the laboratory

- The information obtained from a Frost diagram is for species under standard conditions (pH = 0 for acidic solution and pH = 14 for basic solution).

Changes in pH may change the relative stabilities of the species. The potential of any process involving the hydrogen ion will change with pH because the concentration of this species is changing.

Under basic conditions aqueous Mn^{2+} does not exist. Instead Insoluble $Mn(OH)_2$ forms.

12.3 Solubility product principle

12.3.1 Solubility

When a sparingly soluble ionic substance is dissolved in any solvent, it dissociates into positively charged cations and negatively charged anions. The extent of solubility of the ionic substance depends on different factors like temperature, pressure, presence of common ions etc. The ability of an ionic substance to dissolve in any solvent is called solubility.

12.3.2 Solubility Product Principle

Solubility product of a sparingly soluble electrolyte is defined as the product of its ions in its saturated condition at 25°C. The value of solubility product of a sparingly soluble salt is always constant at given temperature. For example the solubility product of $AgCl$ at 25°C is 1.6×10^{-10}. It represents the level at which a solute dissolve in solution.

Let us consider a sparingly soluble electrolyte AB that dissolves very slightly in water. It dissociates into cations and anions.

$$AB \rightleftharpoons A^+ + B^-$$

At first, AB dissociates to give A^+ and B^-. As the concentration of A^+ and B^- is increased, the backward reaction initiates and the reaction comes under equilibrium. When the solution is saturated at 25°C, the concentration of AB, A^+ and B^- remains constant. Now, we can apply the law of mass action to this equilibrium system.

$K = [A^+][B^-]/[AB]$ or, $K \times [AB] = [A^+][B^-]$, At saturated condition in 25°C,

$K \times [AB] = K_{sp}$ $\quad \therefore K_{sp} = [A^+][B^-]$

The above expression defines the solubility product principle.

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12.3.3 Application of Solubility Product Principle

1. It is used for the precipitatin of :
   - Group I cations [*Pb*, *Hg*(*I*), *Ag*] form precipitates as metal chloride with dilute hydrochloric acid.
   - Group II cations [*Hg*(*II*), *Cu*, *Bi*, *Cd*, *As*(*III*), *Sb*(*V*), *Sn*(*II*)] form precipitate as metal sulfide with hydrogen sulphide.
   - Group III cations [*Co*(*II*), *Ni*(*II*), *Fe*(*II*), *Fe*(*III*), *Cr*(*III*), *Al*(*III*), *Zn*(*II*), *Mg*(*II*)] form precipitate as metal hydroxide with treatment of ammonium chloride in neutral or ammoniacal media.
   - Group IV cations [*Ba*, *Sr*, *Ca*) forms precipitate as carbonates with treatment of ammonium chloride and in ammonium carbonate.
   - Group V cations [*Mg*, *Na*, *K*, NH_4^+] form precipitate as hydrogen phosphate salt by the treatment with NH_4OH, NH_4Cl and HPO_4^{2-} salt.
2. It has wide range of application in qualitative analysis.
3. This principle is usde for the purfication of common salt.

When the solubility product of given salt is less than its ionic product value, then precipitation occurs. This is called solubility product principle.

12.4 Ionic Product

When the temperature of solubility is greater or less than 25°C, then the product of its ion is called ionic product.

$[A^+][B^-]$ = Ionic product

We know that if the product of concentration of ions present in any solution at a given temperature is less than K_{sp}, the solution is called unsaturated and more solute can be dissolved in the solution. Thus,

- When solubility product is greater than ionic product, the solution is unsaturated.
- When solubility product is equal to ionic product, the solution is saturated.
- When ionic product is greater than solubility product, the solution is unsaturated.

12.5 Common Ion Effect

The common-ion effect is a shift in chemical equilibrium that affects solubility, based on Le Chatelier's principle. It occurs when a shared ion in a reacting system suppresses the solubility of an ionic substance, influencing product formation. This effect plays a key role in various chemical processes, including buffering, salt purification, soap production, precipitation, and water treatment. It is widely applied in industries such as pharmaceuticals. This paper presents

a concise literature review on the common-ion effect, highlighting its significance in chemistry. The common-ion effect refers to the decreased solubility of a salt when dissolved in a solution containing a shared ion. It plays a key role in chemical analysis, affecting solubility and dissolution rates. This phenomenon suppresses the dissociation of weak electrolytes when a strong electrolyte with a common ion is added, shifting equilibrium.

Let us consider the dissociation of equalibrium $HA \rightleftharpoons H^+ + A^-$. Dissociation constant $K_a = C_{H+}.C_{A-}/C_{HA}$ [assuming very dilut solution where $f\pm = 1$]. To this solution if we add common ion say H^+ or A^-, then in order to keep K_a constant some of the added ions will combine with opposite ion to produce HA. The net result is an increase in amount of undissociated part i.e. decrease in degree of dissociation. So, effect of common-ion is to depress degree of dissociation.

The presence of Common-ion generally affects the solubility of salts and other weak electrolytes because it basically decreases the solubility of a solute as the ionization of a weak acid or weak base is decreased by any strong electrolyte that provides a common ion. And since the solubility of solids that contain common ions with solvent is lower than solubility in pure solvents, Silver trioxonitrate (iv) $AgNO_3$ salt for instance, is said to be more soluble in pure water than it is in Sodium trioxonitrate (iv) $NaNO_3$ because they have the nitrate ion (NO_3^-)

The common-ion effect can be seen in the reaction between ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl), where NH_4Cl suppresses the ionization of NH_4OH, reducing hydroxide ion concentration, increasing hydrogen ion concentration, and lowering the solution's pH. This phenomenon also occurs in reactions involving ethanoic acid (CH_3COOH) and sodium ethanoate (CH_3COONa), silver sulfate (Ag_2SO_4) and sodium sulfate (Na_2SO_4), sodium chloride (NaCl) and hydrochloric acid (HCl), potassium carbonate (K_2CO_3) and magnesium carbonate (Mg_2CO_3), barium iodate ($Ba(IO_3)_2$) and barium nitrate ($Ba(NO_3)_2$), barium sulfate ($BaSO_4$) and sodium sulfate (Na_2SO_4), as well as sodium fluoride (NaF) and calcium fluoride (CaF_2).

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Dissociation of a Weak Acid

The ionization of ethanoic acid (CH_3COOH), a weak electrolyte, is suppressed when a strong electrolyte like sodium ethanoate (CH_3COONa) is added due to the common-ion effect. Normally, ethanoic acid dissociates in water as:

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

However, when sodium ethanoate dissociates:

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq),$$

it increases the concentration of ethanoate ions (CH_3COO^-) in the solution. According to Le Chatelier's principle, equilibrium shifts left to reduce ionization, maintaining the dissociation constant (Ka) of the acid. As a result, the ionization of CH_3COOH is suppressed, leading to an increase in pH.

Dissociation of a Weak Base

The ionization of ammonium hydroxide (NH_4OH), a weak base, is suppressed when ammonium chloride (NH_4Cl), a strong electrolyte with a common ammonium ion (NH_4^+), is added. Normally, ammonium hydroxide dissociates in water as:

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

However, when ammonium chloride dissociates:

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq),$$

it increases the concentration of NH_4^+ ions in the solution. According to Le Chatelier's principle, the equilibrium shifts left to reduce ionization, maintaining the base dissociation constant (Kb). As a result, the ionization of NH_4OH is suppressed, leading to a decrease in pH.

12.6 Applications of Common ion Effect in Chemistry

The common-ion effect is a crucial phenomenon widely applied in laboratory salt analysis. It plays a key role in various chemical processes, including buffering solutions, salt purification, soap production, salt precipitation, baking soda manufacturing, and water treatment.

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12.6.1 Purification of common salt

The common-ion effect is crucial in salt purification, as adding a common ion to a saturated salt solution induces precipitation. For example, sodium chloride (NaCl) can be purified from sodium sulfate (Na_2SO_4) and magnesium sulfate (Mg_2SO_4) by passing hydrogen chloride (HCl) gas through its solution. The dissociation of HCl increases chloride ion (Cl^-) concentration, shifting equilibrium left and precipitating pure NaCl.

$$NaCl(aq) \longrightarrow Na+ (aq) + Cl- (aq).$$

$$HCl\ (aq) \longrightarrow H+ (aq) + Cl- (aq).$$

Similarly, barium sulfate ($BaSO_4$) can be precipitated by adding sulfuric acid (H_2SO_4) to a barium-containing solution. H_2SO_4 dissociates completely, increasing sulfate ion (SO_4^{2-}) concentration, shifting equilibrium left, and causing $BaSO_4$ to precipitate.

Dissociation of $BaSO_4$: $BaSO4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Dissociation of H_2SO4: $H_2SO_4\ (aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq).$

12.6.2 Precipitation of Sulphides of Group II.

Precipitation occurs when the ion concentration exceeds the solubility product (Ksp). This can be achieved by increasing the concentration of a common ion. For example, to precipitate Group II sulfides, hydrogen sulfide (H_2S) gas is passed through the solution in the presence of hydrochloric acid (HCl):

$$\mathbf{H_2S \longrightarrow 2H^+ + S^{2-}}$$

HCl provides H^+ ions as common ions, shifting equilibrium left and suppressing H_2S ionization. This reduces sulfide ion (S^{2-}) concentration just enough to exceed the solubility product, leading to the precipitation of Group II sulfides like CuS, PbS, and CdS.

12.6.3 Precipitation of Sulphides in Group III

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Group III cations precipitate as hydroxides when ammonium hydroxide (NH_4OH) is added in the presence of ammonium chloride (NH_4Cl). Here, NH_4^+ acts as the common ion, suppressing NH_4OH ionization:

$$NH_4OH \rightarrow NH_4^+ + OH^-$$

The increased NH_4^+ concentration shifts equilibrium left, reducing OH^- concentration. This allows only the hydroxides of aluminum (Al), iron (Fe), and chromium (Cr) to exceed their solubility products and precipitate, while hydroxides of zinc (Zn), nickel (Ni), and cobalt (Co) remain dissolved due to their higher solubility product.

12.6.4 Precipitation of Sulphides of Group IV

In qualitative analysis, Group IV sulfides, which have a higher solubility product, are precipitated using hydrogen sulfide (H_2S) in the presence of ammonium hydroxide (NH_4OH). The OH^- ions from NH_4OH react with H^+ ions from H_2S to form water:

$$H^+ + OH^- \rightarrow H_2O$$

The removal of H^+ shifts the equilibrium of H_2S dissociation to the right:

$$H_2S \rightarrow 2H^+ + S^{2-}$$

This increases the concentration of sulfide ions (S^{2-}) enough to exceed the solubility product, leading to the precipitation of sulfides like CoS, NiS, and ZnS.

12.6.5 Softening of hard water

Hard water, containing dissolved calcium and magnesium salts, can be softened using chemicals like calcium hydroxide (slaked lime) and sodium carbonate (soda ash) or through ion exchange. Adding these chemicals causes the precipitation of sparingly soluble calcium carbonate and magnesium hydroxide via the common-ion effect:

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$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$2NaOH + Ca(HCO_3)_2 + Ca^{2+} \rightarrow 2CaCO_3 \downarrow + 2H_2O + 2Na^+$$

Lime reacts with bicarbonate alkalinity to form calcium carbonate, while magnesium hydroxide precipitates at high pH. However, partial solubility limits cold lime softening, and hot lime softening is not suitable for potable water. After softening, sedimentation and filtration remove precipitates.

The common-ion effect is also useful in treating wine wastewater, aiding in the recovery of organic compounds like tartaric acid, which has applications in the food and pharmaceutical industries.

12.6.6 Manufacture of sodium bicarbonate: Solvay process

The common-ion effect plays a key role in the Solvay process, used for large-scale production of sodium carbonate ($Na_2CO_3 \cdot 10H_2O$). It helps maintain the (NH_3 + NH_4Cl) buffer solution during the precipitation of sodium bicarbonate ($NaHCO_3$).

The process involves reacting brine (NaCl) and limestone ($CaCO_3$) to form soda ash:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$

When a saturated NaCl solution is combined with ammonia (NH_3) and carbon dioxide (CO_2), sodium bicarbonate precipitates due to its reduced solubility in a concentrated NaCl solution:

$$NaCl + CO_2 + NH_3 + H_2O \rightarrow NaHCO_3 + NH_4Cl$$

This principle enables the separation of $NaHCO_3$, which can then be converted into soda ash for industrial and domestic applications.

12.7 Summary

- **Latimer diagrams** display the standard electrode potentials (E°) of different oxidation states, helping predict the tendency of a species to undergo oxidation or reduction.
- **Frost diagrams** plot the relative free energy of oxidation states, aiding in the identification of stable and unstable species and predicting disproportionation reactions.

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These diagrams are widely used in electrochemistry, corrosion studies, and industrial redox processes.

- **Solubility** refers to the maximum amount of a solute that can dissolve in a solvent at a given temperature.
- **Solubility Product Principle (Ksp)** states that for a sparingly soluble ionic compound, the product of the molar concentrations of its ions, each raised to the power of its stoichiometric coefficient, remains constant in a saturated solution.
- **Applications of Ksp** include predicting precipitation, calculating solubility, and controlling the formation of scale in water treatment.
- **Ionic Product** represents the product of ion concentrations in a solution at any moment and helps determine whether precipitation will occur based on Ksp.
- **Common Ion Effect** describes the suppression of the dissociation of a weak electrolyte when a common ion is added, thereby reducing solubility.

