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

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 Elective (DSE)
Course Title: Basic Inorganic Chemistry
Course Code: NEC-CH-03

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Netaji Subhas
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UG : Chemistry

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Unit - 1 ❑ Theories of Atomic Structure

Structure

1.1 Objectives

After reading this unit, we will be able to:

- Postulates of Bohr's Theory and limitations
- The dual behaviours of matter and radiation
- de-Broglie wavelength
- Atomic spectra of hydrogen atoms
- Definition of quantum numbers and their significance
- Electronic configurations of atom

1.2 Introduction

Atoms are made up of particles called protons, neutrons, and electrons, which are responsible for the mass and charge of atoms. Atomic structure refers to the structure of an atom containing nucleus (at the centre) in which there is protons (positively charged) and neutrons (neutral) and electrons (negatively charged) revolving around the nucleus. The history of atomic structure and quantum mechanics restates only one name who first proposed that matter is made up of atoms; the name is Democritus. After Democritus, it is John Dalton who proposed the first scientific theory of atomic structure in 1800.The English chemist Sir Joseph John Thomson was better known for his discovery of electrons for which he got the Nobel Prize. After that Rutherford proposed the atomic model which was further modified by Bohr's Atomic theory. In this chapter Bohr's atomic theory and limitations are presented. The dual nature of matter and radiations is highlighted. Electronic configurations of atoms are shown in this chapter. Quantum numbers and their significances are also discussed in this chapter which are very important to understand the atomic structure.

1.3 Review of Bohr's Theory and its limitation

4. Whenever an electron jumps from one orbit to another, a required amount of energy is absorbed or released.

Limitations of Bohr's theory

- It can explain the spectra of one electron systems like H, He^+, Li^{+2} etc. but can not explain the spectra obtained from multi-electron atoms.
- Bohr's model is a two dimensional (2D) system but the actual atom is three dimensional (3D).
- Formation of chemical bonds between two atoms to form a single molecule is not explained.
- Bohr treated the electron as a particle whereas according to de Broglie's hypothesis electrons also have wave nature.
- It violates the Heisenberg Uncertainty Principle.

1.4 Dual behaviour of matter and Radiation

Observing a light is one of the easiest ways to prove the duality between a particle and a wave. Since light is similar to waves, it is able to diffract, refract, and interface, etc. Albert Einstein's theory of photoelectric effect in 1905 has established that light behaves like discrete packets of energy in addition to classical wave theory of light.

In 1923, Louis de Broglie, a French physicist, proposed a hypothesis that every particle is behaving like a wave and the wave also has its particle nature. The property of particles behaving as waves and the property of waves behaving as particles as well as waves is known as wave-particle duality. Although the duality is not very effective in large matters. The wave characteristic of the electron implicates many of the electron's particle behaviors.

Within a few years, de Broglie's hypothesis was tested by scientists shooting electrons and rays of light through slits. What scientists discovered was that the electron stream acted the same way as light, proving de Broglie correct.

1.5 De Broglie wavelength

De Broglie derived his equation using well established theories through the following series of substitutions:

1. De Broglie first used Einstein's famous equation relating matter and energy:

   $$E = mc^2 \quad \ldots (1)$$

   E = energy, m = mass, c = speed of light
2. Using Planck's theory which states every quantum of a wave has a discrete amount of energy given by Planck's equation:

   $$E = h\nu \quad \ldots (2)$$

   E = energy, h = Plank's constant (6.62607×10^{-34} J s), ν = frequency
3. Since de Broglie believes particles and wave have the same traits, the two energies would be the same:

   $$mc^2 = h\nu \quad \ldots (3)$$
4. Because real particles do not travel at the speed of light, De Broglie subsituted v, velocity, for c, the speed of light.

   $$mv^2 = h\nu \quad \ldots (4)$$
5. Through the equation λ, de Broglie substituted v/λ for ν and arrived at the final expression that relates wavelength and particle speed.

   $$mv^2 = hv/\lambda \quad \ldots (5)$$

   Hence: $\lambda = hv/mv^2 = h/mv = h/p$ ... (6) [$p = mv$]

Although De Broglie was credited for his hypothesis, he had no actual experimental evidence for his conjecture. In 1927, Clinton J. Davisson and Lester H. Germer shot electron particles onto a nickel crystal. What they see is the diffraction of the electron similar to waves diffraction against crystals (x-rays). In the same year, an English physicist, George P. Thomson fired electrons towards thin metal foil providing him with the same results as Davisson and Germer.

De Broglie was awarded the Nobel Prize for Physics in 1929 for his hypothesis. Thomson and Davisson shared the Nobel Prize for Physics in 1937 for their experimental work.

1.6 Heisenberg's Uncertainty Principle

According to Heisenberg's uncertainty principle both position and momentum (or velocity) of a subatomic particle simultaneously can not be determined precisely.

The product of uncertainty in position (Δx) and uncertainty in momentum (Δp) is given by the following equation:

$$\Delta x \cdot \Delta p \geq h/2\pi$$

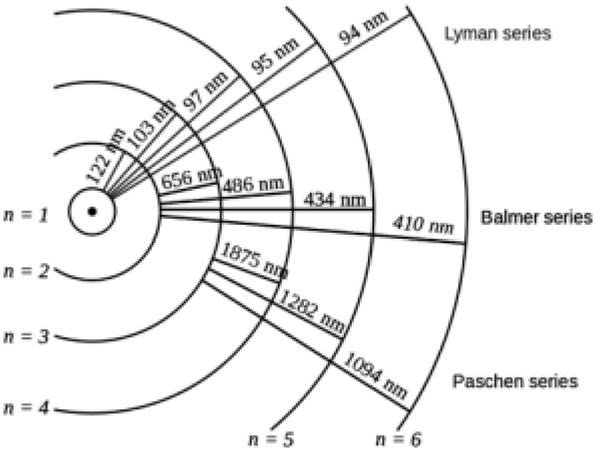
1.7 Hydrogen atom Spectra

The spectral lines observed when an electric current is passed through a sample of hydrogen gas are known as hydrogen spectra. Hydrogen molecules break into hydrogen atoms due to the electrical energy and each electron in each hydrogen atom gets excited. After absorbing energy the electron moves to higher energy levels. Each different electron in different hydrogen atoms (there are a large number of atoms in a hydrogen sample) doesn't move up to the same energy level, depending on energy absorbed they move to different energy levels. Now those electrons in the excited state are unstable and they give up those absorbed energy in the form of radiation. Then those emitted radiation is separated according to their frequency and wavelength and recorded on a plate as lines. This plate containing the lines is known as the hydrogen emission spectrum.

Johann Balmer first proposed a formula to correlate the lines observed in hydrogen spectra The formula is as follows:

$$\bar{\nu} = 109677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

This series of lines he was able to correlate in the observed hydrogen emission spectra is known as the Balmer series. This series falls in the visible region. The value, 109,677 cm^{-1}, is called the Rydberg constant for hydrogen. The Balmer series is the part of the hydrogen emission spectrum obtained when the excited electron comes from any other shell to the 2nd shell. Besieged the Balmer series there are other series. Some of them are listed below,



- Transition from any other shell to the first shell – Lyman series
- Transition from any other shell to the 2nd shell – Balmer series
- Transition from any other shell to the 3rd shell – Paschen series
- Transition from any other shell to the 4th shell – Bracket series
- Transition from any other shell to the 5th shell – Pfund series

1.8 Significance of Quantum numbers, orbital angular momentum

Bohr's model was a two dimensional (2D) model that used only one quantum number to describe the distribution of electrons within the atom. The size of the orbit was described by the n quantum number. But Schrodinger's atomic model is a three dimensional (3D) model which allows the electrons to occupy three dimensional space around the nucleus. Hence It required three coordinates, or three quantum numbers, to describe the electrons within an atom.

The three coordinates that come from Schrodinger's wave equations are the principal (n), angular (ℓ), and magnetic (m_ℓ) quantum numbers. These quantum numbers describe the size, shape, and orientation in space of the orbitals within an atom.

The principal quantum number (n) describes the size of the orbital. If n increases, the size of the atom increases. The principal quantum number indirectly describes the energy of an orbital. The value of principal quantum number (n) can be only integers (1, 2, 3 etc) and can never be zero.

The angular quantum number (ℓ) describes the shape of the orbital. Orbitals have shapes that are best described as spherical ($\ell = 0$), polar ($\ell = 1$), or cloverleaf ($\ell = 2$). They can even take on more complex shapes as the value of the angular quantum number increases. The value angular quantum number (ℓ) can be any integer including zero up to $n - 1$ (where n = principal quantum number). If the value of $\ell = 0$ then the name of the orbital is indicated by s, again for $\ell = 1$, it is indicated by p, for $\ell = 2$, d orbital, for $\ell = 3$, f orbital and so on.

It was observed that orientation of orbitals are affected by the magnetic field. When the value of angular quantum number is zero then only one orientation is possible which is a sphere ($\ell = 0$). Now if the value of angular momentum number is greater than zero ($\ell = 1, 2$ etc) then the orbitals have polar ($\ell = 1$) or cloverleaf ($\ell = 2$) shapes, but oriented in different directions. Therefore, a third quantum number is required to describe the orientation of a particular orbital in three dimensional space. This quantum number is known as magnetic quantum number. The value magnetic quantum number (m_ℓ) can be $-\ell$ to $+\ell$ including zero. As for example if the value of ℓ is 1 then m_ℓ has three values $-1, 0, +1$; according to their orientation in space they also known as p_x, p_y and p_z.

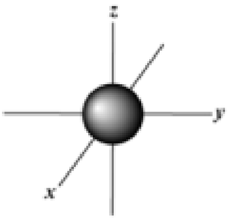
1.8.1 Spin quantum numbers (m_s)

The concept of spin quantum number is given by the two scientists Goudsmit and Ulhenbeck. They postulated that, when an electron rotates around the nucleus within an atom, it also spins about its own axis. Spin is an intrinsic property of matter. Electrons spin with an intrinsic angular momentum that is independent of any orbital angular momentum. The magnetic moment arising due to spin interacts in a quantized manner with the magnetic moment (arising due to the orbital motion) so that spin can either be parallel or antiparallel to orbital angular momentum.

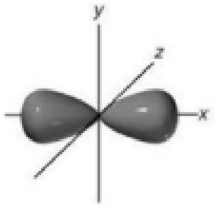
The spin quantum number (m_s) has both a magnitude half and direction (+, –) this is a vector quantity and is called as magnetic spin quantum numbers (m_s) each orbital can only hold 2 electrons one electron will have a positive spin and other will have negative spin so spin quantum numbers (m_s) has + ½ and – ½ values.

1.9 Shapes of s, p and d atomic orbitals

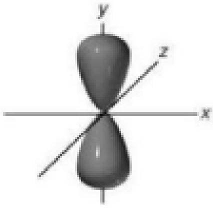
Shapes of *s*, *p* and *d* atomic orbitals, nodal planes: According to the modern concept of orbitals are the region of in three dimensional space where the probability of finding the electron is maximum. The shape of *s*, *p* and *d* orbitals are given below :



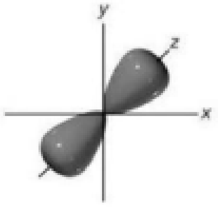
's' orbital



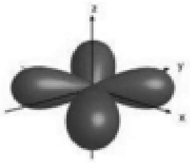
'p_x' orbital



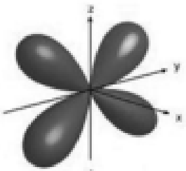
'p_y' orbital



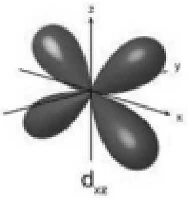
'p_z' orbital



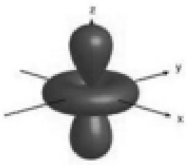
d_{xy}



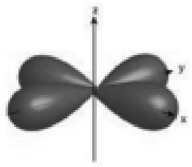
d_{yz}



d_{xz}



d_{z^2}



$d_{x^2-y^2}$

1.10 Discovery of spin (s) and magnetic spin quantum number (m_s)

In 1922, the German physicists Otto Stern and Walther Gerlach conducted an experiment to test the Bohr-Sommerfeld model of the atom. They passed a beam of silver atoms - which have a single electron in their outer shell - through a magnetic field with positive and negative regions. They then measured how the atoms were affected by the field.

If the orbits of electrons can have any orientation, and they are distributed randomly, then they will be deflected by a continuous range of values. This is the classical prediction. If they only have a limited number of orientations, then they will only be deflected by a limited number of angles. The Bohr-Sommerfeld model predicted an odd number of deflections, one in this case.

Stern and Gerlach found that neither theory was correct; although the electron orbits were quantised, the electrons were deflected by two values. This means that outer electrons with the same m_ℓ value were divided into two groups, defined by a new quantum number (m_s).

The maximum number of m values can be found using maximum number = $2\ell + 1$, and so assuming this is also the case for s values,

If the maximum number is equal to two, then s must equal ½. In 1925, the Austrian physicist Wolfgang Pauli described the atom as having a "two-valuedness" that could not be described classically.

The German-American physicist Ralph Kronig and the Dutch-American physicists George Uhlenbeck and Samuel Goudsmit all suggested that these two extra angular momentum values, designated +½ and –½, may be due to the electrons rotating as they orbit the nucleus, just as the Earth rotates as it orbits the Sun. The electrons were considered to be rotating in two directions, either clockwise or anticlockwise, and so this quality was named 'spin'.

1.11 Summary

Bohr's atomic theory, while ground-breaking in explaining the hydrogen atom's spectra and quantized energy levels, was limited by its inability to explain multi-electron systems and lacked an understanding of wave-particle duality. The introduction of wave-particle duality through De Broglie's wavelength and the Heisenberg Uncertainty Principle advanced the understanding of atomic behavior, revealing the probabilistic nature of electron positions and momenta. The concept of quantum numbers, particularly the spin quantum number, added further detail to the description of electrons within atoms, explaining both their spatial distribution and intrinsic angular momentum. The discovery of the shapes of atomic orbitals (s, p, d) and their angular momentum characteristics provided a more complete picture of atomic structure, culminating in a comprehensive quantum mechanical model. This model not only explains the atomic spectra but also lays the foundation for modern quantum chemistry and atomic physics.

1.12 Sample Questions

A. A. Multiple Choice Type Questions

1. Which of the following was a limitation of Bohr’s atomic model?

- A) It explained multi-electron atoms accurately
- B) It could not explain the wave nature of electrons
- C) It described the quantum mechanical nature of electrons
- D) It explained the uncertainty principle

Answer: B) It could not explain the wave nature of electrons

2. The concept of the dual nature of matter was proposed by:

- A) Albert Einstein
- B) Niels Bohr
- C) Louis de Broglie
- D) Werner Heisenberg

Answer: C) Louis de Broglie

3. The de Broglie wavelength of a particle is given by the equation:

- A) $\lambda = \frac{mv}{h}$
- B) $\lambda = \frac{h}{mv}$
- C) $\lambda = \frac{v}{mh}$
- D) $\lambda = \frac{hv}{m}$

Answer: B) $\lambda = \frac{h}{mv}$

4.According to the Heisenberg Uncertainty Principle, it is impossible to simultaneously know the exact:

- A) Energy and mass of an electron
- B) Position and velocity of an electron
- C) Charge and mass of an electron
- D) Position and charge of an electron

Answer: B) Position and velocity of an electron

5. The line spectrum of hydrogen can be explained by:

- A) Bohr’s atomic model
- B) Heisenberg's Uncertainty Principle
- C) De Broglie's hypothesis
- D) The Pauli Exclusion Principle

Answer: A) Bohr’s atomic model

6. Which quantum number determines the shape of an orbital?

- A) Principal quantum number (n)
- B) Magnetic quantum number (m)
- C) Spin quantum number (ms)
- D) Azimuthal quantum number (l)

Answer: D) Azimuthal quantum number (l)

7. The spin quantum number (ms) has values of:

- A) +1 and -1
- B) 0 and 1
- C) +1/2 and -1/2
- D) +2 and -2

Answer: C) +1/2 and -1/2

8. The shape of the p orbital is:

- A) Spherical
- B) Dumbbell-shaped
- C) Cloverleaf-shaped
- D) Circular

Answer: B) Dumbbell-shaped

9. Who is credited with the discovery of electron spin?

- A) Niels Bohr
- B) Wolfgang Pauli
- C) Samuel Goudsmit and George Uhlenbeck
- D) Louis de Broglie

Answer: C) Samuel Goudsmit and George Uhlenbeck

10. The magnetic spin quantum number (m_s) refers to:

- A) The direction of an electron's orbit
- B) The orientation of the electron's spin
- C) The energy level of an electron
- D) The angular momentum of an electron

Answer: B) The orientation of the electron's spin

B. Short Type Questions

1. What are the key postulates of Bohr's atomic model?

Bohr's atomic model is based on the following key postulates:

1. **Electrons move in specific, stable orbits (stationary states)** around the nucleus without radiating energy. These orbits are called quantized orbits.
2. **Quantization of angular momentum:** The angular momentum of an electron in a particular orbit is quantized and is given by $L = n\hbar = \frac{nh}{2\pi}$, where n is a positive integer (the principal quantum number), h is Planck's constant, and $\hbar$ is the reduced Planck's constant.
3. **Energy of electrons in these orbits is quantized:** Electrons can only exist in certain allowed energy levels, and energy is absorbed or emitted when an electron transitions between these levels.
4. **Emission or absorption of energy:** When an electron jumps from a higher energy orbit to a lower one, it emits energy in the form of a photon. The energy of the photon corresponds to the difference in energy between the two orbits.

2. How does Bohr's model explain the stability of atoms?

Bohr's model explains the stability of atoms by proposing that electrons orbit the nucleus in fixed, quantized energy levels, without radiating energy while in these stable orbits. According to classical physics, an accelerating electron should emit radiation and spiral into the nucleus, but Bohr's quantized orbits prevent this continuous energy loss. Electrons can only radiate energy when they transition between discrete energy levels, thus maintaining atomic stability as long as they remain in a stationary state.

3. What is the significance of quantized angular momentum in Bohr's theory?

The quantization of angular momentum is a crucial concept in Bohr's theory. According to classical physics, an electron could have any value of angular momentum, leading to continuous energy loss and an unstable atom. Bohr proposed that only certain discrete values of angular momentum are allowed, with each corresponding to a stable orbit. This quantization condition, $L=n\hbar$, where n is a positive integer, restricts electrons to specific orbits and explains why they don't spiral into the nucleus, thus providing stability to the atom.

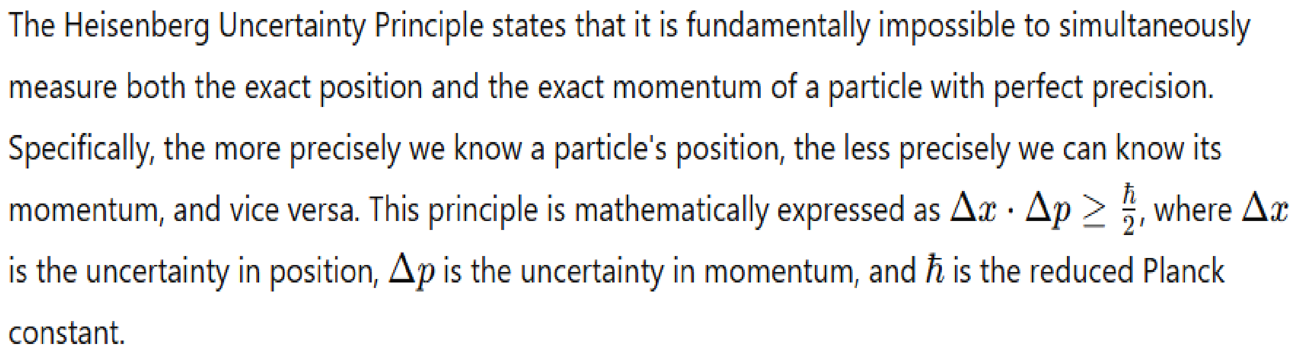
4. What role does the concept of energy levels play in Bohr's atomic model?

Energy levels are fundamental to Bohr's atomic model. Each allowed orbit corresponds to a specific energy level, and electrons in an atom can only occupy these discrete levels. When an electron moves between energy levels, it either absorbs or emits a photon whose energy is equal to the difference between the initial and final energy levels. The existence of these distinct energy levels explains why atoms absorb or emit radiation at specific frequencies, leading to the discrete spectral lines observed in atomic spectra.

5. How does Bohr’s model explain the emission spectrum of hydrogen?

Bohr’s model explains the emission spectrum of hydrogen by proposing that electrons in a hydrogen atom can only occupy certain quantized energy levels. When an electron in a hydrogen atom transitions from a higher energy level to a lower one, it emits a photon whose energy corresponds to the difference between the two energy levels. The frequency of the emitted photon is given by E=hν, where E is the energy difference and h is Planck’s constant. This results in the emission of light at specific wavelengths, which correspond to the spectral lines observed in the hydrogen atom's emission spectrum. The most famous of these is the Balmer series in the visible range.

6. What does the Heisenberg Uncertainty Principle state about the relationship between the position and momentum of a particle?



The Heisenberg Uncertainty Principle states that it is fundamentally impossible to simultaneously measure both the exact position and the exact momentum of a particle with perfect precision. Specifically, the more precisely we know a particle's position, the less precisely we can know its momentum, and vice versa. This principle is mathematically expressed as $\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$, where Δx is the uncertainty in position, Δp is the uncertainty in momentum, and $\hbar$ is the reduced Planck constant.

7. What are the four quantum numbers used to describe an electron in an atom?

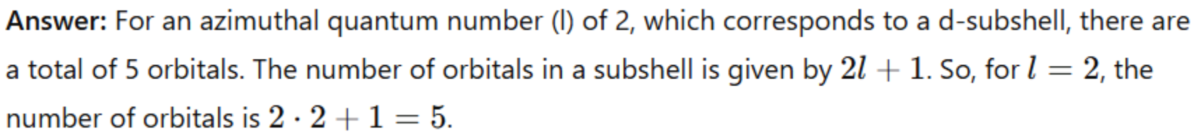
Answer: The four quantum numbers are:

- Principal Quantum Number (n): Indicates the main energy level or shell of the electron.
- Azimuthal Quantum Number (l): Defines the shape of the orbital and is related to the angular momentum of the electron.
- Magnetic Quantum Number (m□): Specifies the orientation of the orbital within a given subshell.
- Spin Quantum Number (m□): Describes the intrinsic spin of the electron, which can be either +1/2 or -1/2.

8. How does the principal quantum number (n) affect the energy of an electron in an atom?

Answer: The principal quantum number (n) determines the energy level of the electron. As 'n' increases, the electron's energy increases, and the electron is further from the nucleus. Higher 'n' values correspond to higher energy levels.

9.What is the maximum number of orbitals in a subshell with an azimuthal quantum number (l) of 2?



Answer: For an azimuthal quantum number (l) of 2, which corresponds to a d-subshell, there are a total of 5 orbitals. The number of orbitals in a subshell is given by $2l + 1$. So, for $l = 2$, the number of orbitals is $2 \cdot 2 + 1 = 5$.

10. What does the magnetic quantum number (m□) represent, and what are its possible values for an s orbital?

Answer: The magnetic quantum number (m□) represents the orientation of the orbital within a given subshell. For an s orbital (where l=0), the only possible value for m□ is 0, meaning there is only one orientation.

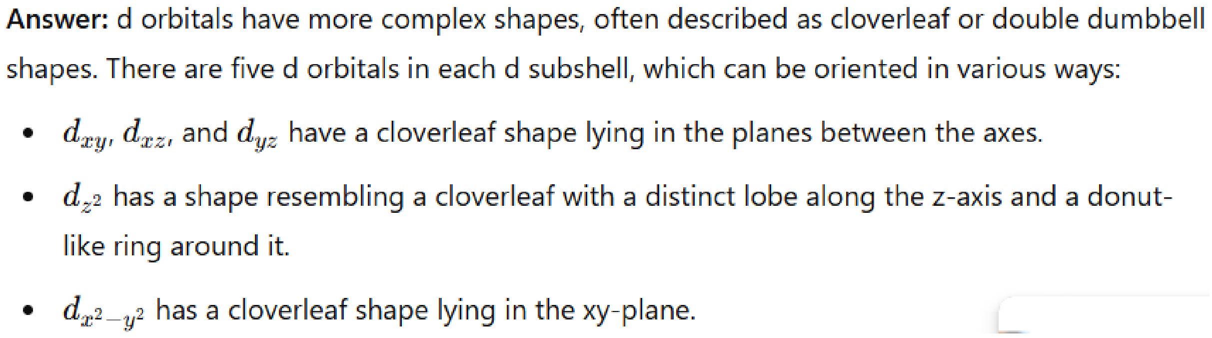
11. What is the shape of an s orbital, and how many orientations does it have?

Answer: The s orbital has a spherical shape. It has only one orientation, meaning there is just one s orbital in each principal energy level.

12. Describe the shape of p orbitals and how many p orbitals are present in each p subshell.

Answer: p orbitals have a dumbbell or figure-eight shape, with two lobes extending along different axes. Each p subshell contains three p orbitals, oriented along the x, y, and z axes (often denoted as p_x, p_y, and p_z).

13. What are the shapes of d orbitals, and how many d orbitals are there in each d subshell?



Answer: d orbitals have more complex shapes, often described as cloverleaf or double dumbbell shapes. There are five d orbitals in each d subshell, which can be oriented in various ways:

- d_{xy}, d_{xz}, and d_{yz} have a cloverleaf shape lying in the planes between the axes.
- d_{z^2} has a shape resembling a cloverleaf with a distinct lobe along the z-axis and a donut-like ring around it.
- $d_{x^2-y^2}$ has a cloverleaf shape lying in the xy-plane.

C. Assay Types Questions

1. Explain the significance of the Heisenberg Uncertainty Principle and its impact on the development of quantum mechanics. How does this principle challenge classical notions of particle behavior?

2. Compare and contrast the Bohr model and the quantum mechanical model of the atom. How did the quantum mechanical model improve upon and refine Bohr's ideas?