1. **Purification of Common Salt** – Addition of HCl gas to impure NaCl solution precipitates pure NaCl.
2. **Precipitation of Sulphides in Group II** – H_2S in acidic conditions precipitates sulfides like CuS and PbS.
3. **Precipitation of Sulphides in Group III** – NH_4OH and NH_4Cl suppress OH^- concentration to selectively precipitate $Al(OH)_3$, $Fe(OH)_3$, and $Cr(OH)_3$.
4. **Precipitation of Sulphides in Group IV** – H_2S in basic conditions increases S^{2-} concentration, precipitating CoS, NiS, and ZnS.
5. **Softening of Hard Water** – Addition of Na_2CO_3 or $Ca(OH)_2$ precipitates Ca^{2+} and Mg^{2+} ions, reducing water hardness.

12.8 Model Questions

A. Multiple Choice Type Questions

1. In a Latimer diagram, what does a more negative reduction potential indicate?

a) A strong oxidizing agent
b) A weak reducing agent
c) A strong reducing agent
d) A stable oxidation state

Answer: c) A strong reducing agent

2. Which of the following statements about Frost diagrams is correct?

a) The y-axis represents oxidation state
b) A species at a higher point is more stable
c) A downward slope indicates a tendency for disproportionation
d) The x-axis represents the free energy of the species

Answer: c) A downward slope indicates a tendency for disproportionation

3. The solubility product constant (Ksp) is used to determine:

a) The rate of a reaction
b) The equilibrium constant for acid-base reactions
c) The solubility of a sparingly soluble salt
d) The amount of excess reagent in a reaction

Answer: c) The solubility of a sparingly soluble salt

4. Which of the following salts has the highest solubility in water?

a) A salt with a very low Ksp
b) A salt with a high Ksp
c) A salt with a common ion present
d) A salt that undergoes hydrolysis

Answer: b) A salt with a high Ksp

5. What happens when NH_4Cl is added to an NH_4OH solution?

a) NH_4OH ionization increases
b) The solution becomes more acidic
c) The solution becomes more basic
d) NH_4OH dissociates completely

Answer: b) The solution becomes more acidic

6. In qualitative analysis, which group of cations is precipitated as sulfides in acidic medium?

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a) Group I
b) Group II
c) Group III
d) Group IV

Answer: b) Group II

7. The solubility of calcium carbonate ($CaCO_3$) in water decreases when:

a) HCl is added
b) NaCl is added
c) $CaCl_2$ is added
d) NH_4OH is added

Answer: c) $CaCl_2$ is added

8. The common ion effect is useful in which of the following processes?

a) Increasing solubility of salts
b) Precipitation of insoluble salts
c) Increasing ionization of weak acids
d) Enhancing the conductivity of solutions

Answer: b) Precipitation of insoluble salts

9. What is the role of ammonium hydroxide in the precipitation of Group III cations?

a) It increases OH^- concentration
b) It decreases NH_4^+ concentration
c) It acts as a strong acid
d) It forms soluble complexes with all cations

Answer: a) It increases OH^- concentration

10. Which method is commonly used to remove hardness from water?

a) Addition of NaCl
b) Addition of $CaCO_3$
c) Addition of $Ca(OH)_2$ and Na_2CO_3
d) Boiling alone

Answer: c) Addition of $Ca(OH)_2$ and Na_2CO_3

B. Short Type Questions

1. What is the significance of a more negative reduction potential in a Latimer diagram?
2. How can a Frost diagram be used to predict disproportionation reactions?
3. Define the solubility product constant (Ksp) and explain its importance.

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4. What is the common ion effect, and how does it influence solubility?
5. Why does the addition of NH_4Cl to NH_4OH solution suppress the ionization of NH_4OH?
6. How is the common ion effect applied in the purification of common salt?
7. What role does hydrogen sulfide (H_2S) play in the precipitation of Group II sulfides?
8. How does the addition of ammonium chloride (NH_4Cl) help in the selective precipitation of Group III hydroxides?
9. Explain how lime ($Ca(OH)_2$) and soda ash (Na_2CO_3) are used for softening hard water.
10. Why does the solubility of sodium bicarbonate decrease in a concentrated NaCl solution during the Solvay process?

C. Assay Type Questions

1. Explain Latimer and Frost diagrams and their significance in predicting redox reactions.
2. Describe the solubility product principle (Ksp) and its role in determining the solubility of sparingly soluble salts.
3. What is the common ion effect? Discuss its mechanism and impact on the solubility of salts.
4. Discuss the application of the common ion effect in the purification of common salt.
5. Explain the role of the common ion effect in the selective precipitation of sulfides in qualitative analysis of cations (Groups II, III, and IV).
6. Describe the process of softening hard water using lime and soda ash, explaining the chemical reactions involved.
7. How does the addition of a common ion affect the dissociation of weak acids and weak bases? Illustrate with suitable examples.

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8. Discuss the industrial applications of the solubility product principle with examples.
9. Explain how the common ion effect is utilized in the Solvay process for the manufacture of sodium bicarbonate and sodium carbonate.
10. Discuss the role of hydrogen sulfide (H_2S) and ammonium hydroxide (NH_4OH) in the precipitation of metal sulfides in qualitative inorganic analysis.

12.9 Further Reading

1. **Atkins' Physical Chemistry** – Peter Atkins, Julio de Paula
   Covers redox reactions, electrochemistry, and solubility equilibria in detail.
2. **Principles of Inorganic Chemistry** – Puri, Sharma & Kalia
   Discusses qualitative analysis, solubility product, and common ion effect with applications.
3. **Vogel's Qualitative Inorganic Analysis** – G. Svehla
   A comprehensive guide on qualitative analysis, including the precipitation of sulfides and common ion effect.
4. **Inorganic Chemistry** – Shriver & Atkins
   Includes redox potential diagrams (Latimer and Frost), solubility equilibria, and ionic equilibria.
5. **General Chemistry: Principles and Modern Applications** – Ralph H. Petrucci

Unit 13: Acid-Base concept

Contents

13.0 Objectives

13.1 Introduction

13.2 Different Types of Acid-Base Concepts and Solvents

13.2.1 Arrhenius concept or water ion concept

13.2.2 Solvent system concept

13.2.3 Bronsted-lowry concept or protonic concept

13.2.4 Lux-flood concept

13.2.5 Lewis electronic concept

13.2.6 Usanovich concept

13.3 Levelling and Differentiating Effect of Solvent

13.4 Relative Strength of Different Acids and Bases

13.5 Relative Strength of Mononuclear Oxyacids: Pauling Rule

13.6 Hard and Soft Acid-base (HSAB) Principle and its Application

13.6.1 Usefulness of SHAB principle

13.7 Summary

13,8 Model Questions

13.9 Further Reading

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13.0 Objectives

After reading this unit, we will be able to:

- Concepts of acid-base theories
- Drago-Wayland equation
- Definition of levelling and differentiating effect
- Concept of relative strength of acids and bases
- Details concept of HSAB theory and its applications
- Definition of super acid, buffer, pH and their significations
- Detail study on acid-base titrations

13.1 Introduction

Acids and bases play a central role in chemistry because, with th exception of redox reactions, every chemical reaction can be classified as an acid-base reaction. Our understanding of chemical reactions as acid-base interactions comes from the wide acceptance of the Lewis definition of acids and bases, which suppliment both the earlier Bronsted-Lowry concept and the first definition the Arrhenius model. Arrhenius first defined acids as proton (H^+) producers in aqueous solution and bases as hydroxide (OH^-) producers. Although this model is intuitively correct, it is limited to substances that include proton and hydroxide groups. Bronsted and Lowry proposed the more general definitions of acids and bases as proton donors and acceptors, respectively. Unlike the Arrhenius conception, the Bronsted-Lowry model accounts for acids in solvents other than water, where the proton transfers do not necessarily involve hydroxide ions. But the Bronsted-Lowry model fails to explain the observation that metal ions make water more acidic. Finally, Lewis gave us the more general definition of acids and bases that we use today. According to Lewis, acids are electron pair acceptors and bases are electron pair donors. Any chemical reaction that can be represented as a simple exchange of valence electron pairs to break and from bonds is therefore an acid-base reaction.

Acid-base chemistry is important to us on a practical level as well, outside of laboratory chemical reactions. Our bodily functions, ranging from the microscopic transport of ions across nerve cell membranes to the macrosopic acidic digestion of food in the stomach, are all ruled by the principles of acid-base chemistry. Homeostasis, the temperature and chemical balances in our bodies, is maintained by acid-base reactions. For example, fluctuations in the pH, or concentration of hydrogen ions, of our blood is moderated at a comfortable level through use of buffers. Learning how buffers work and what their limitations are can help us to better understand our physiology. We will start by introducing fundamentals of acid-base chemistry and the calculation of pH, and then we will cover techniques for measuring pH. We learn about buffers and see how they are applied to measure the acidic content of solutions through titration.

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13.2 Different Types of Acid-Base Concepts and Solvents

Various concepts of acids and bases were developed from time to time, though each concept has its limitation. Latter on, G. N. Lewis listed the following based upon which the definition are to be developed to avoid limitations.

(a) The process of neutralization is a rapid one.

(b) Acid and bases can be titrated one against the other in presence of indicator.

(c) A stonger acid or base can displace a weaker acid or base during reaction.

(d) Acid and bases act as a catalyst in various reaction.

In addition to these Faraday's recognization that the ions carry current and acids-bases are electrolytes, led much foundation for the development of semi-modern and modern concept of acids and bases.

there are six concepts regarding acids and bases, which are discussed below with their advantages and limitations.

13.2.1 Arrhenius concept or water ion concept

According to Arrhenius "acids are hydrogen containing substances which gives H^+ ions in aqueous solution whereas bases are substances which gives OH^- ions in aqueous solution."

The process of neutralization amounts to the combination of H^+ with OH^- to form water

ACID : $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

BASE : $NaOH + H_2O \rightleftharpoons Na^+ + OH^- + H_2O$

Neutralization : $H^+ + OH^- \rightleftharpoons H_2O$

Advantages : (i) This concept readily explains that the heat of neutralization of a strong acid by a strong base should be constant.

(ii) The comcept offered a means of co-relating catalytic behavior with the concentration of H^+ ion.

Limitation : (i) Acid base behavior is restricted to the presence of solvent water only. But acid-base behavior observed in other solvents as well as in absence of solvent.

(ii) The concept can not explain the acidic character of certain salt like $AlCl_3$ in aqueous solution.

13.2.2 Solvent system concept

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In this model, the autoionization of the solvent is considered and any subtance capable of increasing the concentration of the cation (i.e. lyonium) produced by the autoionization of the solvent is regarded as an acid in that solvent. On the other hand, the species which can enhance the concentration of the anion (i.e. lyate) produced in the autoionization of the solvent is considered as a base in the solvent. Hence to characterize the substances as acid or base in a particular solvent, it is required to know the mode of autoionization of the solvent under consideration. Some common solvents with their autoionization modes are given below.

Solvent	Acid		Base
$H_2O + H_2O \rightleftharpoons$	H_3O^+	+	OH^-
$NH_3 + NH_3 \rightleftharpoons$	NH_4^+	+	NH_2^-
$SO_2 + SO_2 \rightleftharpoons$	SO^{2+}	+	SO_3^{2-}
$HF + HF \rightleftharpoons$	H_2F^+	+	F^-

In liquid H_2O, NH_3, SO_2, HF typical acid base reaction are :

$$HCl(acid) + NaOH(base) \rightleftharpoons NaCl(salt) + H_2O(solvent)$$

$$NH_4Cl(acid) + NaNH_2(base) \rightleftharpoons NaCl(salt) + 2NH_3(solvent)$$

$$Na_2SO_3(base) + SOCl_2(acid) \rightleftharpoons NaCl(salt) + SOCl_2(solvent)$$

$$H_2NO_3^+(acid) + F^-(base) \rightleftharpoons HNO_3(salt) + HF(solvent)$$

Advantage : It can extend the concept of acid-base interaction in both protic and aprotic solvents

Limitation : (i) It pays an excessive attention to the idea of autoionization of the solvents ignoring the other physical and chemical properties of the solvents. It even ignores the properties arising from the dielectric constant which is fact, determines the possibility of autoionization.

(ii) It cannot explain many acid-base reactions occuring in the absence of any solvent.

(iii) Many acid base reactions involving the neutral molecules cannot be explained in this model.

13.2.3 Bronsted-lowry concept or protonic concept

Bronsted and Lowry in 1923 independetly proposed a more fruitful concept for acid and bases. According to them "An acid is defined as any hydrogen containing molecule or ions that can release a proton (H^+) to any other substance and a base is any molecule or ion which can accept a proton." In short "An acid is a proton donor and base is a proton acceptor."

Following are some examples :

Protonic acids : $HCl \rightarrow H^+ + Cl^-$ $\quad [Al(H_2O)_6]^{3+} \rightarrow H^+ + [Al(H_2O)_5OH]^{2+}$

Protonic bases : $NH_3 + H^+ \rightarrow NH_4^+$ $\quad HCO_3^- + H^+ \rightarrow H_2CO_3$

An acid and a base that are related by the gain and loss of a proton are called a conjugate acidbase pair. For example, NH_4^+ is the conjugate acid of NH_3, and NH_3 is the conjugate baseof NH_4^+. Every acid has associated with it a conjugate base. Likewise, every base has associated with it a conjugate acid.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

base Acid Conj acid Conj base

AND

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$

Acid base Conj base Conj acid

Advantage : (i) According to this concept acid-base behavior is not made dependent upon the presence or absence of any particular solvent.