3. Analyze the role of quantum numbers in determining the electronic configuration of atoms. How do the principal, azimuthal, magnetic, and spin quantum numbers work together to define the state of an electron in an atom?

4. Discuss the main postulates of Bohr's atomic theory and explain how they addressed the limitations of Rutherford's model. How did Bohr's theory improve our understanding of atomic structure and spectral lines?

5. Analyze the limitations of Bohr's atomic theory, particularly in explaining the spectra of atoms with more than one electron and the fine structure of spectral lines. How did these limitations lead to the development of the quantum mechanical model?

1.13 References

1. "Atomic Structure and Chemical Bonding: An Introduction" by S. S. Mukherjee
2. "Chemistry: The Central Science" by Theodore L. Brown, H. Eugene LeMay, Bruce E. Bursten, and Catherine Murphy
3. "Physical Chemistry: A Molecular Approach" by Donald A. McQuarrie and John D. Simon
4. "Modern Physical Chemistry: An Introduction" by Robert J. Silbey, Robert A. Alberty, and Moungi G. Bawendi
5. "Introduction to Quantum Chemistry" by J. Walter
6. Inorganic Chemistry by R.L. Dutta
7. Essentials of Physical Chemistry by B.S. Bahl
8. Concise Inorganic Chemistry (4th Edition) by J.D. Lee
9. General and Inorganic Chemistry by P.K. Dutta
10. General and Inorganic Chemistry by R. Sarka

Unit - 2 ❑ Electronic Configuration of Atoms

Structure

2.0 Objectives

- To understand the arrangement of electrons in different orbitals of an atom.
- To apply the Aufbau principle, Pauli Exclusion Principle, and Hund's Rule to determine the electronic configuration of atoms.
- To explain how the electronic configuration influences the chemical properties and reactivity of elements.
- To understand the stability associated with half-filled and completely filled orbitals due to symmetrical distribution and exchange energy.
- To analyze why certain electron configurations, exhibit extra stability (e.g., chromium and copper).
- To explore the role of electronic configuration in the stability of elements across the periodic table.
- To understand the reasons behind deviations from the expected Aufbau principle due to factors like stability of half-filled and completely filled orbitals.

2.1 Introduction

The electronic configuration of atoms is a fundamental concept in chemistry that describes the arrangement of electrons within an atom's orbitals. Understanding how electrons are distributed among these orbitals is essential for predicting the chemical behavior, reactivity, and bonding of elements. Several rules, including the Aufbau principle, Pauli Exclusion Principle, and Hund's Rule, govern the filling of electrons in orbitals. Additionally, the relative stability of half-filled and completely filled orbitals, the concept of exchange energy, and the order of orbital energies play crucial roles in determining the overall stability of an atom. Occasionally, certain elements exhibit anomalous electronic configurations, deviating from the expected patterns due to stability considerations. These concepts are vital for understanding atomic structure and the periodic properties of elements.

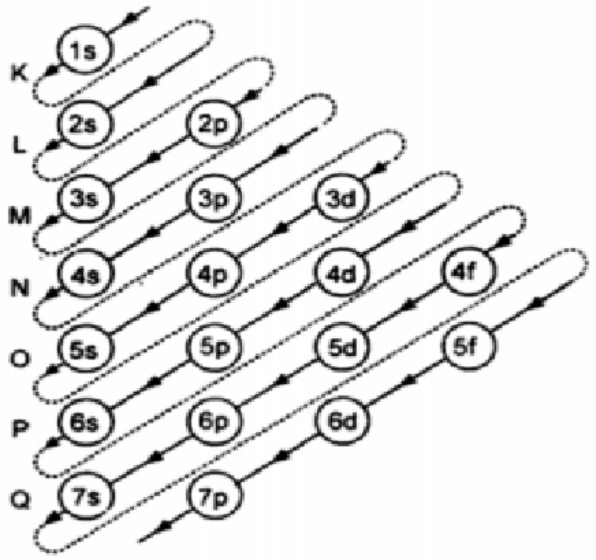
2.2 Electronic Configuration of Atoms Rules for filling electrons in various orbitals

Electrons are filled in the orbitals in an atom based on following rules:

Aufbau principle

Aufbau principle states that electrons are filled into the atomic orbitals in order from lowest energy to highest. The Aufbau (German for *building up, construction*) principle is sometimes referred to as the "building up" principle.

According to aufbau principle the orbitals can be arranged according to their energy in following order: $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$



Hund's rule of maximum spin multiplicity

The rule states that electrons will prefer to remain unpair until the vacant orbitals of the same energy levels are available. For a given electronic configuration, the lowest energy term will be that one with the greatest value of spin multiplicity. This implies that a half filled orbital will have lower energy than partially filled orbitals. As for examples, if 3 electrons are needed to fill in a p orbital then the preferred electronic configuration will be diagram-A rather than diagram-B. This is quite intuitive because electron-electron repulsions would make an atom more unstable if the electrons start filling two at a time in a single orbital.

↑	↑	↑

Diagram-A

↑↓	↑

Diagram-B

Thus electronic configurations with half filled orbital and fulfilled orbitals will be more stable than partially filled orbitals.

As for example, the correct electronic configuration of Cr-atom will be: [Ar] $3d^5 4s^1$

Pauli's Exclusion Principle

Pauli's exclusion principle states that no two electrons in an atom can have the same values of all the four quantum numbers.

As for example if we take two electrons in 1s orbital then the values of quantum numbers are as follows:

n	ℓ	m_{ℓ}	m_s
1	0	0	+½
1	0	0	-½

Though the two electrons of 1s orbital have same values of n, $-\ell$ and m_{ℓ} but they have different m_s values. Thus two electrons have different sets of values of four quantum numbers.

2.3 Electronic configurations of the atoms

Electrons are filled in the orbitals in an atom following the above four principles. Based on these principles we can write electronic configurations of all the atoms.

Electronic configurations of first thirty elements are given below:

Atomic Number	**Name of the Element**	**Electronic Configuration**
1	Hydrogen (H)	$1s^1$
2	Helium (He)	$1s^2$
3	Lithium (Li)	[He] $2s^1$
4	Beryllium (Be)	[He] $2s^2$
5	Boron (B)	[He] $2s^2$ $2p^1$
6	Carbon (C)	[He] $2s^2$ $2p^2$
7	Nitrogen (N)	[He] $2s^2$ $2p^3$
8	Oxygen (O)	[He] $2s^2$ $2p^4$
9	Fluorine (F)	[He] $2s^2$ $2p^5$
10	Neon (Ne)	[He] $2s^2$ $2p^6$
11	Sodium (Na)	[Ne] $3s^1$
12	Magnesium (Mg)	[Ne] $3s^2$
13	Aluminium (Al)	[Ne] $3s^2$ $3p^1$
14	Silicon (Si)	[Ne] $3s^2$ $3p^2$
15	Phosphorus (P)	[Ne] $3s^2$ $3p^3$
16	Sulphur (S)	[Ne] $3s^2$ $3p^4$

17	Chlorine (Cl)	$[\mathrm{Ne}]\ 3s^{2}\ 3p^{5}$
18	Argon (Ar)	$[\mathrm{Ne}]\ 3s^{2}\ 3p^{6}$
19	Potassium (K)	$[\mathrm{Ar}]\ 4s^{1}$
20	Calcium (Ca)	$[\mathrm{Ar}]\ 4s^{2}$
21	Scandium (Sc)	$[\mathrm{Ar}]\ 3d^{1}\ 4s^{2}$
22	Titanium (Ti)	$[\mathrm{Ar}]\ 3d^{2}\ 4s^{2}$
23	Vanadium (V)	$[\mathrm{Ar}]\ 3d^{3}\ 4s^{2}$
24	Chromium (Cr)	$[\mathrm{Ar}]\ 3d^{5}\ 4s^{1}$
25	Manganese (Mn)	$[\mathrm{Ar}]\ 3d^{5}\ 4s^{2}$
26	Iron (Fe)	$[\mathrm{Ar}]\ 3d^{6}\ 4s^{2}$
27	Cobalt (Co)	$[\mathrm{Ar}]\ 3d^{7}\ 4s^{2}$
28	Nickel (Ni)	$[\mathrm{Ar}]\ 3d^{8}\ 4s^{2}$
29	Copper (Cu)	$[\mathrm{Ar}]\ 3d^{10}\ 4s^{1}$
30	Zinc (Zn)	$[\mathrm{Ar}]\ 3d^{10}\ 4s^{2}$

There are two main exceptions to electron configuration: chromium and copper. In these cases, a completely filled or half-filled d orbital is more stable than a partially filled d orbitals, so an electron from the 4s orbital is excited and rises to a 3d orbital. The stabilizing effect is used whenever two or more electrons with the same spin are present in a degenerate orbital as a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is half filled or completely filled. The exchange energy increases with the number of possible exchanges between electrons with the same spin and energy. Thus, half-filled and completely filled orbitals are energetically more stable than the partially filled orbitals.

Here are some examples of exceptional electronic configurations:

Element	**Predicted Electronic Configuration**	**Actual Electronic Configuration**
Cu	$[\mathrm{Ar}]\ 3d^{9}\ 4s^{2}$	$\mathbf{[Ar]\ 3\boldsymbol{d}^{10}\ 4\boldsymbol{s}^{1}}$
Ag	$[\mathrm{Kr}]\ 4d^{9}\ 5s^{2}$	$\mathbf{[Kr]\ 4\boldsymbol{d}^{10}\ 5\boldsymbol{s}^{1}}$
Au	$[\mathrm{Xe}]\ 4f^{14}\ 5d^{9}\ 6s^{2}$	$\mathbf{[Xe]\ 4\boldsymbol{f}^{14}\ 5\boldsymbol{d}^{10}\ 6\boldsymbol{s}^{1}}$
Pd	$[\mathrm{Kr}]\ 4d^{8}\ 5s^{2}$	$\mathbf{[Kr]\ 4\boldsymbol{d}^{10}}$
Cr	$[\mathrm{Ar}]\ 3d^{4}\ 4s^{2}$	$\mathbf{[Ar]\ 3\boldsymbol{d}^{5}\ 4\boldsymbol{s}^{1}}$
Mo	$[\mathrm{Kr}]\ 4d^{4}\ 5s^{2}$	$\mathbf{[Kr]\ 4\boldsymbol{d}^{5}\ 5\boldsymbol{s}^{1}}$

2.4 Stability of half-filled and completely filled orbitals

The stability of half-filled and completely filled orbitals is a key concept in atomic structure, often influencing the electron configurations of elements, particularly in transition metals. This increased stability arises due to two primary factors: symmetrical distribution of electrons and exchange energy.

Symmetrical Distribution of Electrons: Orbitals that are either half-filled or completely filled exhibit greater symmetry. Symmetrical distribution leads to a lower repulsion among electrons, which contributes to the overall stability of the atom. For example, in the case of a half-filled orbital, each electron occupies an individual orbital with parallel spins, reducing electron-electron repulsion.

Exchange Energy: Exchange energy is a stabilization factor that arises from the quantum mechanical property of electrons known as "exchange interaction." When electrons with parallel spins occupy degenerate orbitals (orbitals of the same energy), they can exchange their positions without altering the overall energy. The number of possible exchanges is higher when orbitals are half-filled or completely filled, which leads to increased exchange energy and consequently, greater stability.

Examples in Transition Metals: The stability of half-filled and completely filled orbitals can sometimes result in deviations from the expected electron configuration, particularly in elements like chromium (Cr) and copper (Cu). Instead of following the expected configuration of [Ar] $4s^2\ 3d^4$, chromium adopts [Ar] $4s^1\ 3d^5$, which provides the stability of a half-filled 3d orbital. Similarly, copper adopts [Ar] $4s^1\ 3d^{10}$ instead of the expected [Ar] $4s^2\ 3d^9$, due to the stability of a completely filled 3d orbital.

Impact on Chemical Properties: This stability of half-filled and completely filled orbitals influences the chemical reactivity, oxidation states, and bonding behavior of elements. For example, transition metals often form compounds where their d-orbitals are half-filled or completely filled, contributing to their unique properties in catalysis, magnetism, and coordination chemistry.

2.5 Concept of exchange energy

Exchange energy is a quantum mechanical concept that plays a crucial role in the stability of atoms, particularly in relation to the distribution of electrons within degenerate orbitals (orbitals with the same energy). It arises from the exchange interaction between electrons with parallel spins, which leads to a stabilizing effect on the atom.

Origin of Exchange Energy: The exchange energy originates from the Pauli Exclusion Principle, which states that no two electrons in an atom can have the same set of quantum numbers. Electrons within the same subshell (degenerate orbitals) prefer to occupy different orbitals with parallel spins before pairing up. When electrons have parallel spins in degenerate orbitals, they are indistinguishable from each other in terms of their spin orientation. This allows them to "exchange" their positions without changing the system's energy, which results in a lower energy state.

Electron Exchange: When electrons with parallel spins are present in different degenerate orbitals, there is a higher probability of them exchanging places. This phenomenon increases the system's stability because it minimizes electron-electron repulsion, allowing for a more favorable energy arrangement. The number of possible exchanges is directly proportional to the number of electrons with parallel spins in degenerate orbitals. Therefore, the more exchanges that can occur, the greater the stabilization.