(ii) This concept is useful in according for the acidic or alkalin nature of aqueous solution of certain salts like $FeCl_3$ or Na_2CO_3. The acidic or alkalinity character develop due to hydrolysis.

$$FeCl_3 + 6H_2O \rightleftharpoons [Fe(H_2O)_6]^{3+} + 3Cl^-$$

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H^+$$

(iii) This concept gives idea regarding the relative strength of acids and bases (both qualitative and quantitative).

Limitation : (i) It gives too much emphasis on the proton although the common acids are protonic in nature, yet there are many acids which are not protonic e.g. $AlCl_3$, CO_2, SO_2, etc.

(ii) Although this concept gives a major of the relative strength from the determined K values with respect to a common base or acid. Yet it fails to compare the relative strength of the so called common strong acids like HCl, H_2SO_4, HNO_3 etc. due to the levelling effect of the solvent. In aqueous solution these acids behave equally stronger due to levelling effect of water.

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13.2.4 Lux-flood concept

They put forward a concept for defining acid base character of oxides, according to them acids are oxide ion acceptor and bases are oxide ion donor.

$$\text{Acid} + O^{2-} \rightleftharpoons \text{Base}$$

$$CO_2 + O^{2-} \rightleftharpoons CO_3^{2-}$$

$$SO_3 + O^{2-} \rightleftharpoons SO_4^{2-}$$

This view is particularly-useful in high temperature chemistry, as in the field of ceramics and metallurgy :

$$CaO \rightleftharpoons Ca^{2+} + O^{2-}$$

$$\underline{SiO_2 + O^{2-} \leftrightarrow SiO_3^{2-}}$$

$$CaO + SiO_2 \rightleftharpoons CaSiO_3$$

Base + Acid Salt

Zinc oxides shows amphoterism as it can both donate or accept oxide ions.

Base : $ZnO + S_2O_7^{2-} \rightleftharpoons Zn^{2+} + 2SO_4^{2-}$

Acid : $Na_2O + ZnO \rightleftharpoons Na_2ZnO_2$

This concept is very much limited and it gained very little importance. This concept is unable even to explain the acidic and basic character of very common acids and bases such as HCl, H_2SO_4, HNO_3 etc.

13.2.5 Lewis electronic concept

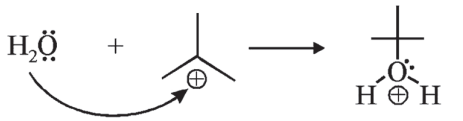
Lewis concept was proposed in 1923 by **Gilbert N. Lewis** which includes reactions with acid-base characteristics that do not involve a hydrogen transfer. A Lewis acid is a species that reacts with a Lewis base to form a Lewis adduct. The Lewis acid accepts a pair of electrons from another species; in other words, it is an electron pair acceptor. Bronsted acid-base reactions involve hydrogen transfer reactions while Lewis acid-base reactions involve electron pair transfers. All Bronsted acids are Lewis acids, but not all Lewis acids are Bronsted acids.

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

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

In the first example BF_3 is a Lewis acid since it accepts an electron pair from the fluoride ion. This reaction cannot be described in terms of the Bwonsted theory because there is no hydrogen transfer. The second reaction can be described using either theory. A hydrogen is transferred from an unspecified Bronsted acid to ammonia, a Bronsted base; alternatively, ammonia acts as a Lewis base and transfers a lone pair of electrons to form a bond with a hydrogen ion. Lewis acids and bases are defiened in terms of electron pair transfers. A Lewis base is an electron pair donor, and a Lewis acid is an electron pair acceptor. An organic transformtion (the creation of products from reactants) essentially results from a process of breaking bonds and forming new ones. This process basically amounts to electron pair transfers. Ionic mechanisms involve electron pair transfers and are therefor described by the Lewis acid-base theory. The Lewis definition implies the presence of high electron density centers in Lewis bases, and a Lewis base the electron pair donated by the base is used to form a new sigma bond to the electron deficient center in the acid. The identification of Lewis bases follows basically the same guidelines as the identification of Bronsted bases. They frequently contain atoms that have nonbonding electrons, or *lone pairs*. On the other hand, Lewis acids frequently contain atoms with an incomplete octet, a full positive charge, or a partial positive charge. Water is an example of a Lewis base. Carbocations are examples of Lewis acids. When water reacts with a carbocation as shown below, one of the electron pairs from oxygen is used to form a new sigma bond to the central carbon in the carbocation. As with Bronsted acid-base reactions, curved arrow is used to indicate the movement of electron pairs during the reaction process. The arrow always originates with the Lewis base and moves towards the area of electron deficiency in the Lewis acid. To avoid confusion between the Lewis and the Bronsted definitions of acids and bases, Lewis bases are sometimes called nucleophiles, and Lewis acids are called electrophiles. In the example above, water acts as a nucleophile (donates electrons), and the carbocation acts as an electrophile (receives electrons). Since Bronsted acids and bases are a sub category of the more encompassing Lewis definition, It can be said that most Bronsted bases are also nucleophiles, and that the proton ia a Lewis acid, or an electrophile, There are however some subtle differences to keep in mind.

E-copy



Lewis base | Lewis acid | Addition product

Recognizingnucleophiles : For the most part, the same criteria used for identifying Bronsted bases can also be used to identify nucleophiles. Here is a summary.

1. The most common type of nucleophiles are those containing atoms with unshared electron pairs, such as the following. Notice that nonbonding electrons are frequently omitted from formulas. Always remember their presence on oxygen, nitrogen, and negatively charged carbon atoms. H_2O, OH^-, NH_3, RNH_2, CN^-

2. A negatively charged species is usually a stronger nucleophile or base than its neutral analog. Thus, hydroxide ion is stronger, both as a base and as a nucleophile, than water.

3. Carbon bonded to a metal has strong negative character, revealed when writing resonance structures. The carbon atom in such molecules is conidered a strong nucleophile. Recall the molecules is structures of *n*-butyllithium and Grignard (organo-magnesium) reagents from previous notes.

4. The pi bond is a region of high electron density. Pi bonds are not as strong as sigma bonds, which means that pi electrons are more available for reactions because pi bonds are more easily broken. Molecules containing pi bonds are considered weak nucleophiles or bases, because they can react with strong acids or electrophiles. See examples under Bronsted acid-base chemistry.

5. Periodic trends in nucleophilicity are such that, other factors being similar, nucleophilicity increases from right to left across the same row, and from top to bottom across the same period or group. Make a note that this trend is different from the basicity trend, which increases in the same way across a row, but from bottom to top within a period.

E-copy

Nucleophilicity trends

Same row $OH^{\ominus} > F^{\ominus}$ and $NH_3 > H_2O$

Same group $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ and $CH_3S^{\ominus} > CH_3O^{\ominus}$

6. Basic vs. nucleophilic behavior. There are some differences between Bronsted bases and nucleophiles. First, the term base is reserved for substances seeking acidic protons, whereas the term nucleophile is used for substances seeking electron-deficient centers, be they protons or other atmos (most commonly carbon).

Second, in acid-base reactions the size (or bulk) of the base seldom matters. In nucleophilic reactions, the size of the nucleophile can be an important (steric) factor. Smaller is more effective. Thus, although the nucleophilic atom in the two species below is the same (oxygen) and they have similar structures, methoxide ion is a more effective nucleophile than *t*-butoxide ion, even though they are about equally effective as bases. The larger *t*-butoxide ion has more difficulty reaching an electrophilic center, which is typically a carbon buried at the core of the molecular structure. That is not a problem when it acts as a base because acidic protons usually lie in the periphery of the molecule and are easily accessible.



methoxide ion
smaller ion
better nucleophile

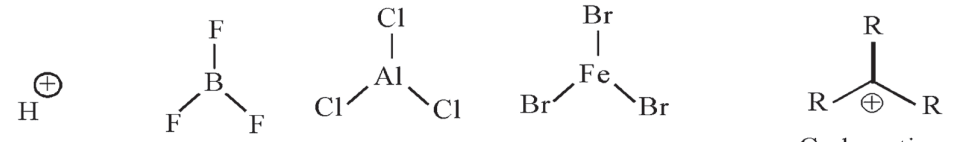
t-butoxide ion
larger ion,
poorer nucleophile

Recognizing electrophiles : There are two requirements for a molecule to be considered a good electrophile. First, it must contain an electrophilic center or atom. Second, the electrophilic atom must be able to accommodate a new sigma bond. Please keep in mind the difference between electrophile and electrophilic center. The term electrophile refers to the modlecule. The term electrophilic center refers to the particular part of the molecule susceptible to nucleophilic attack. To avoid confusion, the term *substrate* is frequently used in reference to electrophiles. This term denotes a molecule being acted upon by another agent. For example, an enzyme substrate is

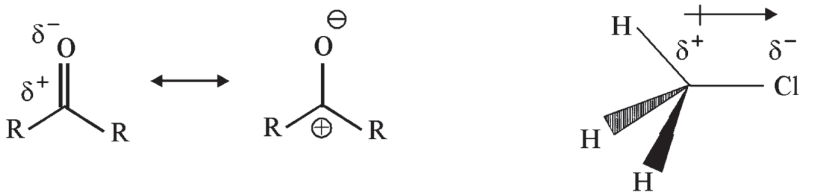
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a molecule being modified by an enzyme. Likewise, an electrophile can be thought of as the substrate of a nucleophile when the latter "attacks" its electrophilic center. *Electrophilic centers are areas of low electron density.* Most often they are atoms which (a) *contain an incomplete octet,* and/or (b) *carry a full or a partial positive charge.* A partial positive charge can be revealed by writing resonance structures, or by identifying a polar bond.

1. The following are examples of electrophiles containing atoms with incomplete octets :



2. These are examples of electrophiles containing atoms with partial positive charges :



3. Atoms of the second row like oxygen and nitrogen, which are more electronegative than carbon, seldom act as electrophilic centers, even if they carry a positive charge. In that situation they seek to lessen their positive character by sharing the charge with adjacent atoms, causing them to become acidic (protons) or electrophilic (carbon for instance). Resonance structures can reveal this shift of positive charge.



The ammonium and hydronium are of moderate high acidity because the highly negative oxygen and nitrogen seek to transfer the positive charge to adjacent proton, to make acidic. In addition, those atoms cannot accommodate another bond without violating the octate rule.

E-copy



The reaction with a base (B^-) is an equilibrium process that normally has low activation energy and is therefore relatively fast.

Advantage : (i) This concept is more general than the other concepts because the acid base behavior is not dependent upon the presence or absence of any solvent.

(ii) It explains the long accepted basic properties of metallic oxides and acidic properties of nonmetallic oxides.

(iii) This theory can explain those acid-base reaction which occur at the high temperature in the gas phase and in absence of solvent.

Limitation : (i) Since the strength of Lewis acids and bases depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

(ii) According to phenomenological criteria the process of neutralization is a rapid one. But those are many reaction Lewis acid-base reactions are slow.

13.2.6 Usanovich concept'

Actually, this concept (1934) extents and generalizes the idea of Lewis acid-base concept. It does not get confined within the domain of electron pair donation and acceptance. It defines acids bases as follows.

An acid is a substance capable of accepting anions or electrons or giving up cations, and a base is a substance which can combine with the cations or give up anions or electrons. Thus the redox reactions (i.e. electron transfer reactions) are also regarded as acid-base reactions. Here it is worth mentioning that both the Lewis and Usanovich concepts are identical in terms of kind but they may differ on the degree of the process. In Lewis acid base interactions, the donated electron pair is commonly shared by the reactants in the adduct but in Usanovich concept, the electrons might be completely or partially transferred. There are some reactions which may be considered as redox reactions (i.e. Usanovich's acid base reactions) as well as Lewis acid base adduct formation. These are,

$$O + :SO_3^{2-} \rightleftharpoons SO_4^{2-}, \quad C_6H_5N: + O \rightleftharpoons C_6H_5N^+ \rightarrow O^-$$

Practically, Usanovich concept includes all the reactions as acid-base reactions. These are illustrated by considering some specific examples.

E-copy

(i) $SiO_2 + CaO \rightleftharpoons Ca^{2+}SiO_3^{2-}$ Here SiO_2 takes up the anion, O^{2-} which is given up by CaO

(ii) $Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$ Here Fe^{2+} combines with the anion CN^-

(iii) $2Fe^{3+} + Sn^{2+} \rightleftharpoons Sn^{4+} + 2Fe^{2+}$ Here Sn^{2+} gives up electrons which are taken up by Fe^{3+}. Thus Sn^{2+} act as a base while Fe^{3+} act as an acid.

13.3 Levelling and Differentiating Effect of Solvent

In water, no stronger than H_3O^+ can survive. Thus, water levels off all such stronger acids to the acidity of H_3O^+. The effective proton affinity of H_2O in water 1130 $kJ\ mol^{-1}$. Hence, all acids (HA) for which effective proton affinity of their conjugate bases (A^-) is smaller than 1130 $kJ\ mol^{-1}$ are levelled off in water (i.e. $HA + H_2O \rightarrow H_3O^+ + A^-$).

In water, any base stronger than OH^- cannot survive. The effective proton affinity of OH^- in water is 1188 $kJ\ mol^{-1}$. Thus any base (B) for which the effective proton affinity is greater than 1188 $kJ\ mol^{-1}$ will be completely converted into the conjugate acid (BH^+) with the release of OH^- in water ($B + H_2O \rightarrow BH^+ + OH^-$).

This is why, we cannot study NH_2^- or CH_3^- in water as these get completely protonated as follows : $LiCH_3 + H_2O \rightarrow Li^+ + OH^- + CH_4$

For liquid NH_3, the proton affinity of NH_3 is greater than that of H_2O and consequently the acids which are weaker and differentiated in water may be levelled off in liquid NH_3. The proton affinity of NH_2^- is greater than that of OH^- and consequently, the stronger bases which are levelled off in water may not be levelled off in liquid NH_3.

13.4 Relative Strength of Different Acids and Bases

To measure the proton donating strength of an acid, a reference must be taken into consideration, as the extent of proton transfer definitely depends on two factors : (i) the proton donating power of the acid and (ii) the proton accepting power of the reference base participated in proton transfer equilibrium. Generally, to measure the proton donating strength (i.e. acid strength) of an acid, the solvent is taken as the refence base. This is an aqueous solution the following proton transfer equilibrium is to be considered.

E-copy

$Acid_1$ (A_1) + $Base_2$ (H_2O) $\rightleftharpoons$ $Base_1$ (B_1) + H_3O^+ $(Acid_2)$

$K_{eq} = [H_3O^+][B_1]/[A_1][H_2O]$

The extent of proton transfer is measured by the equilibrium constant (in dilute solution), K. The conventional acid dissociation constant (K_a) is given by :

$K_a = K_{eq}[H_2O] = [H_3O^+][B_1]/[A_1]$

In dulute solution, $[H_2O]$ can be taken as 55.5 moles per litre. Thus, $K_a = K_{eq} x$ 55.5. Thus in general, the acid dissociation constant can be defined as follows :

The acid dissociation constant is the product of the equilibrium constant of the proton transfer process and the concentration of the reference base (generally the pure solvent) with respect to which the extent of proton transfer is being measured.

Strongest acids are classified as $Ka > 1$ and usually $Ka >> 1$ (i.e. negative pKa values), while weak acids are classified as $Ka < 1$ (i.e. positivepKa values).

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression :

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H_3O^+ and A^- when the acid ionizes in water; Table 1 lists several strong acids. A weak acid gives small amounts of H_3O^+ and A^-.

Table 1 : *Some of the common strong acids and bases are listed here.*

Strong acid		Strong base	
$HClO_4$	perchloric acid	$LiOH$	lithium hydroxide
HCl	hydrochloric acid	$NaOH$	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

E-copy

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a grater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA :

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

we write the equation for the ionization constant as :

$$K_a = \left[H_3O^+\right]\left[A^-\right]/\left[HA\right]$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include [H_2O] in the equation. The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength

$CH_3CO_2H < HNO_2 < HSO_4^-$

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) K_a = 1.8 \times 10^{-5}$$

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO^{-2}(aq) K_a = 4.6 \times 10^{-4}$$

$$HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{-2}(aq) K_a = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is the percent ionization. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100 :

$$\%\text{ionization} = ([H_3O^+]_{eq}/[HA]_0) \times 100$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

E-copy

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yield 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

Table 2 : Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25°C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}

As we did with acids, we can measure the relative strengths of bases by measuring their base ionization constant (K_b) in aqueous solutions. In solutions of the saem concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B :

$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$,

We write the equation for the ionization constant as :

E-copy

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Where the concentrations are those at equilibrium. Again, we do not include [H_2O] in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are :

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq) K_b = 2.17 \times 10^{-11}$$

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) K_b = 5.6 \times 10^{-10}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) K_b = 1.8 \times 10^{-5}$$

A table of ionization constants of weak bases appears in TAble 3. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Tabl 3. : Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25°C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2 + + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.3×10^{-10}

Consider the ionization reactions for a conjugate acid-base pair, HA, A^- :

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O + (aq) + A^-(aq), K_a = [H_3O^+][A^-]/[HA]$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + HO^-(aq)$$

As shown in the previous chapter on equilibrium, the *k* expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' *K* expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that :

$$K_a \times K_b = [H_3O^+][A^-]/[HA] \times [HA][OH^-]/[A^-] = [H_3O^+][OH^-] = K_w$$

For example the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = Kw$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+– the acid is strong. Stong acids from very weak conjugate bases, and weak acids from stronger conjugate bases (Figure 1)

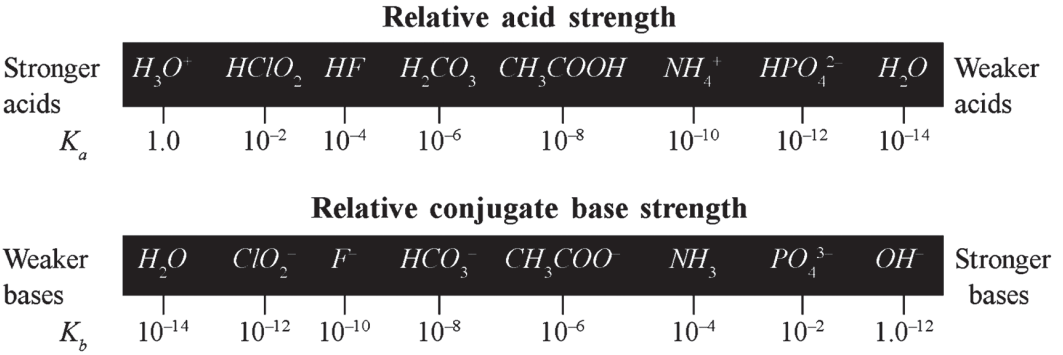


Figure 1 : This diagram shows the relative strengths of conjugate acid-base pairs, as inicated by their ionization constants in aqueous solution.

Figure 3. lists a series of acids an bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

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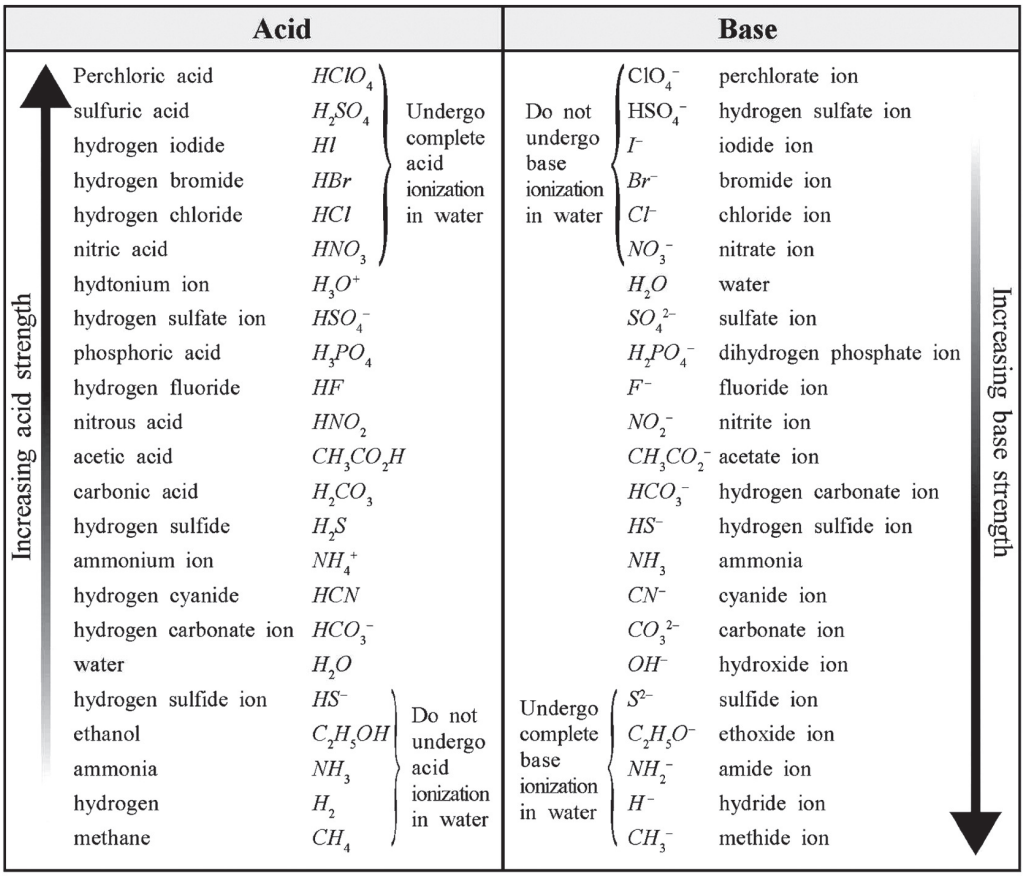


Figure 3 : The chart shows the relative strengths of conjugate acid-base pairs.

The first six acids in Table 1 are the most common strong acidss These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water form conjugate bases that can complete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Table 2 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

E-copy

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in the Table. 3. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

13.5 Relative Strength of Mononuclear Oxyacids: Pauling Rule

In H_nXO_m all the oxygen atoms are directly linked with the central atom X and ome of which are present as *OH* groups. Thus from the structural view point H_nXO_m can be represented as $O_{m-n}X(OH)_n$. Hence it is assumed that all *H-s* exist as *OH* groups. Each *X-OH* bond is formed by using one *X* electron and one *O* electron while in each $X \rightarrow O$ bond, there is a net loss of electron from *X*. In this way, the formal positive charge accumulated on the central atom is given by the number of $X \rightarrow O$ bonds and it becomes (*m-n*). With the increase of (*m-n*), the central atom becomes more and more electron deficient and it facilitate the removal of the proton from the *-O-H* bonds due to the enhanced electron withdrawing inductive effect towards the central atom. An empirical relationship between the values of (*m-n*) and acid strength measured by pK_1(i.e. first acid dissociation constant) has been proposed by Pauling as follows : $pk_1 \approx 8 - 5(m\text{-}n)$

(*m-n*)	0	1	2
pk_1 (observed)	~8.5	~2.8	<< 0
k_1 (observed)	$\sim 10^{-8}$–10^{-9}	$\sim 10^{-3} - 10^{-4}$	very strong

The successive pK values differ by 5 units. In many cases, the prediction has been supported experimentally.

E-copy

(*m-n*)	Acid	pK_1	pK_2	pK_3
0	$HClO_4$	7.5	—	—
	$HBrO_4$	8.7	—	—
	H_3AsO_3	9.2	—	—
	H_6TeO_6	8.8	—	—
	H_3PO_3	1.8	6.15	—
1	H_3PO_4	2.1	7.2	12.0
	H_3PO_2	2	—	—
	H_3AsO_4	3.5	7.2	12.5
	H_5IO_6	3.3	6.7	—
	H_2SO_3	1.9	7.3	—
	H_2SeO_3	2.6	6.6	—
	HNO_2	3.3	—	—
	H_2CO_3	6.4	10.3	—
2	HNO_3	Highly negative	—	—
	H_2SO_4	do	1.9	—
	H_2SeO_4	do	2.0	—
3	$HClO_4$	do	—	—
	$HMnO_4$	do	—	—

13.6 Hard and Soft Acid-base (HSAB) Principle and its Application

According to Lewis concept acid base reaction involves the formation of coordination complex. A strong acid strong base will form a stable complex.

$$A + : B = A \leftarrow B$$

R. G. Person (1963) introduced the soft and hard or hard and soft concept of acids and bases for determining the strengths of Lewis acids and bases. According to this concept, "a hard acid prefers to combine with a hard base and a soft acid prefers to combine with a soft base to form a more stable adduct." This is known as SHAB or HSAB concept. Hardness and softness refer to firmly and loosely bound electron respectively.

For the determining the hardness and softness of bases R. G. Pearson measured the equilibrium constant of the following exchange reaction.

$$BH^+ + CH_3Hg(H_2O)^+ \rightleftharpoons [CH_3HgB]^+ + H_3O^+$$

It was found that bases having more electronegative donors (*O*, *N*, and *F*) prefer to bind to the proton but bases with less electronegative donors (*P*, *S*, *I*, *Br*, *Cl*) prefer to bind to CH_3Hg^+. The former bases are hard bases and the later are soft bases.

6.9.1. Classification of acids and bases

From the measured K values R. G. Person classified Lewis bases as hard and soft having the following criteria. Bases with intermediate character are said to be boarder line.

Hard base	Soft base
(i) High electronegatively	(i) Low electronegativity
(ii) Low polarisibility	(ii) High polarsibility
(iii) Presence of filled orbital, empty may exist at higher energy level	(iii) Parially filled orbitals, empty orbitals are low lying.
e.g., H_2O, OH^-, F^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, NH_3, $R\text{-}NH_2$, $R\text{-}OH$, R_2O, etc.	e.g, H^-, I^-, SCN^-, $S_2O_3^{2-}$, CO, C_2H_4, C_6H_6, R_2S, R_3P, etc,

Border line : $C_6H_5 - NH_2$, C_5H_5N, N_2, N_3^-, NO_2^-, Br^-, etc.

Lewis acids also classified as hard, soft and boarder line having the following characteristics :

Hard acid	Soft acid
(i) Small size	(i) Large size
(ii) High positive oxidation state	(ii) Zero or low positive oxidation stae
(iii) Absence of any outer electrons which easily excited to higher states.	(iii) Presence of several exicitable valency electrons.
e.g., H^+, Li^+, Na^+, K^+, Mg^{2+}, Fe^{3+}, CO_2, SO_3, BF_3, $AlCl_3$, etc.	e.g, Cu^+, Ag^+, Hg^+, Hg^{2+}, I^+, I_2, Cl, M^0, etc,

Border line : Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, SO_2 etc.

13.6.1 Usefulness of SHAB principle

Hard –hard and soft-soft principle can be used as guide lines for predicting various chemical reactions. Following are some examples.