Stabilization Effect: Exchange energy is most significant in cases where orbitals are either half-filled or completely filled. In a half-filled subshell, each orbital has one electron with parallel spins, maximizing the number of possible exchanges. Similarly, in a completely filled subshell, all orbitals are paired, and the exchange energy contributes to the system's overall stability. This is why atoms with half-filled or fully filled subshells exhibit greater stability compared to other configurations.

Relation to Electron Configurations: Exchange energy plays an important role in the formation of anomalous electronic configurations, especially in transition metals. For example, elements like chromium (Cr) and copper (Cu) deviate from the expected Aufbau principle configuration because the exchange energy gained from half-filled (in Cr) and completely filled (in Cu) d-orbitals compensates for the energy difference.

- Chromium (Cr) has a configuration of [Ar] $4s^1$ $3d^5$ rather than [Ar] $4s^2$ $3d^4$, as the half-filled 3d subshell is stabilized by exchange energy.
- Copper (Cu) has a configuration of [Ar] $4s^1$ $3d^{1}$□ rather than [Ar] $4s^2$ 3d□, where the completely filled 3d subshell is stabilized by the exchange interactions.

Impact on Chemical Behavior: Exchange energy is significant in determining the chemical behavior of elements. It explains why atoms with half-filled or completely filled orbitals often display greater resistance to changes in their electronic structure, influencing properties such as magnetism, ionization energies, and preferred oxidation states in chemical reactions.

2.6 Relative energies of atomic orbitals

The relative energies of atomic orbitals play a crucial role in determining the electron configuration of atoms and, subsequently, the chemical and physical properties of elements. Atomic orbitals are regions of space around the nucleus where the probability of finding an electron is high. These orbitals differ in shape, size, and energy. Understanding the relative energies of these orbitals is essential for explaining atomic behavior, bonding, and molecular structures.

The energy of an atomic orbital depends on several quantum numbers, specifically:

1. **Principal Quantum Number (n)**: It indicates the size and energy level of the orbital. Orbitals with a higher value of *n* are generally larger and have higher energy because the electron is, on average, farther from the nucleus. For example, the 3s orbital has higher energy than the 2s orbital.
2. **Azimuthal Quantum Number (l)**: It determines the shape of the orbital. For a given value of *n*, orbitals with higher *l* values (p, d, f orbitals) typically have higher energy than orbitals with lower *l* values (s orbitals), due to increased electron shielding and reduced nuclear attraction. The order of energy for orbitals with the same *n* is: s < p < d < f.
3. **Electron Shielding and Penetration**: Electrons in lower-energy orbitals can shield electrons in higher orbitals from the full attraction of the nucleus. Orbitals with a higher penetration ability (such as s orbitals) experience greater nuclear attraction, leading to lower energy compared to p, d, or f orbitals within the same energy level.

Relative Energy Ordering

For multi-electron atoms, the relative energies of orbitals do not follow a simple order due to electron-electron interactions and shielding effects. However, a general trend in increasing energy of orbitals is as follows:

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p

This order is based on both the principal quantum number (*n*) and the azimuthal quantum number (*l*), with some deviations due to electron-electron repulsion and shielding. The 4s orbital, for example, has lower energy than the 3d orbital due to the higher nuclear penetration of the 4s electrons.

Factors Affecting Orbital Energy

1. **Effective Nuclear Charge (Z_eff)**: As the atomic number increases, the nucleus exerts a stronger attractive force on electrons, pulling them closer and reducing their energy. However, electron shielding moderates this effect, especially for outer electrons.
2. **Electron-Electron Repulsion**: In multi-electron atoms, repulsion between electrons in the same orbital or shell increases the energy of those orbitals. This effect is more pronounced in orbitals with more angular momentum (p, d, f).
3. **Hund’s Rule and Exchange Energy**: When electrons occupy degenerate (same-energy) orbitals, they tend to maximize the number of unpaired electrons, as unpaired electrons in parallel spins lower the overall energy through exchange interaction.

Applications in Chemistry

The relative energies of atomic orbitals help explain the periodic table’s structure, chemical bonding, and molecular geometry. They are crucial for predicting electron configurations (e.g., $1s^2\ 2s^2\ 2p^6\ 3s^2$ for magnesium) and understanding the nature of chemical bonds in molecules, especially in molecular orbital theory.

2.7 Anomalous electronic configurations

Anomalous electronic configurations refer to cases where the expected electron configuration of an atom, based on the principles of Aufbau's rule, Hund's rule, and Pauli's exclusion principle, is not followed. These anomalies arise due to the subtle balance between electron-electron interactions, exchange energy, and the stability conferred by certain electron arrangements.

Expected Electron Configurations

Under the **Aufbau principle**, electrons fill atomic orbitals in order of increasing energy. According to this rule, the lower energy orbitals (1s, 2s, 2p, etc.) are filled before higher energy orbitals (3s, 3p, 3d, etc.). The general filling order can be predicted using the (n + l) rule, where *n* is the principal quantum number and *l* is the azimuthal quantum number.

However, **anomalous configurations** occur in certain elements, particularly among transition metals and heavier elements, where the actual electron configuration deviates from what would be expected.

Causes of Anomalous Electronic Configurations

1. **Exchange Energy and Stability of Half-filled and Fully-filled Subshells**: A key factor in anomalous configurations is the enhanced stability associated with half-filled or fully-filled subshells. Orbitals such as *d* or *f* that are exactly half-filled (e.g., $3d^5$) or fully filled (e.g., $3d^{1}$□) are more stable due to **exchange energy**, which arises from parallel spins of unpaired electrons. This stability can sometimes outweigh the energy cost of promoting an electron from a lower energy orbital to a higher one.

   For example:

   - Chromium (Cr): The expected configuration is [Ar] $3d^4\ 4s^2$, but the observed configuration is [Ar] $3d^5\ 4s^1$. A half-filled 3d subshell is more stable due to exchange energy.
   - Copper (Cu): The expected configuration is [Ar] $3d^9\ 4s^2$, but the actual configuration is [Ar] $3d^{1}$□ $4s^1$. A fully filled 3d subshell provides extra stability.

Relativistic Effects: In heavier elements, particularly those with high atomic numbers, relativistic effects become significant. As electrons approach relativistic speeds near the nucleus, their effective mass increases, leading to a contraction of inner orbitals (like 6s). This changes the energy levels of orbitals and can result in anomalous electron configurations in heavier elements, especially in the lanthanide and actinide series.

Small Energy Differences Between Orbitals: The energy difference between *s* and *d* orbitals in transition metals is small. This makes it easy for an electron to be promoted from the *s* orbital to the *d* orbital to achieve a more stable configuration, often leading to deviations from the expected pattern.

For example:

Molybdenum (Mo): Expected configuration [Kr] $4d^4\ 5s^2$, but the actual configuration is [Kr] $4d^5\ 5s^1$, again due to the stability of a half-filled 4d subshell.

Silver (Ag): Expected configuration [Kr] $4d^9$ $5s^2$, but the actual configuration is [Kr] $4d^{10}$ $5s^1$, due to the stability of a fully filled 4d subshell.

Examples of Anomalous Configurations

Chromium (Cr):

Expected: [Ar] $3d^4$ $4s^2$

Observed: [Ar] $3d^5$ $4s^1$

Copper (Cu):

Expected: [Ar] $3d^9$ $4s^2$

Observed: [Ar] $3d^{10}$ $4s^1$

Molybdenum (Mo):

Expected: [Kr] $4d^4$ $5s^2$

Observed: [Kr] $4d^5$ $5s^1$

Silver (Ag):

Expected: [Kr] $4d^9$ $5s^2$

Observed: [Kr] $4d^{10}$ $5s^1$

Gold (Au):

Expected: [Xe] $4f^{14}$ $5d^9$ $6s^2$

Observed: [Xe] $4f^{14}$ $5d^{10}$ $6s^1$

Why Are These Configurations Important?

1. **Chemical Reactivity**: Anomalous electron configurations can influence the chemical properties of elements. For example, copper (Cu) has a configuration of [Ar] $3d^1$ $4s^1$, which affects its ability to form different oxidation states (+1, +2).
2. **Magnetism**: The electron configuration, especially the presence of unpaired electrons in d or f orbitals, plays a significant role in determining whether an element exhibits magnetic properties. For example, elements with half-filled *d* orbitals, such as chromium (Cr), often exhibit unique magnetic behavior.
3. **Catalytic Properties**: Transition metals with anomalous configurations often have partially filled d orbitals, which make them effective catalysts. The ease with which

these metals can exchange electrons in reactions contributes to their ability to catalyze various chemical reactions.

2.8 Summary

Electronic Configurations of Atoms:

The electronic configuration of an atom describes the distribution of electrons in different orbitals (s, p, d, f). Electrons fill these orbitals following three key rules:

- **Aufbau Principle**: Electrons occupy the lowest energy orbitals first.
- **Pauli Exclusion Principle**: No two electrons can have the same set of four quantum numbers, meaning each orbital can hold a maximum of two electrons with opposite spins.
- **Hund's Rule**: In degenerate orbitals (orbitals with the same energy), electrons are distributed singly with parallel spins before pairing occurs.

a) **Stability of Half-Filled and Completely Filled Orbitals**:

- Orbitals that are either half-filled or completely filled exhibit greater stability. This is due to symmetrical electron distribution and a maximization of exchange energy (a stabilizing interaction between electrons with parallel spins). Half-filled (e.g., p^3, d^5) and fully filled (e.g., p^6, d^{10}) orbitals lower the energy of the atom, contributing to its stability.

Concept of Exchange Energy:

- Exchange energy is the energy released due to the exchange of positions between electrons with parallel spins within the same subshell. The more such exchanges occur, the lower the energy of the atom. This energy is significant in half-filled and fully filled orbitals, where the number of exchanges is maximized, further stabilizing the configuration.

Relative Energies of Atomic Orbitals:

The energy of atomic orbitals increases as the principal quantum number (n) and angular momentum quantum number (l) increase. However, orbitals of higher n (e.g., 3d) may sometimes have lower energy than orbitals of a lower n (e.g., 4s) due to electron shielding and penetration effects. Thus, electrons may fill orbitals in an order that is not strictly based on their principal quantum number.

Anomalous Electronic Configurations:

Some elements exhibit electronic configurations that deviate from the expected order due to enhanced stability associated with half-filled or fully filled orbitals. Examples include chromium ([Ar]$3d^5 4s^1$) and copper ([Ar]$3d^{10} 4s^1$), where the electron configurations prioritize a more stable d-subshell configuration over the expected arrangement. This deviation is explained by the stability derived from exchange energy and the symmetry of half-filled or fully filled orbitals.

2.9 Sample Questions

2.10 Further Reading

A. Multiple Choice Type Questions

1. Which rule states that no two electrons in an atom can have the same set of four quantum numbers?

A. Hund’s rule
B. Pauli Exclusion Principle
C. Aufbau Principle
D. Bohr's rule

Answer: B. Pauli Exclusion Principle

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2. According to the Aufbau Principle, electrons fill orbitals in which order?

A. From higher to lower energy levels
B. From lower to higher energy levels
C. Randomly
D. Based on atomic size

Answer: B. From lower to higher energy levels

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3. Hund's Rule states that electrons will occupy orbitals singly before pairing up to maximize which property?

A. Atomic number
B. Total energy

C. Spin multiplicity
D. Total magnetic moment

Answer: C. Spin multiplicity

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4. The electronic configuration of Nitrogen (Z = 7) is $1s^2\ 2s^2\ 2p^3$. Which property makes this configuration particularly stable?

A. Completely filled orbitals
B. Half-filled 2p orbitals
C. Full d-orbital
D. Full f-orbital

Answer: B. Half-filled 2p orbitals

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5. Which of the following elements has an anomalous electronic configuration?

A. Scandium
B. Chromium
C. Calcium
D. Hydrogen

Answer: B. Chromium

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6. What is the reason for the stability of half-filled and completely filled orbitals?

A. Lower exchange energy
B. Higher exchange energy
C. High potential energy
D. Maximum number of paired electrons

Answer: B. Higher exchange energy

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7. In which orbital do electrons experience the least shielding effect, thus having relatively higher energy?

A. 2p
B. 3s
C. 3d
D. 4s

Answer: C. 3d

---

8. Exchange energy is dependent on which of the following factors?

A. The number of unpaired electrons with parallel spins
B. The number of paired electrons
C. The atomic number
D. The total number of protons

Answer: A. The number of unpaired electrons with parallel spins

---

9. What is the correct electronic configuration of Copper (Z = 29), considering anomalous electronic configurations?

A. [Ar] $4s^2\ 3d^9$
B. [Ar] $4s^1\ 3d^{1\square}$
C. [Ne] $3s^2\ 3p^6$
D. [Ar] $4s^2\ 3d^{1\square}$

Answer: B. [Ar] $4s^1\ 3d^{1\square}$

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10. What is the order of relative energies for the following orbitals: 3d, 4s, 4p?