(i) BF_3 being a hard acid prefer to combine with hard base F^- and BH_3 being a soft acid prefer to combine a soft base H^-. So the following reactions proceeds to the right.

$$BF_3H^- + BH_3F^- \rightarrow BF_4^- + BH_4^-$$

E-copy

For similar reason the following reaction proceeds to the right.

$CF_3H + CH_3F \rightarrow CF_4 + CH_4$

(ii) Hard-hard and soft-soft combination can be used to explain the 'Pearson-Pauling paradox' of chemistry. According to the Pauling concept of electronegativity, *Cs* and *Hg* should form more stable bond with *F* as their electronegativity difference is greater. So the following reaction should not proceed to the right.

$LiI + CsF \rightleftharpoons LiF + CsI$

$HgF_2 + BeI_2 \rightleftharpoons BeF_2 + HgI_2$

In fact both the reactions proceed to the right and this anomaly can be explained by SHAB principle. On the left hand side there hard-soft and soft-hard combination (Li^+ – hard acid, I^- –soft base, Cs^+ – soft acid, F^- – hard base). To attain more stable hard-hard and soft-soft combination these reactions proceeds to the right.

(iii) The concept can explain the existance and non-existance of certain ion like AgI_2^-, is known for soft-soft combination whereas AgF_2^- does not exist as it involves soft-hard combination.

(iv) SHAB principle can be used to explain the existance of certain type of compounds as metal ores and non-existance of others. Thus hard acid like Mg^{2+}, Ca^{2+} and Al^{3+} occur in nature as $MgCO_3$, $CaCO_3$, and Al_2O_3 i.e. combining with a hard bases (CO_3^{2-}, O^{2-}). But they do not occur as sulphides because S^{2-} is a soft base. Soft acids such as Cu^+, Ag^+ and Hg^{2+} occur as their sulphides for soft-soft combination. On the otherhand border line acids like Ni^{2+}, Cu^{2+}, Pb^{2+} occur in nature both as carbonates and sulfides.

13.7 Summary

Acid-base theories have evolved to explain acid-base behavior in different contexts. Two significant concepts among them are the **Arrhenius concept** and the **solvent system concept**.

1. Arrhenius Concept (Water Ion Concept)

Proposed by Svante Arrhenius, this concept defines acids as substances that increase hydrogen ion (H^+) concentration in water, while bases increase hydroxide ion (OH^-) concentration. This

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theory is limited to aqueous solutions and does not account for acid-base reactions in non-aqueous solvents or gas phases.

2. Solvent System Concept

This concept extends acid-base behavior beyond aqueous solutions. It defines acids as substances that increase the concentration of cations characteristic of the solvent and bases as substances that increase the concentration of anions characteristic of the solvent. For example, in liquid ammonia (NH_3), NH_4^+ acts as an acid, while NH_2^- acts as a base. This approach allows acid-base reactions to be studied in a variety of solvents beyond water.

Levelling and Differentiating Effect of Solvents

Different solvents influence acid and base strength. A **levelling effect** occurs when strong acids or bases completely dissociate in a solvent, making them indistinguishable in strength. For example, in water, HCl, HNO_3, and H_2SO_4 are all equally strong because they fully ionize to form H_3O^+. In contrast, a **differentiating effect** occurs in less ionizing solvents, where differences in acid or base strengths are more apparent.

Relative Acid-Base Strength and Pauling Rule

The relative strength of acids and bases depends on their ability to donate or accept protons or electrons. In mononuclear oxyacids, Pauling's rule states that acid strength increases with higher electronegativity and oxidation state of the central atom.

Hard and Soft Acid-Base (HSAB) Principle

Proposed by Pearson, the HSAB principle classifies acids and bases as "hard" or "soft" based on their polarizability and charge density. Hard acids prefer to bind with hard bases, and soft acids prefer soft bases. This principle is widely used in predicting reaction pathways, stability of complexes, and biological interactions.

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13,8 Model Questions

A. Multiple Type Questions

1. According to the Arrhenius concept, a base is a substance that:
A) Increases H^+ concentration in water
B) Increases OH^- concentration in water
C) Donates a proton to another substance
D) Accepts a proton from another substance

2. Which acid-base concept is applicable in both aqueous and non-aqueous solvents?
A) Arrhenius concept
B) Bronsted-Lowry concept
C) Solvent system concept
D) Lewis concept

3. In liquid ammonia, NH_4^+ acts as an acid because it:
A) Donates an H^+ ion
B) Accepts an OH^- ion
C) Produces NH_2^- ions
D) Increases the concentration of H_3O^+

4. The levelling effect of a solvent is due to:
A) The formation of different acid-base pairs
B) The complete dissociation of strong acids and bases
C) The inability of weak acids to ionize
D) The formation of weaker conjugate bases

5. Which of the following statements is true about the Bronsted-Lowry concept?
A) Acids are electron pair acceptors
B) Acids are proton donors, and bases are proton acceptors
C) Acids increase OH^- concentration in water
D) It only applies to aqueous solutions

6. According to Pauling's rule, the strength of mononuclear oxyacids depends on:
A) The number of hydrogen atoms
B) The oxidation state and electronegativity of the central atom
C) The solvent used
D) The presence of hydroxide ions

7. Which acid-base concept is based on the transfer of an electron pair?
A) Arrhenius concept
B) Bronsted-Lowry concept
C) Lewis's concept
D) Lux-Flood concept

8. The HSAB principle is useful in predicting:
A) Acid-base neutralization in water
B) The strength of aqueous acids and bases
C) The stability of metal-ligand complexes
D) The pH of strong acids

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9. Which of the following acids is not affected by the levelling effect of water?
A) HCl
B) HF
C) H_2SO_4
D) HNO_3

10. In the Lux-Flood concept, which of the following is considered a base?
A) SO_3
B) H_2O
C) O^{2-}
D) NH_3

Answer Key:
1 - B
2 - C
3 - A
4 - B
5 - B
6 - B
7 - C
8 - C
9 - B
10 – C

B. Short Type Questions

1. Define the Arrhenius concept of acids and bases.
2. How does the Bronsted-Lowry concept differ from the Arrhenius concept?
3. What is the solvent system concept of acids and bases?
4. Explain the levelling effect of solvents with an example.
5. What is the differentiating effect of solvents?
6. State Pauling's rule for the strength of mononuclear oxyacids.
7. What is the main idea behind the Lewis acid-base concept?
8. How does the HSAB principle classify acids and bases?
9. Give an example of a base according to the Lux-Flood concept.
10. Why do strong acids like HCl, HNO_3, and H_2SO_4 appear to have the same strength in water?

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C. Assay Type Questions

1. Explain the Arrhenius concept of acids and bases. Discuss its limitations and how other acid-base concepts overcome these limitations.
2. Describe the Bronsted-Lowry concept of acids and bases. How does it extend the definition of acids and bases beyond aqueous solutions?
3. What is the solvent system concept of acids and bases? Explain with suitable examples.
4. Discuss the Lux-Flood acid-base concept and compare it with the Bronsted-Lowry and Lewis concepts.
5. Explain the Lewis acid-base concept with examples. How is it different from the Bronsted-Lowry concept?
6. What is the levelling and differentiating effect of solvents? Explain how these effects influence acid and base strengths in different solvents.
7. Describe the factors affecting the relative strength of acids and bases. How does Pauling's rule help predict the strength of mononuclear oxyacids?
8. Explain the Hard and Soft Acid-Base (HSAB) principle. Discuss its applications in predicting chemical reactivity and stability.
9. Compare and contrast the different acid-base concepts (Arrhenius, Bronsted-Lowry, Lewis, Lux-Flood, and Usanovich) with suitable examples.
10. Discuss the importance of solvent choice in acid-base chemistry. How does the solvent influence the strength and behavior of acids and bases?

13.9 Further Reading

1. Atkins' Physical Chemistry – Peter Atkins, Julio de Paula
2. Principles of Inorganic Chemistry – Puri, Sharma, Kalia
3. General Chemistry: Principles and Modern Applications – Ralph H. Petrucci, F. Geoffrey Herring, Jeffry D. Madura, Carey Bissonnette

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4. Acids and Bases: Their Reactions, Properties, and Uses – Brian G. Cox

5. Inorganic Chemistry – Gary L. Miessler, Paul J. Fischer, Donald A. Tarr

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Unit 14: Thermodynamic acidity parameters

Contents

14.0 Objectives

14.1 Introduction

14.2 The Drago-Wayland Equation

14.3 Hammett Acidity Function and Super Acid

14.4 Gas phase acidity and proton affinity

14.5 Acid-base equilibria in aqueous solution: Proton transfer equilibria in water

14.6 pH

14.7 Buffer and Buffer Capacity

14.8 Acid-base neutralization curves

14.9 Indicator, choice of indicators

14.10 Model Questions

14.11 Further Reading

14.0 Objectives

1. Understand the Drago-Wayland equation and its application in predicting acid-base interactions.
2. Explain the concept of the Hammett acidity function and its significance in measuring strong acid strength.
3. Define gas-phase acidity and proton affinity and their significance in physical chemistry.
4. Describe acid-base equilibria in aqueous solutions and factors affecting them.

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5. Understand proton transfer mechanisms in aqueous solutions.
6. Interpret acid-base titration curves for different types of acid-base systems.

14.1 Introduction

Acid-base chemistry plays a fundamental role in various chemical and biological processes. Understanding acid-base equilibria, proton transfer mechanisms, and acidity functions is essential for studying reaction mechanisms, catalysis, and analytical chemistry. The Drago-Wayland equation provides a quantitative approach to predicting acid-base interactions based on electrostatic and covalent contributions. The Hammett acidity function extends the concept of acidity beyond aqueous solutions, helping define the strength of superacids, which are crucial in industrial and organic reactions. In the gas phase, acidity and proton affinity provide insights into molecular stability and ionization behavior. Additionally, concepts such as pH, buffer solutions, and acid-base titration curves are essential for controlling and measuring acidity in laboratory and industrial settings. This discussion explores these topics to provide a comprehensive understanding of acid-base chemistry and its applications.

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14.2 The Drago-Wayland Equation

Consider the gas phase reaction : $A(g) + : B(g) \rightarrow A\text{–}B(g)$

Drago and Wayland proposed the equation : $-\Delta H = E_A E_B + C_A C_B$

where ΔH is the standard enthalpy of the reaction, and E_A, E_B and C_A, C_B values represent the abilities of the acid and base to participate respectively in ionic and covalent interactions. Large enthalpies result from combinations of acids and bases with either large E or large C values.

Predictions using this equation typically agree with experimental values (for uncharged species) unless there is spacial interference of groups attached to the donor or acceptor atoms.

Drago-Wayland E and C Paramenters for Uncharged Lewis Acids and Bases

Acid	Acceptor atom	E_A	C_A	C/E
Iodine	I	1.00	1.00	1.00
Iodine monobromide	I	2.41	1.56	0.65
Iodine monochloride	I	5.10	0.830	0.16
Sulfur dioxide	S	0.92	0.808	0.88
Antimony pentachloride	Sb	7.38	5.13	0.70
Chlorotrimethylstanname	Sn	5.76	0.03	0.01
Boron trifluoride	B	9.88	1.62	0.16
Trimethylborane	B	6.14	1.70	0.28
Trimethylaluminium	Al	16.9	1.43	0.08
Trimethylgallium	Ga	13.3	0.881	0.07
Trimethylindium	In	15.3	0.654	0.04
Water	H	1.64	0.571	0.35

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Base	Donor atom	E_B	C_B	C/E
Phenol	H	4.33	0.422	0.10
Thiophenol	H	0.99	0.198	0.20
Ethanol	H	3.88	0.451	0.12
(Tetraphenylporphyrinato)zinc(II)	Zn	5.15	0.620	0.12
Tetraphenylporphyrinato)cobalt(II)	Co	4.44	0.58	0.13
Dimethyl selenide	SE	0.217	8.33	38.4
Dimethyl sulfide	S	0.343	7.46	21.8
Diethyl sulfide	S	0.339	7.40	21.8
Diethyl ether	O	0.936	3.25	3.5
Acetone	O	0.937	2.33	2.5
Ethyl acetate	O	0.975	1.74	1.8
Telrahydrofuran	O	0.978	4.27	4.4
Trimethylphosphine	P	0.838	6.55	7.8
Trimethylamine	N	0.808	11.54	14.2
Pyridine	N	1.17	6.40	5.5
Dimethylamine	N	1.09	8.73	8.0
Methylamine	N	1.30	5.88	4.5
Ammonia	N	1.15	4.75	4.1
Acetonitrile	N	0.886	1.34	1.5
1-Azabicyclo [2.2.1] octanc	N	0.700	13.2	18.9

In water, any base stronger than OH^- cannot survive. The effective proton affinity of OH^- in water is 1188 $kJ\ mol^{-1}$. Thus any base (B) for which the effective proton affinity is greater than 1188 $kJ\ mol^{-1}$ will be completely converted into the conjugate acid (BH^+) with the release of OH^- in water ($B + H_2O \rightarrow BH^+ + OH^-$).

This is why, we cannot study NH_2^- or CH_3^- in water as these get completely protonated as follows : $LiCH_3 + H_2O \rightarrow Li^+ + OH^- + CH_4$

For liquid NH_3, the proton affinity of NH_3 is greater than that of H_2O and consequently the acids which are weaker and differentiated in water may be levelled off in liquid NH_3. The proton affinity of NH_2^- is greater than that of OH^- and consequently, the stronger bases which are levelled off in water may not be levelled off in liquid NH_3.

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14.3 Hammett Acidity Function and Super Acid

The concept of pH measuring the acidity is only meaningful in aqueous dilute solutions of acid and bases. But in concentrated solutions of the so-called strong acids and bases and in nonaqueous media, a new parameter called the Hammett acidity function (H) has been defined to measure the acidity of the solution. To express the Hammett acidity function, protonation deprotonation equilibria of an indicator base (B) are to be considered. Depending on the charge of the indicator base, the Hammett acidity function are denoted by H_0, H_+, H_- for neutral (B), cationic (B^+) and anionic (B^-) indicator bases respectively. To measure the H_0, p-nitroanilline (a neutral base) is used. For particular solution, H_0, H_+ and H_- values differ but these run parallel.

Let us illustrate H_0 (i.e. reference base is neutral) by considering the following equilibrium :

$$BH^+ \rightleftharpoons B + H^+$$

$$K_{BH^+} = a_B a_{H^+} / a_{BH^+} = (a_{H^+}[B] f_B) / ([BH^+] f_{BH^+})$$

$$H_0 = -\log(a_{H^+} f_B) / (f_{BH^+}) = -\log h_0 = pK_{BH^+} + \log[B]/[BH^+]$$

Here, a denotes the activity term and f denotes the corresponding activity coefficient. In dilute solutions, the ratio of activity coefficients (i.e. f_B/f_{BH^+}) becomes unity and it leads to :

$$H_0 = -\log a_{H^+} = pH = pK_{BH^+} + \log[B]/[BH^+]$$

Which is the Henderson's equation.

It is evident that the Hammett acidity function measures the effective pH of the solution and it is formally equivlent to

$H_O = -\log h_O = -\log(a_H + f_B)/(f_{BH}+)$

Similarly, H_+ and H_- may be defined as follows :

$$B^+ + H^+ \rightleftharpoons BH^{2+}$$

$$H_+ = -\log(a_{H^+} f_{B^+}) / (f_{BH^{2+}}) = -\log h_+ = pK_{BH^{2+}} + \log[B^+]/[BH^{2+}]$$

$$B^- + H^+ \rightleftharpoons BH$$

$$H_- = -\log(a_{H^+} f_{B^-}) / (f_{BH}) = -\log h_- = pK_{BH} + \log[B^-]/[BH]$$

In general, organic bases used as indicator bases posses different colours in their protonated and deprotonated forms. Thus the ratio $[B]/[BH^+]$ or $[B^+]/[BH^{2+}]$ or $[B^-]/[BH]$ can be determined spectrophotometrically. By using suitable organic bases, it is possible to determine the Hammett acidity functions of different solutions. Acidity functions of some solutions are given below in table.

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In aqueous media, the strongest acid which can survive is H_3O^+. Hence, the idea of superacid only exists in nonaqueous media. Generally, the superacids are 10^6 to 10^{10} times more acidic than the fairly concentrated (1*M*) aqueous solution of strong acids like H_2SO_4, HNO_3, etc. The powerful proton donating property of superacids can protonate even very weak bases and stabilize the species susceptible to the base attack. Superacids are produced by concentrated solutions of very strong Bronsted acids, like $H_2S_2O_7$(i.e. $SO_3 + H_2SO_4$), FSO_3H or combination of a Bronsted acid and Lewis acid (e.g.SbF_5) acting as the acceptor of conjugate base of the Bronsted acid.

Hammett acidity function of some solutions

Solution/Pure acid	H_0	Solution	H_-
6M HNO_3(aq)	–1.5	5 M KOH (aq)	15.4
HSO_3H + SbF_5(14.1 mol %)	–26.5	10 M KOH (aq)	16.9
HSO_3H	–15.0	15 M KOH (aq)	18.2
HF + SbF_5(0.6 mol%)	–21.1		
HF	–11.0		
HF + NaF (1M)	–8.4		
7 M HCl (aq)	–2.0		
8 M $HClO_4$ (aq)	–2.63		
H_2SO_4 (63% in water)	–4.9		
H_2SO_4	–12.0		
Oleum	–15.0		
F_3CSO_3H	–15.1		
H_3PO_4	–5.0		
HCO_2H	–2.2		

(i) Bronsted acid + Lewis acid : It is noticed that the acidity of HF increases by the addition of Lewis acid SbF_5.

$$2HF \rightleftharpoons H_3F^+ + F-, SbF_5 + F- \rightleftharpoons SbF_6^-$$

(ii) Strong Bronsted acid + Lewis acid : SbF_5 also increases the acidity of fluorosulfonic acid (HSO_3F) and it produces superacid.

$$2HSO_3F + SbF_5 \rightleftharpoons H_2SO_3F^+ + FSO_2O - SbF_5^-$$

(iii) Triflic acid (F_3CSO_3H) can act as powerful strong acid (H_0 = – 15.1). It acts as like superacid.

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14.4 Gas phase acidity and proton affinity.

The proton affinity and gas phase acidity are quite similar in this contest. The term proton affinity of a species B is determined from the enthalpy change of the following process :

$B_{(g)} + H^+_{(g),} \rightleftharpoons BH^+_{(R)} - \Delta Hp = PA$ of B; $HA(g) \rightleftharpoons H^+_{(g)} + A^-_{(g),}$ (Gas phase acidity of HA)

ΔHp can be estimated by constructing a suitable Borm-Haber cycle. If A^- is the conjugate base of HA, then the higher proton affinity of A– indicates the weaker gas phase acidity of HA. In terms of Born – Haber cycle, gas phase acidity of HA depends on the three energy terms i.e. HA bond dissociation energy, ionization energy of H and electron affinity (EA) of A. Higher stability of A-(g) will enhance the gas phase acidity of HA. In the case of aqueous phase acidity, solvation of the involved species is to be considered.

Gas phase acidity of the hydrides of 2nd period elements run as :

PA affinity : $CH_3 > NH_2 > OH > F^-$

Gas phase acidity : $HF^- > H_2O > NH_3 > CH_4$, (same sequence in aqueous phase)

Beside the A-H bond strength (which does not change remarkably in a period), the electron affinity of A is also an important factor to determine the gas phase acidity. The higher electron affinity (or electronegativity roughly) of A will favour the process more. In a period, EA increases from left to right. This reflected in above series.

A-H bond strength decreases for the heavier congeners in a particular group because of the increasing trend of $A - H$ bond length. In fact, the heavier congenrs, the valence orbitals of larger size cannot effectively overlap with the small 1s orbital of H. Thus the bond strength decreases in the following sequence :

$H - O(H_2O) > H - S(H_2S) > H - Se(H_2Se) > H - Te(H_2Te)$;

$H - N(NH_3) > P - S(PH_3)$; $H - F > H - Cl > H - Br > H - I$

Gas phase acidity : $H_2Te > H_2Se > H_2S > H_2S > H_2O$;

$HI > HBr > HCl > HF$; $PH_3 > NH_3$

Proton affinity : $OH^- > HS^- > HSe^- > HTe^-$; $F^- > CI^- > Br^- > I^-$;

$NH_2^- > PH_2^-$

In a group in general electron affinity decreases in moving from top to bottom. Thus in terms of EA, hydrides of heavier congeners should show reduced gas phase acidity. The observed reverse sequence can be explained by considering the bond strength which decreases for the heavier congeners, Thus we can conclude :

(i) In a period, the gas phase acidity (and also aqueous phase acidity) of the hydrides increases in moving from left to right and it is mainly due to the increasing trend of electron affinity.

(ii) In a group, the gas phase acidity (and also aqueous phase acidity) of the hydrides increases from top to bottom and it is governed mainly by the bond strength sequence though opposed by the electron affinity sequence.

Gas phase acidity : $C_2H_5OH > CH_3OH > H_2O$ (opposite sequence in aqueous phase)

The alkyl groups are the better electron pushing grups compared to hydrogen. Thus H_2O is expected to be stronger acid than ROH but it is not true in gas phase. To explain the sequence, we are to consider the relative stability of the conjugate bases i.e. $C_2H_5O^-$, CH_3O^- and OH^-. Now let us consider the inherent group electronegativity(a1) and charge capacity parameters ($\sigma \infty 1/b$)

$a : H(2.1) < Me(2.3) < Et(2.32)$; $\sigma : H(1) < Me(2.8) < Et(3.9)$

Thus inherent electronegativities of the groups H, Me and Et are more or less the same but their charge capacity parameters are quite different. In terms of the σ values, the charge accommodating capacity of the groups is in the sequence : Et > Me > H. The ion induced dipole interaction due to the polarization of the R-group in R-O^- also follows the same trend. Thus stability of the conjugate bases due to charge delocalization through the polarization of R run in the sequence : $EtO^- > MeO^- > OH^-$.

Gas phase acidity order of primary, secondary and tertiary alcohols : It runs in the sequence $R(3°)OH > R(2°)OH > R(1°)OH$.

The sequence can not be explained in terms of simple electron pushing inductive effect of R but it can be explained in terms of electron capacity charge parameters of the R groups and the resultant stability sequence of the conjugate bases. The charge capacity is large for the more branched chain alkyl groups and consequently such alkyl groups are the better moieties to accommodate the charge. Thus the stability order of the conjugate base in terms of charge delocalization runs as $R(3°)O > R(2°)O^- > R(1°)O^-$

Gas phase acidity $CH_3OH > H_2O$ but $CH_3SH < H_2S$

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The size of the orbitals of carbon and sulfur differ significantly while the orbitals of carbon and oxygen are comparable in size. Thus stabilization of CH_3S^- through charge delocalization by hyperconjugation is not efficient but CH_3O^- is efficiently stabilized through charge delocalization by hyperconjugation.

Similarly, the gas phase acidity orders are $CHCl_3 > CHF_3$; $C_6H_5CH_3 > CH_4$; $CH_3NO_2 > CH_4$

Relationship Between Gas Phase Acidity and Proton Affinity

Gas phase acidity and proton affinity are related but describe opposite processes:

- Strong acids have **low gas phase acidity values** (more negative ΔG°acid).
- Strong bases have **high proton affinity values** (more positive PA).

14.5 Acid-base equilibria in aqueous solution

We are going to be working with acid-base equilibria in aqueous solution, and we will use the Bronsted-Lowry definitions that an acid is a source of H^+ and a base is an acceptor of H^+.

Acid ionization constant *Ka*

A convenient way to write the reaction of an acid HA in water is

$$HA(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Here water is acting as a base, accepting the H^+; the result, H_3O^+, called the conjugate acid of H_2O, since H_3O^+ can donate H^+ to reform H_2O. In a similar way, A^- is called the conjugate base of the acid HA, since A^- can accept H^+ to reform HA. The equilibrium constant is known as the acid ionization constant *Ka,*

$$K_a = [H_3O^+][A^-]/[HA]$$

with the understanding that [....] stands for the numerical value—without units—of the concentrationin mol/L. As usual K_a is unit-less.

An example acid ionization is

$$CH_3COOH(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = [H_3O^+][CH_3COO^-]/[CH_3COOH]$$

If *Ka* is much greater than 1, the acid is mostly dissociated and so is said to be a *strong acid.* If *Ka* is much less than 1, the acid is dissociated only to a small extent and so is said to be a *weak acid.*

Base Ionization constant K_b

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Similarly, we can write the reaction of a base B in water as

$$B(aq) + H_2O(1) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

Here water is acting as an acid, donating the H^+; the result, OH^-, is called the conjugate base of H_2O, since OH^- can accept H^+ to reform H_2O. Analogously, HB^+ is called the conjugate acid of the base B, since HB^+ can donate H^+ to reform B. The equilibrium constant is konwn as the base ionization constant K_b,

$$K_b = [HB^+][OH^-]/[B]$$

where we have used the abbreviated form. Here is an example of base ionization,

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = [NH_4^+][OH^-]/[NH_3]$$

If K_b is much greater than 1, the base reacts nearly completely with water and so is said to be a strong base. If K_b is much less than 1, the base reacts hardly at all with water and so is said to be a weak base.

Water Autoionization Constant K_w

In this analysis of acid and base ionizaton we see that water in one case plays the role of a base and the other plays the role of an acid. Indeed, the role that water plays in an aqueous equilibrium can be used as another definition of acid or base.

A consequence of this dual role of water is that its equilibrium with H_3O^+ and OH^- is the reference standard against which aqueous acidity and basicity are defined.

Here is how this works. A general base ionization reaction is

$$B(aq) + H_2O(1) \rightleftharpoons BH^+(aq) + OH^-(aq), \quad K_b$$

and the ionization reaction of its conjugate acid is

$$HB^+(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + B(aq), \quad K_a$$

The sum of these two reactions is $2H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq), \qquad K_w$

This equation is called the autoionization of water and its equilibrium constant is known as the water autoionization constant *Kw*. At 25°C it is equal to

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Now, we have seen that the equilibrium constant of a sum of two reactions is the product of the equilibrium constants of the summed reactions. Therefore, we know that water autoionization constant can be expressed as $K_w = K_a K_b$.

This means we can compute the base ionization constant from the ionization constant of its conjugate acid,

$K_b = K_w/K_a = 10^{-14}/Ka$, where the last equality is for 25°C. It is for this reason that base ionization constants are generally not tabulated.

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14.6 pH

Because K_w is so small, water is ionized only very slightly. We an compute the concentration of H_3O^+ and OH^- by solving the autoionization equilibrium.

	$[H_3O^+]/M$	$[OH^-]$/M
Initial	0	0
Equilibrium	x	x

Initial and equilibrium activities for the autoionization of liquid water. The equilibrium expression is then $K_w = 1.0 \times 10^{-14} = x^2$ and so the concentration of H_3O^+ and OH^- are each 1×10^{-7} M at 25°C.