A. $3d > 4p > 4s$
B. $4s > 3d > 4p$
C. $4s > 4p > 3d$
D. $4p > 4s > 3d$

Answer: A. $3d > 4p > 4s$

B. Short Type Questions

1. Write the electron configuration of Ni^{2+} and Cr^{3+} ions.

Answer: Ni^{2+} (Nickel ion)

The atomic number of Ni (Nickel) is 28, and its neutral electronic configuration is: Ni: $[Ar]3d^8 4s^2$

To form the Ni^{2+} ion, two electrons are removed, and they are taken from the 4s orbital first: Ni^{2+}: $[Ar]3d^8$

Cr^{3+} (Chromium ion)

The atomic number of Cr (Chromium) is 24, and its neutral electronic configuration is: Cr: $[Ar]3d^5 4s^1$

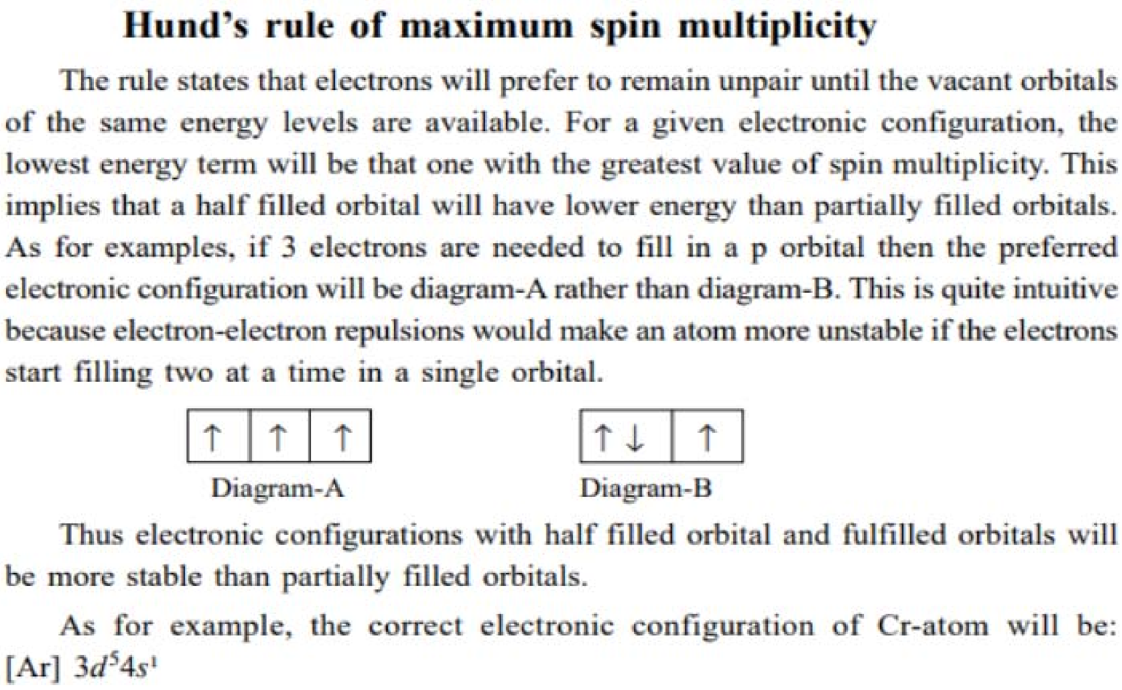
To form the Cr^{3+} ion, three electrons are removed —first from the 4s orbital and then from the 3d orbital: Cr^{3+}:[Ar]$3d^3$

Thus, the electronic configurations are:

- **Ni^{2+}:** [Ar]$3d^8$
- **Cr^{3+}:** [Ar]$3d^3$

2. **Discuss the following: (a) Hund's Rule of Maximum multiplicity. (b) Pauli's Exclusion Principle.**

Answer: (a) Hund's Rule of Maximum multiplicity.



Hund's rule of maximum spin multiplicity

The rule states that electrons will prefer to remain unpair until the vacant orbitals of the same energy levels are available. For a given electronic configuration, the lowest energy term will be that one with the greatest value of spin multiplicity. This implies that a half filled orbital will have lower energy than partially filled orbitals. As for examples, if 3 electrons are needed to fill in a p orbital then the preferred electronic configuration will be diagram-A rather than diagram-B. This is quite intuitive because electron-electron repulsions would make an atom more unstable if the electrons start filling two at a time in a single orbital.

↑	↑	↑

Diagram-A

↑↓	↑

Diagram-B

Thus electronic configurations with half filled orbital and fulfilled orbitals will be more stable than partially filled orbitals.

As for example, the correct electronic configuration of Cr-atom will be: [Ar] $3d^5 4s^1$

(b) Pauli's Exclusion Principle.

Pauli's Exclusion Principle is a fundamental rule in quantum mechanics, proposed by Wolfgang Pauli in 1925. It states that:

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

Explanation:

- Each electron in an atom is described by four quantum numbers: n, l, m□, and m□.
    1. n: Principal quantum number (energy level)
    2. l: Azimuthal quantum number (subshell: s, p, d, f)
    3. m□: Magnetic quantum number (orientation of the orbital)
    4. m□: Spin quantum number (+½ or -½)

In any given orbital, two electrons can coexist, but they must have opposite spins (i.e., their spin quantum numbers, m□, must be different: one +½ and the other -½). This ensures that each electron is unique in its quantum state.

3. State Pauli's exclusion principle. Based on this principle, the maximum number of electrons that can be accommodated in an orbit is 8 when n = 2

2. Answer: Explanation for the maximum number of electrons when n = 2:

The principal quantum number, n, specifies the energy level (or shell). When n = 2, the electrons can be accommodated in two subshells: 2s and 2p.

For the 2s subshell:

- l = 0 (s-orbital)
- m□ = 0 (only one orientation)
- Each orbital can accommodate 2 electrons (with opposite spins: m□ = +½ or -½).
- So, the 2s subshell can hold 2 electrons.

For the 2p subshell:

- l = 1 (p-orbitals)
- m□ = -1, 0, +1 (three orientations, p_x, p_y, and p_z)
- Each of the three p-orbitals can accommodate 2 electrons (with opposite spins).
- So, the 2p subshell can hold 6 electrons.

Therefore, the total number of electrons in the second energy level (n = 2) is:
2 (from 2s)+6 (from 2p)=8

Thus, a maximum of 8 electrons can be accommodated when n = 2.

4. State Pauli's exclusion principle and show that the maximum number of electrons in a given shell is $2n^2$ where n is the principal quantum number of the shell.

Answer: Pauli's Exclusion Principle:

"No two electrons in an atom can have the same set of four quantum numbers (n, l, m□, and m□)."

This principle implies that in an atom, each electron must have a unique quantum state, meaning that no two electrons can occupy the same orbital with the same spin.

Explanation of Maximum Number of Electrons in a Given Shell ($2n^2$):

The principal quantum number n defines the shell or energy level in which electrons reside. The maximum number of electrons in a given shell can be calculated using the formula $2n^2$, where n is the principal quantum number.

Step-by-Step Justification:

1. Subshells in a shell: Each shell (defined by the quantum number n) contains n subshells, where the number of subshells corresponds to the values of the azimuthal quantum number l (ranging from 0 to $n-1$).
2. Number of orbitals in each subshell: Each subshell has orbitals, where the number of orbitals in a subshell is given by $2l+1$, corresponding to the magnetic quantum number m□ values (ranging from $-l$ to $+l$).
3. Electrons in each orbital: Each orbital can hold a maximum of 2 electrons (due to the two possible values of spin quantum number m□, which are +½ and -½), according to Pauli's Exclusion Principle.

Example for $n = 2$:

- For $n = 2$, there are two subshells:
    - 2s (where $l = 0$) has 1 orbital → can hold 2 electrons.
    - 2p (where $l = 1$) has 3 orbitals → can hold 6 electrons.

So, for $n = 2$, the total number of electrons = $2+6=8$.

General Formula for Maximum Number of Electrons:

To determine the maximum number of electrons in a given shell, we add up all the orbitals and electrons across all subshells for a particular value of n.

- For a given n, the total number of orbitals in the shell is:
  n^2 (from summing the number of orbitals in all subshells) n^2
    - The maximum number of electrons in each orbital is 2 (due to Pauli's Exclusion Principle).

Thus, the maximum number of electrons in a shell is:

$$2\times n^2=2n^2$$

B. Assay Type Questions

1. Explain the Pauli Exclusion Principle in detail and discuss its significance in the arrangement of electrons in atoms. How does this principle influence the structure of the periodic table and chemical behavior of elements?

3. **Answer:**Introduction to Pauli Exclusion Principle

- Define the principle:
  - No two electrons in an atom can have the same set of four quantum numbers (n, l, m□, m□).
  - Named after Wolfgang Pauli, proposed in 1925.
- Explain the quantum numbers:
  - n (principal quantum number) — describes the energy level.
  - l (azimuthal quantum number) — describes the shape of the orbital.
  - m□ (magnetic quantum number) — describes the orientation of the orbital.
  - m□ (spin quantum number) — describes the spin direction (+½ or -½).

2. Significance in the Arrangement of Electrons in Atoms

- Maximum of 2 electrons per orbital:
  - Due to the two possible values for the spin quantum number (□m = +½ or -½), only 2 electrons can occupy the same orbital, but they must have opposite spins.
  - Example: $1s^2$ in hydrogen and helium.
- Unique quantum state for every electron:
  - Each electron in an atom must occupy a unique quantum state.
  - Prevents overcrowding of electrons in lower energy states, leading to structured electron configurations across different energy levels and orbitals.

3. Influence on the Periodic Table

- Electron configuration determines position in the periodic table:
  - The arrangement of electrons into shells and subshells (s, p, d, f) creates a structured periodic table.
  - Elements in the same group (vertical columns) have similar valence electron configurations, which gives them similar chemical properties.
  - For example, alkali metals (Group 1) have a single electron in the outermost s-orbital (ns^1 configuration).
- Filling order of orbitals (Aufbau Principle):
  - Electrons fill orbitals in increasing energy order (1s, 2s, 2p, 3s, etc.).

    - The Exclusion Principle, combined with other rules like Hund's rule and the Aufbau principle, governs the periodic trends in electron configurations.

4. Chemical Behavior of Elements

- Influence on reactivity and bonding:
    - The arrangement of electrons, especially the valence electrons, determines an element's reactivity and how it bonds with other elements.
    - Elements with a full outer shell (like noble gases) are chemically inert due to their stable electron configuration.
    - Elements with incomplete valence shells (like alkali metals and halogens) are highly reactive, seeking to lose, gain, or share electrons to achieve stability.
- Stability of half-filled and fully-filled orbitals:
    - Due to Pauli's Exclusion Principle and the related concept of exchange energy, half-filled and fully-filled subshells are often more stable.
    - Example: Nitrogen's configuration ($1s^2\ 2s^2\ 2p^3$) is particularly stable due to its half-filled 2p orbitals.

2. Discuss the rules for filling electrons in various orbitals of an atom (Aufbau Principle, Hund's Rule, and Pauli Exclusion Principle). Provide examples to illustrate how these rules determine the electronic configuration of elements.

Answer: The electronic configuration of an atom describes the arrangement of electrons in its orbitals, which is governed by three key principles: the Aufbau Principle, Hund's Rule, and the Pauli Exclusion Principle. These principles help determine the most stable arrangement of electrons in an atom. Let's discuss each rule with examples.

1. Aufbau Principle

The Aufbau Principle states that electrons fill orbitals starting from the lowest energy level and move to higher energy orbitals as needed. This rule is based on the idea that electrons occupy the most stable (i.e., the least energetic) configuration possible.

The order in which orbitals are filled is determined by their relative energies. The energy levels are filled according to the following order:

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p$, etc.

Example: For carbon (atomic number 6), the electrons fill the orbitals as follows:

- The first two electrons go into the 1s orbital ($1s^2$),
- The next two fill the 2s orbital ($2s^2$),
- The remaining two electrons go into the 2p orbitals ($2p^2$).

Thus, the electronic configuration of carbon is:
$1s^2\ 2s^2\ 2p^2$.

2. Hund's Rule

Hund's Rule states that when electrons fill degenerate orbitals (orbitals of the same energy, like the three 2p orbitals), they first fill them singly with parallel spins before pairing up. This minimizes electron-electron repulsion and leads to a more stable arrangement.

Example: For nitrogen (atomic number 7), the electrons fill as follows:

- The first two electrons go into the 1s orbital ($1s^2$),
- The next two fill the 2s orbital ($2s^2$),
- The remaining three electrons go into the 2p orbitals. According to Hund's Rule, the three electrons occupy the three 2p orbitals singly with parallel spins.

Thus, the electronic configuration of nitrogen is:
$1s^2\ 2s^2\ 2p^3$.
In the 2p sublevel, each p orbital has one unpaired electron.

3. Pauli Exclusion Principle

The Pauli Exclusion Principle states that no two electrons in an atom can have the same set of four quantum numbers. This means that an orbital can hold at most two electrons, and if it does, the two electrons must have opposite spins.

Example: For helium (atomic number 2), both electrons are in the 1s orbital. According to the Pauli Exclusion Principle, one electron will have spin-up (+½) and the other spin-down (−½).