Now, as we will see in a moment, strong acids can have H_3O^+ concentrations of 1 M or more. This means that H_3O^+ varies over many powers of 10 (orders of magnitude), and so it is convenient to measure $[H_3O^+]$ on a logarithmic scale. Also, for weak acids and bases, which is what we will be interested in primarily, concentrations of H_3O^+ and OH^- are generally much less than 1 M, which means their

logarithms are negative, and so it is more convenient to work with the negative logarithms so that we have a positive quantity and in particular pH and pOH are defined as $pH = -\log_{10} H_3O^+$, and $pOH = -\log_{10} OH^-$ where in each case the second equality is written with undersanding that [...] stands for the numerical value—without units—of the concentration of mol/L.

Since acids produce additional H_3O^+, their pH is always less than 7. Similarly, since bases produce additional OH^-, their pOH is always less than 7. We can relate pH and pOH. By calculating pK_w

$$pK_w$$
$$= -\log_{10} K_w$$
$$= -\log_{10}(H_3O^+ + OH^-)$$
$$= -\log_{10} H_3O^+ - \log_{10} OH^-$$
$$= pH + pOH$$

This means that at 25°C

$$pH = 14 - pOH.$$

so that bases have pH greater than 7, at 25°C.

It is important always to be mindful of the temperature being used. The reason is that equilibrim constants in general, and the value of K_w in particular, are different at different tempratures. This means that the pH of pure water will be different at different temperatures. For this reason, saying a solution has $pH = 7$ does not, by itself, mean the solution is "neutral" (has equal concentrations of H_3O^+ and OH^-. More generally, the acidic or basic character of a solution is due to the relative concentrations of H_3O^+ and OH^-, rather than a particular numerical value of pH.

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14.7 Buffer and Buffer Capacity

Before we get into what a buffer capacity is, we should first understand buffers. A buffer is a mixture that resists changes in pH when a limited amount of acid or base is added to it. The chemical composition of a buffer solution usually entails a weak acid or a weak base accompanied by its conjugate salt.

For example :

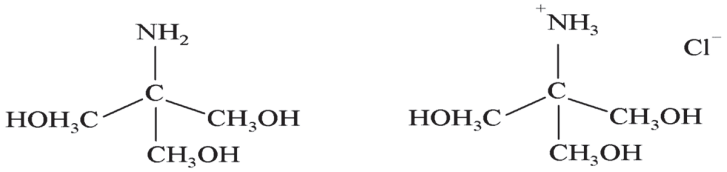
Acetate buffer : CH_3COOH (the weak acid) +

CH_3COONa (the salt, conjugated base)

Phosphate buffer : NaH_2PO_4 (the weak acid) +

Na_2HPO_4 (the salt, conjugated base)

Tris buffer :



Tris (free base) + TrisHCl (the salt, conjugated acid)

(Tris : Tris [2-amino-2-(hydroxymenthyl)-propan-1, 3-diol)1, an organic base)

Now, Buffer Capacity can be defined as the measure of the efficiency of a buffer in resisting its change in pH. This definition does present a bit of a problem as to 'what is the significant change?' Sometimes, a change of 1 unit does not bring about any significant change. At other times, even a 0.1-unit change can cause a significant difference. So, to give clear definition, buffer capacity may be defined as the quantity of a strong acid or strong base that must be added to one litre of a solution to change it by one pH unit. The buffer capacity equation is as follows :

$$\beta = dn/dpH$$

where n is some equivalents of added strong base (per 1 L of the solution). Note that the addition of n moles of acid will change the pH by the same value, but in the opposite direction. We will derive a formula connecting buffer capacity with pH, pK_a and buffer concentration.

It can be shown that the buffer capacity is maximum when the concentration of the weak acid and the base participating in the major proton transfer process in the buffer solution are same.

Let us have a buffer solution prepared by mixing a weak acid (HA) with a strong base (MOH) having their initial equivalent concentration a and b (where $a > b$) respectively. Thus in the buffer prepared, concentrations of the unconsumed weak acid and its conjugate base are : $[HA] = a - b$; $[A] = b$. From the Henderson's equation,

$$pH = pK_A + \log[A^-]/[HA] = pK_A + \log[b/(a-b)]$$

$$pH = pK_A + (1/2.303)\ \text{In}\ [b/(a-b)]$$

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Therefore, $d(pH)/db = (1/2.303)[(a-b)/b][a/(a-b)^2]$

$d(pH)/db = (1/2.303)[a/(a-b)b]$

$db/d(pH) = 2.303[b(a-b)/a]$

$\beta = 2.303[b(a-b)/a]$

$d\beta/db = 2.303(a-2b)/a$

for maximum β, $d\beta/db = 0$, Then $b = a/2$

Hence, for b = a/2 (i.e., at half neutralization), β is maximum or minimum. Therefore, at half neutralization, the buffer capacity is maximum.

Importance of buffer solution

(1) In biological processes : The pH of our blood is maintained constant inspite of various acid and base producing reactions going on in our body. The buffer action is due to the presence of carbonic acid, bicarbonate ion and carbon dioxide in the blood.

(2) In industrial processes : The use of buffers is an important part of many industrial processes, e.g., in electroplating, in the manufacture of leather, dyes, photographic materials.

(3) In analytical chemistry : (i) in the removal of acid radicals such as phosphae, oxalate and borate which interfere in the precipitation of radicals of group 3.(ii) in complexometric titration(iii) to calibrate the pH metres

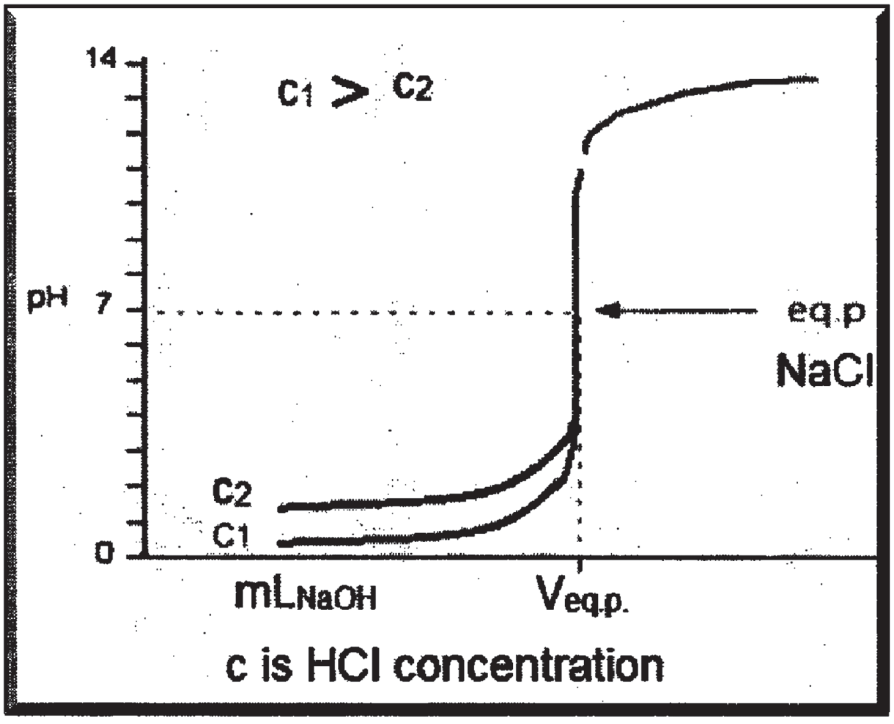
(4) In bacteriological research, culture media are generally buffered to maintain pH required for the growth of the bacteria being studied.

14.8 Acid-base neutralization curves

Acid – base titration, which is sometimes called neutralization titration is used to titrate any species having an acidic characteristic enough ($Ka > 1 \times 10^{-8}$) where it can be titrated with a standard solution of a strong base. Like wise any species that has basic property enough ($K_b > 1 \times 10^{-8}$) can be titrated with a standard solution of a strong acid. The most important characteristics of a neutralization titration can be ummarized in the titration curve (usually pH as a function of volume of the titrant). The titration curve can be calculated theoretically, whereupon conclusion can be drawn from it for the feasibility and the expected accuracy of a titration, and the selection of the proper indicator. The most common approach for the calculation of

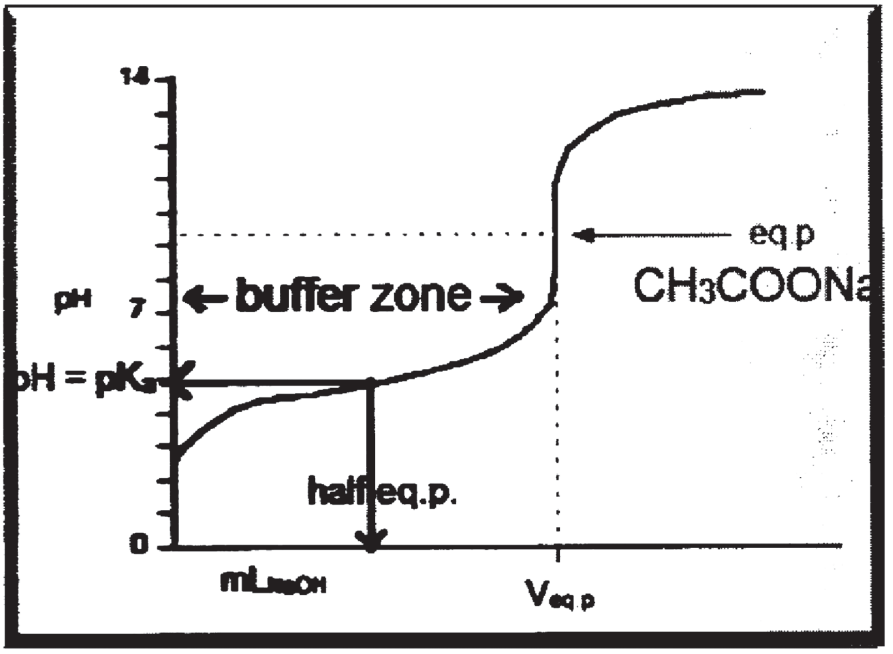
titration curves is based on approximations depending on the relative strength of the acid and base, the concentration levels, and the actual region of the titration curve relatively to the equivalence point.

Strong acid and strong base titration curve

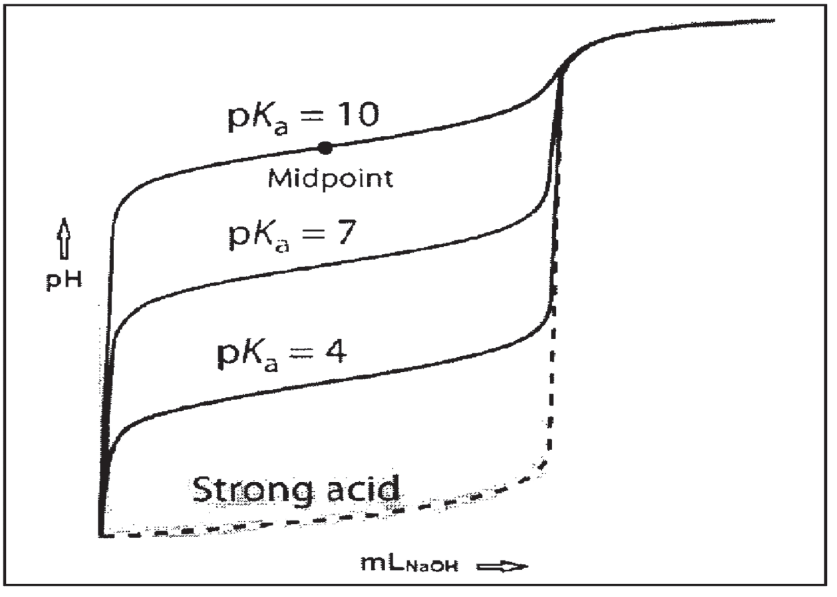


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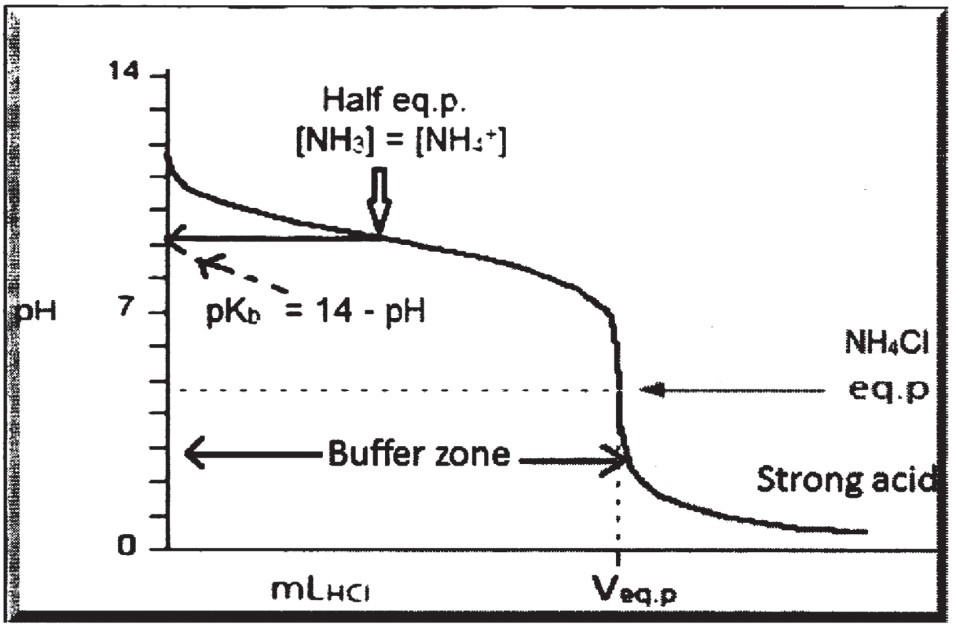
Weak acid and strong base titration curve

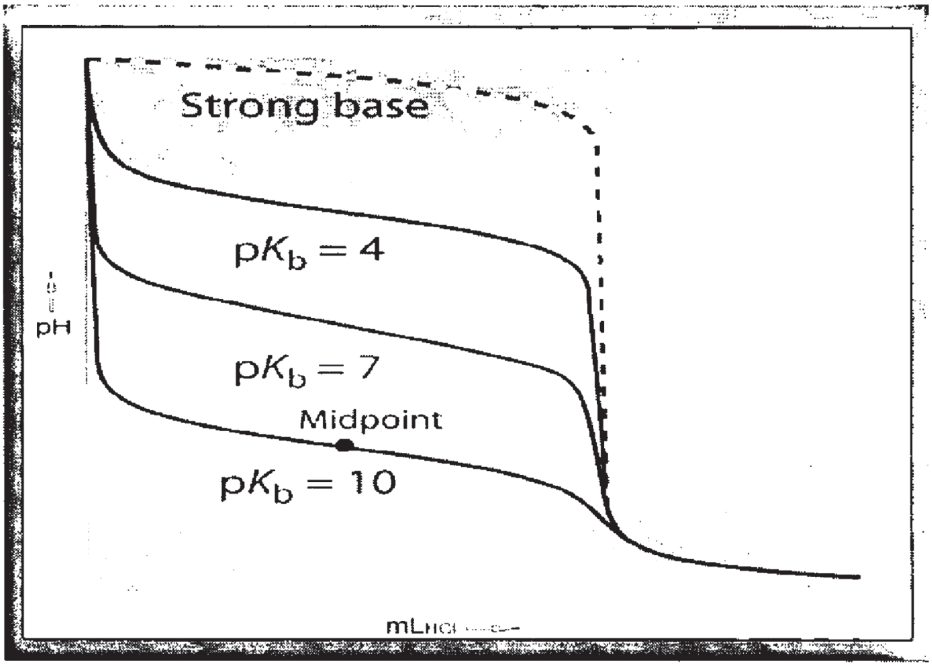


Weak acid and strong base titration curve

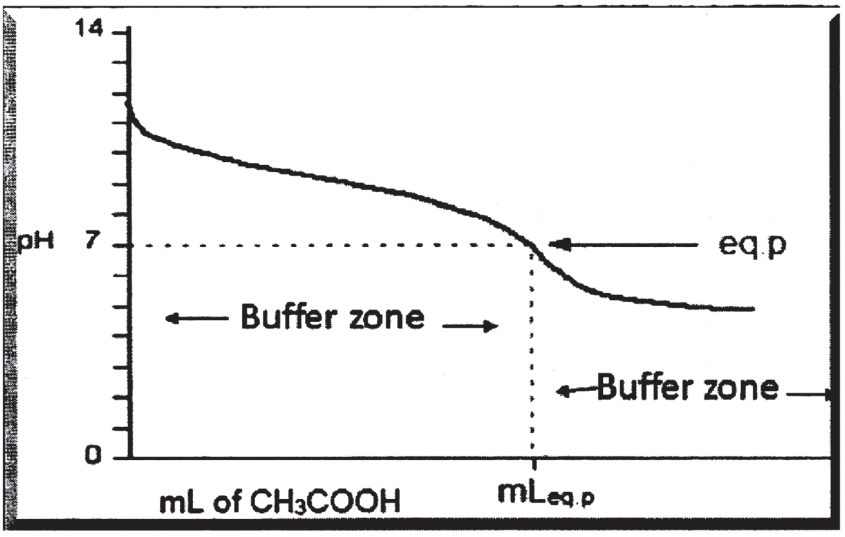


Weak base and strong acid titration curve

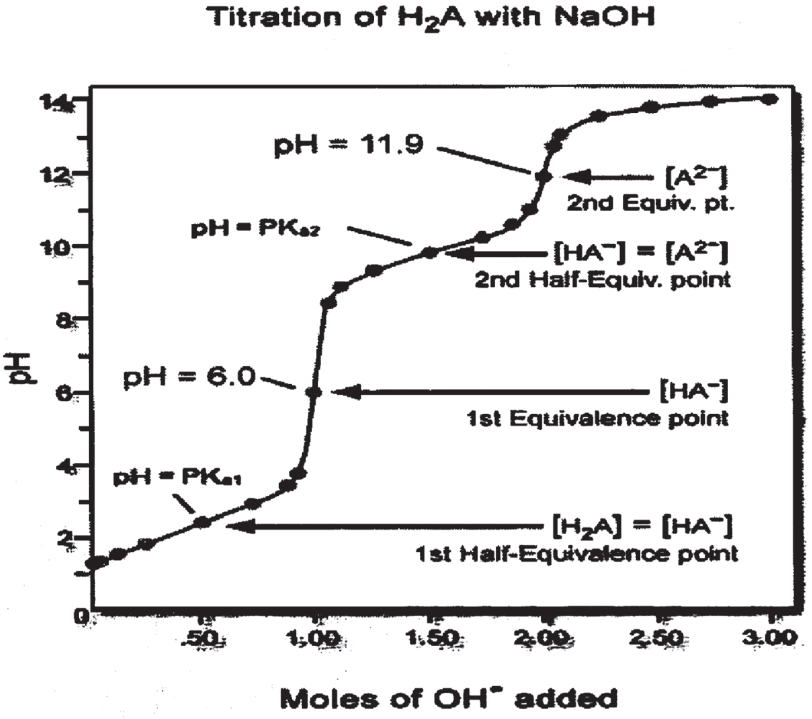




Weak base and weak acid titration curve



Curves for polyprotic acids titration



14.9 Indicator, choice of indicators.

Acid-base titration indicators are usually weak acids (HIn) which ionise as follows :

$$HIn(aq) \overset{Ka}{\rightleftharpoons} H^+(aq) + In^-(aq)$$

(colour 1) (colourless) (colour 2)

$$pH = pKa + \log[In^-(aq)]/[HIn(aq)]$$

For the reaction mixture to impart colour 1 with confidence, $[In–(aq)]/[HIn(aq)]$has to be $\leq 1/10$

For the reaction mixture to impart colour 2 with confidence, $[In– (aq)]/[HIn(aq)]$has to be ≥ 10.

In other words, for the reaction mixture to impart colour 1 with confidence, *pH* value of the solution should be *pKa*–1 or lower, and for the reaction mixture to impart colour 2 with confidence, *pH* value of the solution should be *pKa*+1 or higher. Hence *pH* range of an indicator = *pKa* ± 1.

14.10 Summary

Drago and Wayland equation: $\Delta H = E_A E_B + C_A C_B$ for reaction $A_{gas} + B_{gas} \rightarrow AB_{gas}$

In this study the leveling and differentiating effect are discussed.

Here many examples of the relative acid strengths are shown. Like $CH_3COOH < HNO_2 < HSO_4^-$;

$HF < HC1 < HBr < HI$; $H_3PO_4 > H_3PO_3 > H_3PO_2$ etc.

Hammett acidity function is used to measure the acidity function of super acids. According to HSAB principle a hard acid prefers to combine with a hard base and a soft acid prefers to combine with a soft base to form a more stable adduct.

When acid dissociation constant is greater than 1, then it is called strong acid and when acid dissociation constant less than 1, then it is weak acid. pH is a negative logarithm of hydrogen ion $[H^+]$ concentration. It is given as: pH = 14 – pOH at 25°C. A buffer is a mixture that resists changes in pH when a limited amount of acid or base is added to it. Buffer capacity can be defined as the measure of the efficiency of a buffer in resisting its change in pH. The most common approach for the calculation of titration curves is based on approximations depending on the relative strength of the acid and base, concentration levels, and the actual region of the titration curve relatively to the

equivalence point. Gas phase acidity of the second period elements run as:

$HF > H_2O > NH_3 > CH_4$;

$H_2Te > H_2Se > H_2S > H_2O$; $HI > HBr > HCl > HF$; $PH_3 > NH_3$

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14.10 Model Questions

A. Multiple Type Questions

1. The Drago-Wayland Equation describes:

A) The solubility of weak acids
B) The enthalpy of acid-base interactions
C) The rate of acid-base neutralization
D) The stability of superacids

Answer: B) The enthalpy of acid-base interactions

2. The Hammett Acidity Function (H_0) is used to measure:

A) The concentration of acids in water
B) The strength of acids in non-aqueous solutions
C) The pH of a solution
D) The ionization energy of acids

Answer: B) The strength of acids in non-aqueous solutions

3. Superacids are defined as acids that have an acidity stronger than:

A) Hydrochloric acid
B) Sulfuric acid
C) 100% pure nitric acid
D) 100% pure sulfuric acid

Answer: D) 100% pure sulfuric acid

4. Gas-phase acidity is best defined as:

A) The ability of a molecule to donate a proton in the gas phase
B) The dissociation of an acid in water
C) The tendency of a gas to form acidic solutions
D) The ability of a gas to react with bases

Answer: A) The ability of a molecule to donate a proton in the gas phase

5. Proton affinity is a measure of:

A) The energy released when an acid donates a proton
B) The energy required to remove a proton from a base
C) The tendency of a molecule to accept a proton
D) The solubility of an acid in water

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Answer: C) The tendency of a molecule to accept a proton

6. In aqueous acid-base equilibria, the proton transfer equilibrium is governed by:

A) The Bronsted-Lowry theory
B) The Arrhenius concept
C) The solubility constant
D) The Lewis acid-base theory

Answer: A) The Bronsted-Lowry theory

7. The pH of a solution is defined as:

A) The concentration of hydroxide ions in solution
B) The negative logarithm of the hydrogen ion concentration
C) The positive logarithm of the hydrogen ion concentration
D) The ratio of acid to base in a buffer solution

Answer: B) The negative logarithm of the hydrogen ion concentration

8. Buffer capacity is:

A) The amount of acid or base required to change the pH by 1 unit
B) The maximum amount of acid a buffer can neutralize
C) The pH of a solution at equilibrium
D) The resistance of a solution to oxidation

Answer: A) The amount of acid or base required to change the pH by 1 unit

9. Which of the following represents the correct acid-base neutralization curve for a strong acid and a strong base?

A) A steep rise in pH near the equivalence point
B) A gradual increase in pH with no equivalence point
C) A steady pH value with no sudden change
D) A sharp decrease in pH throughout the titration

Answer: A) A steep rise in pH near the equivalence point

10. The choice of indicator for a titration depends on:

A) The solubility of the indicator in water
B) The temperature of the reaction
C) The pH range over which the indicator changes color
D) The volume of acid used in the titration

Answer: C) The pH range over which the indicator changes color

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B. Short Type Questions

1. Write the general form of the Drago-Wayland equation and explain its significance.
2. Define the Hammett Acidity Function (H_0) and explain its use in determining acid strength.
3. What are superacids? Give one example.
4. How is gas-phase acidity different from aqueous acidity?
5. Define proton affinity and mention its importance in acid-base chemistry.
6. What is the significance of proton transfer equilibria in aqueous solutions?
7. How is pH mathematically defined?
8. What is a buffer solution, and how does it resist changes in pH?
9. Describe the shape of a strong acid–strong base neutralization curve.
10. What factors should be considered while selecting an indicator for a titration?

C. Assay Type Questions

1. Explain the Drago-Wayland Equation and discuss its significance in predicting the enthalpy of acid-base interactions. Provide examples of its application.
2. Discuss the Hammett Acidity Function (H_0) in detail. How is it used to measure the strength of acids in non-aqueous solutions? Explain with suitable examples.
3. What are superacids? Explain their properties, methods of preparation, and applications in chemistry.
4. Compare and contrast gas-phase acidity and aqueous-phase acidity. How does proton affinity influence gas-phase acidity?
5. Explain acid-base equilibria in aqueous solutions with reference to proton transfer equilibria. How do different factors affect this equilibrium?
6. Define and explain the concept of pH. How is pH measured, and why is it an important parameter in chemical and biological systems?

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7. Describe the working and significance of buffer solutions. What factors affect buffer capacity, and how can buffer solutions be prepared for different pH ranges?
8. Explain acid-base neutralization curves. How do they differ for strong acid–strong base, strong acid–weak base, weak acid–strong base, and weak acid–weak base titrations?
9. What are acid-base indicators? Discuss their types, working principle, and criteria for selecting a suitable indicator for a titration.
10. Describe the role of acid-base equilibria in biological and industrial processes. Provide examples of its significance in biochemical reactions, environmental chemistry, and industrial applications.

14.11 Further Reading

1. **Atkins' Physical Chemistry** – Peter Atkins, Julio de Paula

   Covers acid-base equilibria, pH, buffers, and thermodynamic principles.
2. **Principles of Acid-Base Chemistry** – James N. Butler

   A detailed resource on acid-base equilibria, superacids, and Hammett acidity function.
3. **Modern Physical Organic Chemistry** – Eric V. Anslyn, Dennis A. Dougherty

   Discusses acidity, proton transfer, and gas-phase acidity in depth.
4. **Acid-Base Behavior in Chemistry** – Brian G. Cox

   Provides insights into acid-base neutralization, buffer capacity, and related equilibria.
5. **Superacid Chemistry** – George A. Olah, Douglas A. Klumpp

   A comprehensive guide on superacids, their properties, and applications.

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