The electronic configuration of helium is:
$1s^2$, where the two electrons have opposite spins.

Example of All Principles Combined: Oxygen (Atomic number 8)

- First, apply the Aufbau Principle: the first two electrons go into 1s, the next two into 2s, and the remaining four into 2p.
- Apply Hund's Rule: The three 2p orbitals are first filled with one electron each before pairing occurs.
- Apply Pauli Exclusion Principle: In each filled orbital (1s, 2s, and one of the 2p orbitals), the two electrons must have opposite spins.

Thus, the electronic configuration of oxygen is:
$1s^2 2s^2 2p^4$.

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3. Describe the concept of half-filled and completely filled orbitals. Why are these configurations considered more stable than other configurations? Use examples such as nitrogen and chromium to support your explanation.

Answer: The concept of half-filled and completely filled orbitals refers to the stability that arises when a set of degenerate orbitals (orbitals with the same energy, such as p, d, or f orbitals) are either exactly half-filled or fully occupied by electrons. These configurations are considered more stable due to a combination of exchange energy, symmetry, and electron-electron repulsion minimization. Let's explore why this happens and use examples like nitrogen and chromium to illustrate these points.

1. Half-Filled Orbitals

A half-filled orbital configuration occurs when each degenerate orbital within a subshell contains one electron. This situation leads to greater stability due to:

- Exchange energy: Electrons with parallel spins can exchange places between degenerate orbitals, resulting in exchange energy, which stabilizes the atom. The greater the number of parallel spins, the higher the exchange energy, and hence, the stability.
- Symmetry: A half-filled configuration is more symmetrical, which also contributes to its stability.
- Minimized electron-electron repulsion: When electrons occupy separate orbitals (as in a half-filled configuration), they minimize repulsion, which makes the arrangement more stable.

Example: Nitrogen (Atomic number 7)

The electronic configuration of nitrogen is $1s^2\ 2s^2\ 2p^3$. In this configuration, the 2p subshell has three orbitals, and each orbital contains one electron. Since the three electrons in the 2p orbitals are unpaired and have parallel spins, this is a half-filled configuration, which is relatively stable.

Nitrogen has a higher stability compared to elements where the 2p orbitals are partially filled but not half-filled (e.g., oxygen, with a configuration of $2p^4$).

2. Completely Filled Orbitals

A completely filled orbital configuration occurs when each orbital in a degenerate set is fully occupied by two electrons. This is another highly stable arrangement due to:

- Maximized exchange energy: Fully filled orbitals benefit from both exchange energy and the pairing of electrons in a balanced and stable manner.
- Symmetry and pairing: Completely filled orbitals are highly symmetrical, and paired electrons tend to balance the forces in an atom, leading to greater stability.

Example: Chromium (Atomic number 24)

Chromium's expected electronic configuration based on the Aufbau Principle would be [Ar] $3d^4\ 4s^2$. However, experimentally, chromium has the configuration [Ar] $3d^5\ 4s^1$. This deviation occurs because the 3d subshell is now half-filled ($3d^5$), which provides extra stability.

Instead of following the expected pattern, one electron from the 4s orbital is promoted to the 3d orbital, creating a half-filled 3d subshell ($3d^5$), which is more stable than the $3d^4\ 4s^2$ configuration. The stability arises from the increased exchange energy and symmetrical distribution of the electrons across the five 3d orbitals.

Why Are Half-Filled and Completely Filled Configurations More Stable?

The enhanced stability of half-filled and completely filled orbitals arises from:

1. Exchange energy: Electrons with parallel spins in separate orbitals can "exchange" positions, which lowers the total energy of the atom. Half-filled and completely filled orbitals maximize exchange energy.
2. Symmetry: These configurations are more symmetrical, which leads to lower energy states due to balanced electron distribution.
3. Electron-electron repulsion: In half-filled orbitals, electrons occupy separate orbitals, reducing repulsion. In completely filled orbitals, the pairing of electrons balances the repulsion.

Example: Copper (Atomic number 29)

Similar to chromium, copper also deviates from the expected configuration. Instead of [Ar] $3d^9\ 4s^2$, copper has the configuration [Ar] $3d^{10}\ 4s^1$, where the 3d subshell is completely filled. The full 3d subshell provides extra stability, making this configuration more favorable.

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4. Explain the concept of exchange energy and its role in stabilizing half-filled and completely filled orbitals. How does exchange energy affect the distribution of electrons in orbitals?

Answer: Exchange energy is a quantum mechanical phenomenon that arises due to the Pauli exclusion principle and the indistinguishability of electrons. It plays a significant role in determining the distribution of electrons in orbitals, particularly in the stabilization of half-filled and completely filled orbitals.

Concept of Exchange Energy:

- Pauli Exclusion Principle: No two electrons in an atom can have the same set of quantum numbers, which means that electrons in the same orbital must have opposite spins.
- Exchange: Electrons with parallel spins (same spin direction) in different orbitals can "exchange" places in a quantum mechanical sense, which leads to a lower overall energy. This is due to a phenomenon known as exchange interaction, which arises from the symmetry of the wave function for fermions (particles like electrons that follow the Pauli exclusion principle).

The exchange energy is the energy released when electrons with parallel spins are distributed in degenerate (same energy level) orbitals. More exchange interactions lead to greater stability, lowering the energy of the atom.

Role in Stabilizing Half-Filled and Completely Filled Orbitals:

1. Half-Filled Orbitals:
    - In a half-filled subshell, electrons occupy different orbitals with parallel spins (due to Hund's rule), maximizing the number of exchange interactions.
    - Since exchange interactions lower the energy, a half-filled configuration (e.g., d^5 or p^3) is stabilized due to the maximum possible number of such interactions.
2. Completely Filled Orbitals:
    - When orbitals are completely filled (e.g., d^{10}or p^6), there are still significant exchange interactions among electrons with parallel spins in different orbitals.
    - The full occupation leads to a symmetric distribution and maximizes exchange energy, providing additional stability to the completely filled orbitals.

How Exchange Energy Affects Electron Distribution:

- Hund's Rule of Maximum Multiplicity: This rule states that electrons will occupy degenerate orbitals singly with parallel spins before pairing. This is a direct consequence of the desire to maximize exchange energy, as it leads to a lower energy configuration.

For example:

- In the case of a carbon atom ($1s^2 2s^2 2p^2$), the two $2p^2$ electrons will occupy different p-orbitals with parallel spins to maximize exchange interactions.
- In transition metals, the stability of half-filled (d^5) and completely filled (d^{10}) configurations in d-orbitals is similarly explained by the high exchange energy associated with these configurations.

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5. Discuss the anomalous electronic configurations of certain transition elements like chromium (Cr) and copper (Cu). Why do these elements deviate from the expected electronic configurations based on the Aufbau Principle?

Answer: The electronic configurations of transition elements such as chromium (Cr) and copper (Cu) exhibit some deviations from what might be expected based on the Aufbau Principle. To understand these deviations, let's first review the expected configurations and then explore why the deviations occur.

Expected Electronic Configurations

According to the Aufbau Principle, electrons fill orbitals in order of increasing energy. For transition elements, this generally means filling the 4s orbital before the 3d orbitals. For example:

- Chromium (Cr) is in the 4th period, and its atomic number is 24. Based on the Aufbau Principle, its configuration should be:

  Cr: [Ar] $4s^2\ 3d^4$

- Copper (Cu) is also in the 4th period, and its atomic number is 29. Its expected configuration would be:

Cu: [Ar] $4s^2$ $3d^9$

Actual Electronic Configurations

However, the actual configurations are:

- Chromium (Cr):

  Cr: [Ar] $4s^1$ $3d^5$

- Copper (Cu):

  Cu: [Ar] $4s^1$ $3d^{10}$

Reasons for Deviations

1. Stability of Half-Filled and Fully Filled Orbitals:

   The primary reason for these deviations lies in the stability associated with half-filled and fully filled d orbitals. Both configurations offer additional stability due to electron-electron repulsions and exchange energy.

   - Chromium (Cr): In the case of Cr, having a half-filled 3d subshell ($3d^5$) is more stable than having a $3d^4$ configuration. The exchange energy associated with having one electron in each of the five 3d orbitals compensates for the energy required to promote one electron from the 4s to the 3d orbital. Thus, Cr prefers the configuration [Ar] $4s^1$ $3d^5$.
   - Copper (Cu): For Cu, a completely filled 3d subshell ($3d^{10}$) provides additional stability compared to having $3d^9$. By promoting one electron from the 4s orbital to the 3d orbital, Cu achieves a fully filled d subshell, which is energetically more favorable. Therefore, Cu adopts the configuration [Ar] $4s^1$ $3d^{10}$.
2. Electron-Electron Repulsion:

   Electron-electron repulsion plays a significant role in these deviations. In a partially filled d subshell, electrons are repelled more strongly due to their mutual repulsion.

Thus, configurations that alleviate this repulsion (by having half-filled or fully filled d orbitals) are energetically more favorable.

3. Exchange Energy:

   Exchange energy, which arises due to the quantum mechanical property of electrons (their spin), contributes to the stability of half-filled or fully filled orbitals. For Cr and Cu, the gain in exchange energy by having half-filled or fully filled 3d orbitals outweighs the energy cost of promoting an electron from the 4s orbital.

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6. Explain the relative energies of atomic orbitals and how this affects the order of electron filling in multi-electron atoms. Why do 4s electrons fill before 3d electrons, but 3d electrons are removed first during ionization?

Answer: The relative energies of atomic orbitals play a crucial role in determining the order in which electrons fill these orbitals and how they are removed during ionization. Understanding these concepts involves a few key principles related to electron configurations, orbital energies, and the effects of electron-electron interactions in multi-electron atoms.

Relative Energies of Atomic Orbitals

In multi-electron atoms, the relative energies of atomic orbitals are influenced by several factors, including the effective nuclear charge, electron-electron repulsions, and shielding effects. Here’s how these factors come into play:

1. Effective Nuclear Charge (Z_eff):
   - The effective nuclear charge is the net positive charge experienced by an electron in an atom. It accounts for the actual nuclear charge minus the shielding effect of other electrons.
   - As electrons are added to an atom, the effective nuclear charge increases, which affects the energy of the orbitals. Orbitals that are more shielded or further from the nucleus generally have higher energy.

2. Shielding Effect:
    - Inner electrons shield outer electrons from the full effect of the nuclear charge. This shielding means that the outermost electrons experience a reduced effective nuclear charge compared to what would be expected if there were no other electrons present.
    - Electrons in the same shell (e.g., 4s) do not shield each other very effectively compared to electrons in different shells.
3. Orbital Penetration:
    - Orbitals that are closer to the nucleus (such as s orbitals) penetrate the electron cloud of inner orbitals more effectively. This penetration reduces the energy of the orbital relative to those that are more shielded by other electrons.

Order of Electron Filling

- 4s vs. 3d Orbitals:
    - In the Ground State:
        - For a neutral atom, the 4s orbital is filled before the 3d orbitals. This is because the 4s orbital is slightly lower in energy than the 3d orbitals when the atom is in its ground state. This can be attributed to the 4s orbital's better penetration and less shielding compared to the 3d orbitals.
        - The order of filling is generally [n]s < [n]p < [n-1]d for orbitals of the same principal quantum number (n), though there are exceptions, such as the filling of 4s before 3d.

Ionization and Removal of Electrons

- Why 4s Electrons Are Removed First:
    - For Ionization:
        - When an atom loses electrons to form a cation, the 4s electrons are typically removed before the 3d electrons, even though the 4s orbitals were filled before the 3d orbitals. This is because, as electrons are added to the atom, the 4s orbital's energy becomes higher than that of the 3d orbitals due to increased electron-electron repulsion and effective nuclear charge.

- Once the 3d orbitals are occupied, the added electron-electron repulsions and increased shielding effects cause the 4s orbital to be slightly higher in energy compared to the 3d orbitals. Thus, the 4s electrons are removed first when ionization occurs.

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7. Discuss the significance of electronic configuration in determining the chemical properties of elements. How do elements in the same group of the periodic table exhibit similar chemical behavior based on their electronic configurations?

Answer: The electronic configuration of an element is crucial in determining its chemical properties because it dictates how atoms interact, bond, and react with other substances. Key points include:

1. Valence Electrons:
    - Chemical behavior is largely influenced by the number and arrangement of valence electrons (the electrons in the outermost shell). Elements with similar valence electron configurations exhibit similar chemical properties.
2. Periodic Table Groups:
    - Elements in the same group (column) of the periodic table have the same number of valence electrons, leading to similar chemical behavior. For instance, alkali metals (Group 1) all have a single valence electron, making them highly reactive and leading them to form similar types of compounds.
3. Chemical Bonding and Reactivity:
    - The tendency to gain, lose, or share electrons to achieve a stable electronic configuration (often a noble gas configuration) drives chemical reactions. Elements in the same group have similar tendencies due to their comparable valence electron configurations.

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8. How does the concept of shielding and penetration influence the energy levels of electrons in multi-electron atoms? Explain with reference to the s, p, d, and f orbitals.

Answer: The concepts of shielding and penetration significantly influence the energy levels of electrons in multi-electron atoms. These concepts help explain why orbitals within the same principal energy level have different energies and why the order of filling orbitals can vary. Here's a breakdown of how shielding and penetration affect the energy levels of s, p, d, and f orbitals:

Shielding

Shielding refers to the phenomenon where inner-shell electrons partially block the effective nuclear charge felt by outer-shell electrons. The effectiveness of shielding depends on the electron distribution in various orbitals:

- s Orbitals:
  - s orbitals are spherical and have a high probability density near the nucleus. They are less shielded by other electrons because they penetrate through other electron shells effectively. As a result, s orbitals experience a strong effective nuclear charge and generally have lower energy compared to p, d, and f orbitals in the same principal energy level.
- p Orbitals:
  - p orbitals have a dumbbell shape and are located further from the nucleus compared to s orbitals. They are more shielded by inner electrons and have less penetration through other orbitals, leading to higher energy compared to s orbitals in the same principal energy level.
- d Orbitals:
  - d orbitals are more complex in shape and are further away from the nucleus than s and p orbitals. They experience significant shielding due to their location in higher principal energy levels and also due to their less effective penetration through inner electrons. Consequently, d orbitals generally have higher energy than s and p orbitals in the same period.
- f Orbitals:
  - f orbitals have even more complex shapes and are located further from the nucleus. They experience the most shielding and have the least penetration through inner electron shells. Thus, f orbitals are the highest in energy among s, p, d, and f orbitals in the same principal energy level.

Penetration

Penetration refers to how well an orbital can approach the nucleus. Orbitals with higher penetration experience a stronger effective nuclear charge, which lowers their energy:

- s Orbitals:
  - s orbitals have the highest penetration because their spherical shape allows them to get close to the nucleus. They experience less shielding from other electrons and therefore have lower energy.
- p Orbitals:
  - p orbitals have moderate penetration compared to d and f orbitals. They are somewhat shielded by s orbitals but can still get relatively close to the nucleus.
- d Orbitals:
  - d orbitals have lower penetration than s and p orbitals, as their complex shapes make it more difficult for them to approach the nucleus closely. They are more shielded and hence have higher energy.
- f Orbitals:
  - f orbitals have the lowest penetration due to their complex shapes and location in higher principal energy levels. They are heavily shielded and thus have the highest energy among s, p, d, and f orbitals in the same period.

9. Describe the role of quantum numbers in determining the position and energy of an electron in an atom. How do quantum numbers help in predicting the possible electronic configurations of atoms?

Answer: Quantum numbers play a fundamental role in determining the position, energy, and arrangement of electrons in an atom. Each quantum number provides specific information about an electron's state within an atom. Here's how quantum numbers influence the electron's characteristics and how they help predict electronic configurations:

Quantum Numbers and Their Roles

1. Principal Quantum Number (n):
   - Role: Indicates the main energy level (shell) of an electron and its relative distance from the nucleus. It is a positive integer (n=1,2,3,….)
   - Energy: Higher n values correspond to higher energy levels.
   - Position: Determines the general size of the orbital and the average distance of the electron from the nucleus.
2. Azimuthal Quantum Number (lll):
   - Role: Defines the shape of the orbital and is also known as the angular momentum quantum number. It can take integer values from 0 to n−1.
   - Energy: Orbitals with different l values have different energies within the same principal energy level, with s orbitals (l=0) being lower in energy than p (l=1), d (l=2l), and f (l=3l) orbitals.
   - Position: Affects the shape of the electron cloud (spherical for s, dumbbell-shaped for p, and more complex shapes for d and f).
3. Magnetic Quantum Number (m_l):
   - Role: Specifies the orientation of the orbital in space relative to the other orbitals. It can take integer values from −l to +l, including zero.
   - Energy: In a given subshell, m_l values do not affect the energy of orbitals; however, they determine the number of orbitals and their spatial orientation.
4. Spin Quantum Number (m_s):
   - Role: Describes the intrinsic spin of the electron, which can be either +1/2 or -1/2. This quantum number accounts for the magnetic properties of electrons.
   - Energy: Spin does not directly affect the energy of an orbital but is crucial for determining electron pairing and the magnetic properties of atoms.

Predicting Electronic Configurations

The quantum numbers together determine the arrangement of electrons in an atom. Here's how they help in predicting electronic configurations:

1. Principal Quantum Number (n):
   - Determines the overall energy level and shell in which electrons are found.
2. Azimuthal Quantum Number (l):
   - Defines the type of orbital (s, p, d, f) and thus helps in organizing electrons within the shells into different subshells.
3. Magnetic Quantum Number (m_l):

  - Specifies how many orbitals exist in a given subshell (e.g., sss has 1 orbital, p has 3 orbitals, d has 5 orbitals, f has 7 orbitals).
4. Spin Quantum Number (m_s):
  - Determines how electrons fill the orbitals, ensuring that no two electrons in the same orbital have the same spin (Pauli Exclusion Principle).

Example: Hydrogen Atom

- Hydrogen (1 electron):
  - $n=1$ (first energy level)
  - $l=0$ (s orbital)
  - $ml=0$ (one orientation for s orbital)
  - $m_s=+1/2$ or $-1/2$ (one of two possible spins)

Example: Carbon Atom

- Carbon (6 electrons):
  - $n=1$ (2 electrons in 1s orbital)
  - $n=2$ (4 electrons in 2s and 2p orbitals)
  - Configuration: $1s^2\ 2s^2\ 2p^2$
  - $l=0$ for 1s and 2s; $l=1$ for 2p
  - m_l determines the arrangement of 2p electrons in the three 2p orbitals
  - m_s decides the spin state of each electron, following Hund's rule to maximize unpaired spins.

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10. Discuss the periodic trends in the atomic and ionic radii, ionization energy, and electron affinity in relation to electronic configuration. How do changes in electronic configuration across periods and groups affect these properties?

Answer: Periodic trends in atomic and ionic radii, ionization energy, and electron affinity are deeply linked to the electronic configuration of elements. Understanding these trends helps explain the reactivity and bonding characteristics of elements. Here's how changes in electronic configuration affect these properties across periods and groups in the periodic table:

1. Atomic Radius

Definition: The atomic radius is the distance from the nucleus of an atom to the outermost electron shell.

- Across a Period (Left to Right):
  - Trend: The atomic radius decreases.
  - Reason: As you move across a period, the number of protons in the nucleus increases, resulting in a greater effective nuclear charge. This increased positive charge pulls the electrons closer to the nucleus, reducing the atomic radius. Despite the increase in the number of electrons, these are added to the same principal energy level, so the increased nuclear charge has a stronger effect on pulling the electrons inward.

- Down a Group (Top to Bottom):
    - Trend: The atomic radius increases.
    - Reason: As you move down a group, additional electron shells (or energy levels) are added. Although the effective nuclear charge increases, the added electron shells increase the distance between the nucleus and the outermost electrons. Moreover, the shielding effect of inner-shell electrons partially offsets the increased nuclear charge, resulting in a larger atomic radius.

2. Ionic Radius

Definition: The ionic radius is the radius of an ion in a compound. It can be different from the atomic radius depending on whether the ion is a cation or an anion.

- Cations (Positively Charged Ions):
    - Trend: Cationic radius is smaller than the atomic radius.
    - Reason: When an atom loses one or more electrons to become a cation, the electron-electron repulsion decreases, and the remaining electrons are drawn closer to the nucleus due to the higher effective nuclear charge.
- Anions (Negatively Charged Ions):
    - Trend: Anionic radius is larger than the atomic radius.
    - Reason: When an atom gains one or more electrons to become an anion, there is increased electron-electron repulsion among the additional electrons, which causes the electron cloud to expand. The effective nuclear charge per electron decreases, leading to a larger ionic radius.
- Across a Period:
    - Trend: Ionic radii generally decrease for cations and increase for anions, though this is more noticeable among elements forming similar types of ions (e.g., comparing cations to anions of the same period).
- Down a Group:
    - Trend: Ionic radii increase as you move down a group, similar to atomic radii, due to the addition of electron shells.

3. Ionization Energy

Definition: Ionization energy is the energy required to remove an electron from an atom in its gaseous state.

- Across a Period:
    - Trend: Ionization energy increases.
    - Reason: As you move across a period, the effective nuclear charge increases, making it more difficult to remove an electron due to the stronger attraction between the nucleus and the electrons. Additionally, electrons are added to the same energy level, so the increased nuclear charge outweighs any additional electron-electron repulsion.
- Down a Group:
    - Trend: Ionization energy decreases.
    - Reason: Moving down a group increases the number of electron shells, which results in greater distance between the nucleus and the outermost electrons. The increased shielding effect reduces the effective nuclear charge felt by the outer electrons, making them easier to remove.

4. Electron Affinity

Definition: Electron affinity is the amount of energy released when an electron is added to a neutral atom to form an anion.

- Across a Period:
    - Trend: Electron affinity generally becomes more negative (i.e., increases) across a period.
    - Reason: As the effective nuclear charge increases, atoms have a greater tendency to attract additional electrons. The added electrons experience a stronger attraction from the nucleus, which leads to a greater release of energy when they are added.
- Down a Group:
    - Trend: Electron affinity generally becomes less negative (i.e., decreases) down a group.
    - Reason: Adding more electron shells means that the added electron is further from the nucleus and experiences less effective nuclear charge due to increased shielding. Thus, atoms have a lower tendency to attract additional electrons, and less energy is released.

2.10 References

1. Inorganic Chemistry by R.L. Dutta

2. Essentials of Physical Chemistry by B.S. Bahl

3. Concise Inorganic Chemistry (4th Edition) by J.D. Lee

4. General and Inorganic Chemistry by P.K. Dutta

5. General and Inorganic Chemistry by R. Sarkar

Unit - 3 ❑ Ionic Bonding

Structure

3.0 Objectives

After reading this unit, we will be able to:

- Definition of different types of Bonds
- Definition of lattice energy
- Born Haber cycle
- The applications of Born Haber cycle: determination of lattice energy
- Concept on solvation energy
- Fajan's Rule and it's applications
- Definition of dipole moment

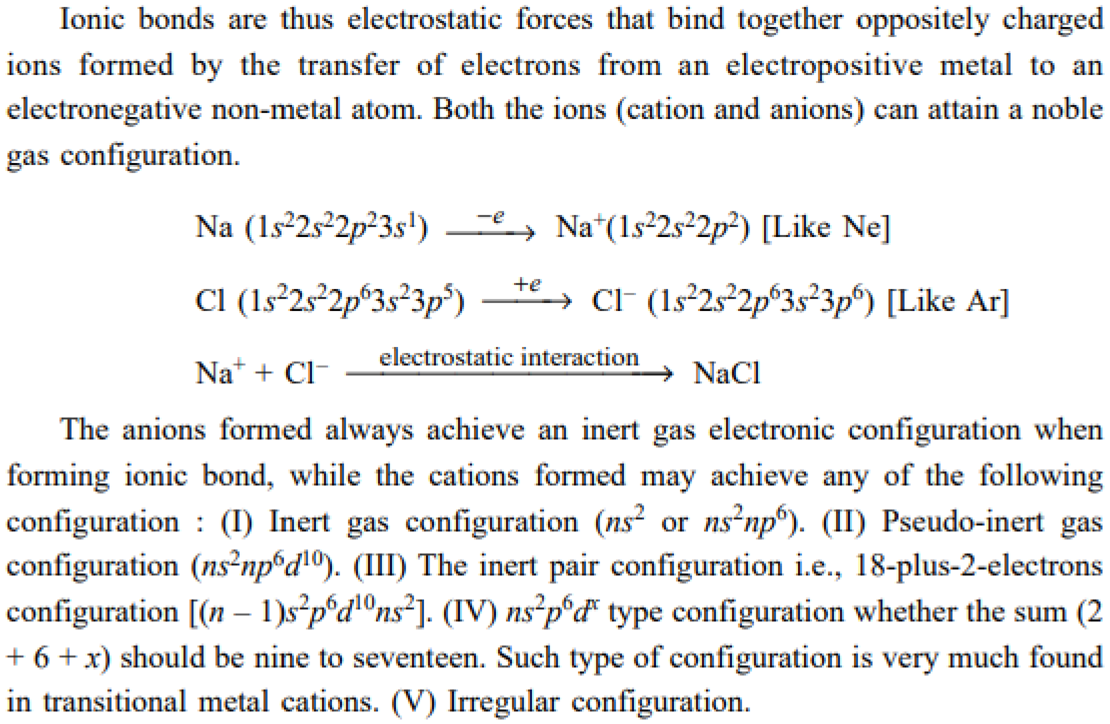
3.1 Introduction

Ionic bonding is a fundamental type of chemical bond that forms between atoms when electrons are transferred from one atom to another. This process results in the formation of positively charged cations and negatively charged anions, which are held together by electrostatic forces of attraction. Ionic bonds typically form between metals and non-metals, where metals lose electrons to become cations and non-metals gain those electrons to become anions. The general characteristics of ionic bonding include high melting and boiling points, electrical conductivity in molten or dissolved states, and the formation of crystalline lattice structures. The formation of ionic bonds involves several energy considerations. The process is driven by the lattice energy, which is the energy released when gaseous ions form a solid ionic compound, and the ionization energy, which is the energy required to remove an electron from an atom to form a cation. Additionally, the electron affinity, or the energy released when an electron is added to an atom to form an anion, plays a crucial role. The overall stability of an ionic compound is determined by the balance between these energy changes. The lattice energy of an ionic compound is the energy released when gaseous ions come together to form a solid lattice. The solvation energy is the energy change associated with the dissolution of an ionic compound in a solvent, such as water. The Born-Haber cycle is a thermochemical cycle used to determine the lattice energy of an ionic compound. It involves breaking down the formation process into a series of steps, including ionization, electron affinity, and lattice formation. By applying Hess's law, the lattice energy can be calculated using the enthalpy changes of these steps. This cycle is crucial for understanding the stability of ionic compounds and predicting their formation.

3.2 General characteristics of ionic bonding

According to Pauling a chemical bond existing between two atoms the binding forces between them, of such a strength that leads to an aggregate of sufficient stability, warranting their consideration as independent molecular species. The following types of bonding forces (in order decreasing strength) are convenient and sufficient to describe the chemical compounds-ionic, covalent and metallic, hydrogen bonds and Vander Waals forces.

3.2.1 Ionic Bond



Ionic bonds are thus electrostatic forces that bind together oppositely charged ions formed by the transfer of electrons from an electropositive metal to an electronegative non-metal atom. Both the ions (cation and anions) can attain a noble gas configuration.

$$\text{Na}\ (1s^2 2s^2 2p^2 3s^1) \xrightarrow{-e} \text{Na}^+(1s^2 2s^2 2p^2)\ [\text{Like Ne}]$$

$$\text{Cl}\ (1s^2 2s^2 2p^6 3s^2 3p^5) \xrightarrow{+e} \text{Cl}^-\ (1s^2 2s^2 2p^6 3s^2 3p^6)\ [\text{Like Ar}]$$

$$\text{Na}^+ + \text{Cl}^- \xrightarrow{\text{electrostatic interaction}} \text{NaCl}$$

The anions formed always achieve an inert gas electronic configuration when forming ionic bond, while the cations formed may achieve any of the following configuration : (I) Inert gas configuration (ns^2 or ns^2np^6). (II) Pseudo-inert gas configuration ($ns^2np^6d^{10}$). (III) The inert pair configuration i.e., 18-plus-2-electrons configuration [$(n-1)s^2p^6d^{10}ns^2$]. (IV) $ns^2p^6d^x$ type configuration whether the sum ($2 + 6 + x$) should be nine to seventeen. Such type of configuration is very much found in transitional metal cations. (V) Irregular configuration.

3.2.2 Conditions for formation of an ionic compound

1. Lower the charge on the cation i.e., lower is I.P., better is the chance that an ionic compound will formed.

2. Higher the size of cation lower is the I.P., better is the chance that an ionic compound will be formed.

3. Small size and low charge on the anion. i.e., higher electron affinity and electronegativity of an anion favors ionic compound.

3.2.3 Characteristic of ionic compound

1. The cations and anions in the compounds are held together by electrostatic lines of forces.
2. Since electrostatic forces of attraction are no directional i.e., extended in all directions. So "giant molecules" are formed. Ionic hands are non-directional.
3. Ionic compounds are hard, high m.p. and b.p.
4. Due to ionization ionic compounds conduct electricity in fused or in solution.
5. Due to ionization compounds are soluble in polar solvents.

3.3 Energy considerations in ionic bonding

Lattice Energy

The Lattice energy (U_0) is the amount of energy released in the formation of one mole of a solid crystal from the constituent free gaseous ions at infinite distance from one another.

$M^+ (g) + X^- (g) \longrightarrow MX (s) +$ Lattice energy (U_0)

Born-Lande Equation of Lattice Energy

$$U_0 = (-)\ \frac{N_A A Z_e^+ Z_e^-}{r_0}\left(1-\frac{1}{n}\right);\ \text{This is the Born-Lande Equation}$$

U_0 = Lattice energy; N_A = Avogardo No.; A = Madelung Constant; Z_e^+ = Point charge of cation; Z_e^- = Point charge of anion; n = Born exponent.

3.4 Lattice energy and solvation energy and their importance in the context of stability and solubility of ionic compounds

Lattice Energy:

- Definition: Lattice energy is the amount of energy released when gaseous ions come together to form a solid ionic lattice. It reflects the strength of the ionic bonds within the crystal structure of the compound.
- Importance:
  - Stability: High lattice energy indicates a strong attraction between the ions in the solid state, contributing to the stability of the ionic compound. A compound with high lattice energy is typically more stable and has a higher melting point.

  - Solubility: While high lattice energy generally makes a compound less soluble (because it requires more energy to break apart the lattice), the actual solubility also depends on the solvation energy.

Solvation Energy:

When one mole of cation or one mole of anion in the gaseous state reacts with a solvent in the liquid state, energy is liberated. This liberated energy is termed salvation energy. When the solvent concerned is water liberated energy is called hydration energy.

$$Z^{\pm x}\ (g) + H_2O\ (l) \longrightarrow Z^{\pm x}\ (aq) + \text{Hydration energy}$$

The hydration/solvation energy of anion is a function of $\frac{(Ze)^2}{r}$, where Ze is the charge and r is radius. Thus greater the charge on the ion and the lower the radius, the greater will be the amount of energy liberated. It can be stated that the greater the $\frac{e}{r}$ ratio (i.e., the charge density) of the ion the greater will be the amount of energy liberated. This explains why Li^+ has a higher hydration energy than either Na^+ or K^+. Again Mg^{2+} has higher hydration energy than Ba^{2+} or Li^+.

N.B. : Though both F^- and K^+ have same ionic radii, but hydration energy of $F^- > K^+$. This is deu to the cact of F^- interacts with the small hydrogen atom (with $\delta+$ charge) of H_2O while K^+ has to interacts with the much larger oxygen atom (with $\delta-$). So more hydrogen atoms can get around a F^- ion compared to oxygen atoms around the K^+ ion. Thus there is a scope of strong hydrogen bonding in the case of F^- but not in the case of K^+.

- **Importance:**
  - **Solubility:** High solvation energy favors the dissolution of an ionic compound. When the energy released upon solvation exceeds the lattice energy required to break the ionic bonds, the compound is more soluble in the solvent.
  - **Overall Stability in Solution:** The balance between lattice energy and solvation energy determines the compound's solubility. If the solvation energy is significantly high compared to the lattice energy, the compound is likely to dissolve readily.

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3.5 Born-Haber cycle and its applications

Experimental determination of lattice energy, The Born-Haber cycle:

Since direct experimental determination of lattice energies are not so easy. These are determined indirectly with the help of thermochemical cyclic process known as Born-Haber cycle. We illustrative this with NaCl. The various steps involved in the formation of NaCl (s) in crystalline state as follows:

- **Conversion of metallic Na into gaseous Na atoms:**

  The energy required for the conversion of 1 mole of metallic Na into gaseous Na atoms is called Heat of sublimation and represented by ‘‘S’’

  $$\text{Na (s)} + \text{S} \longrightarrow \text{Na (g)}$$

  1 mole heat of sublimation

- **Dissociation of gaseous Cl_2 molecules into gaseous Cl atoms:**

  This step involves the dissociation of gaseous Cl_2 molecules into gaseous Cl atoms. The amount of energy required to dissociate one mole of Cl_2 molecules into gaseous atoms is called dissociation energy and denoted by ‘‘D’’.

  $$Cl_2\text{ (g)} + \text{D} \longrightarrow 2Cl\text{ (g)}$$

  The energy required to produce one mole of gaseous Cl atoms would be D/2.

- **Conversion of gaseous Na atom into Na^+ ions:**

  The amount of energy required to convert one mole of gaseous state of ions is called ionization energy. This is represented by ‘I.E’

  Na (g) + I.E. ⟶ Na+ (g) + e^-

- **Conversion of gaseous Cl atom into Cl^- ion:**

  The amount of energy released when one mole of gaseous Cl atoms is converted into Cl– ions in the gaseous state is called electron affinity and donated by ‘‘E.A’’.

  $$\text{Cl (g)} + e– \longrightarrow Cl^-\text{ (g)} + \text{E.A}$$

☐**Combination of gaseous ions to form a solid crystal:**

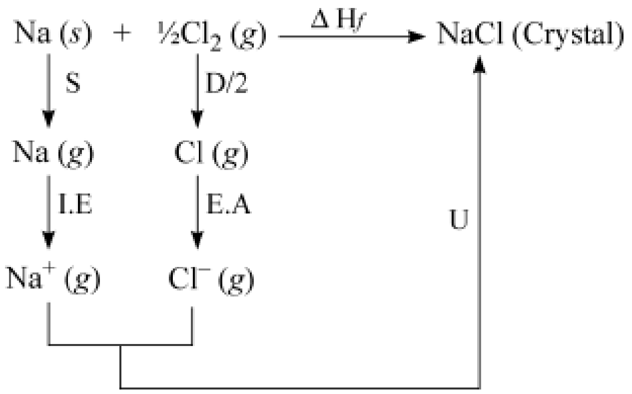
This step involves the combination of gaseous Na+ and Cl– ions to give one mole of NaCl crystal. The amount of energy released when 1 mole of solid crystalline compound is formed from gaseous ions of opposite charges is called lattice energy and is denoted by ‘‘U’’.

$$Na^+\text{ (g)} + Cl^-\text{ (g)} \longrightarrow \text{NaCl (s)} + \text{U}$$

The overall change may be represented as, Na (s) + 1 2 Cl_2 (g) ⟶ NaCl (s)

The enthalpy change for this reaction is called enthalpy of formation and denoted by ΔH_f.

The various steps may be represented in the form of Born-Haber cycle.



Born Haber Cycle for NaCl

According to Hess's law the enthalpy of formation of NaCl should be same irrespective of the fact whther it takes place directly in one steps or through a no of steps illustrated above.

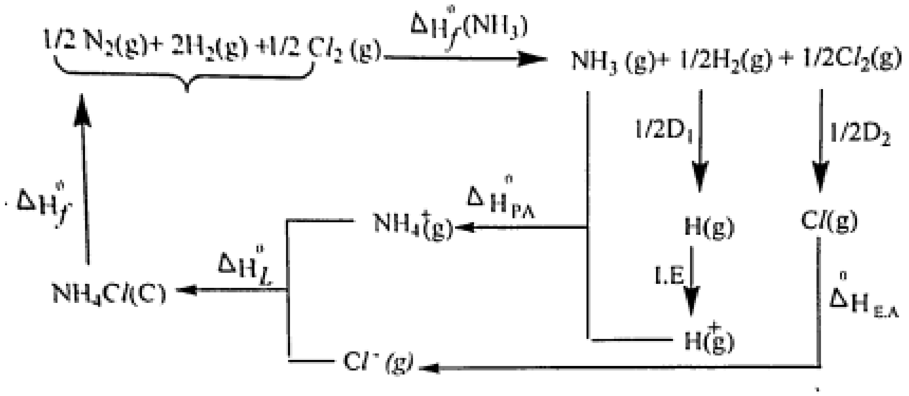
Hence, $\Delta H_f = S + \frac{D}{2} + I.E + E.A + U.$

Using (+ve) sign for energy absorbed and (–ve) sign for energy released we have for NaCl.

S = 108.5 kj mol^{-1}, D = 243.0 kj mol^{-1}, I.E = 495.2 kj mol^{-1}, E.A = –348.3 kj mol^{-1}, $\Delta H_f = -381.8$ kj mol^{-1}. Substituting the various values in the above equation. We get U = –758.7 kj.

Q 1. Draw Born Haber cycle of NH_4Cl.

Ans.



Born Haber cycle for NH_4Cl

$$-\Delta H_f^0(NH_4Cl) + \Delta H_f^0(NH_3) + \Delta H_{PA}^0 + 1/2D_1 + 1/2D_2 + I.E + \Delta H_{EA}^0 - \Delta H_L^0 = 0$$

Q 2. "MgO is a stable ionic solid though large amount of energy is required to form Mg to Mg^{2+} and to dissociate O_2 into atomic oxygen and thereafter to form O^{2+} ion"—account for the fact (2)

Ans. Born-Haber cycle is useful in analyzing and correcting the stability of various ionic compount. It explains why MgO is a stable ionic compount in spite of the fact that very large amount of energies are required to vaporize MgO to Mg^{2+} ion, to dissociate O_2 into atomic oxygen and finally to form O^{2+} ion. Both of these process are highly endothermic. The heat of formation for MgO is highly negative $[(\Delta H_{for})_{MgO} = -143.8$ kcal/mole] inspite of the unfavourable factors mentioned above. This high negative value is due to the very high lattice energy of MgO $[(U)_{MgO} = -935$kcal/mole] which is more than compensates the energy expenditure.

Q 3. Calculate the electron affinity of iodine with the help of following data (given kcal/mole) $(\Delta H_{for})_{NaI} = -68.8$, $(\Delta H_{sub})_{Na} = 25.9$, $\frac{1}{2}(\Delta Hdiss)I_2 = 25.5$, $(IP)_{Na} = 118.4$, $(U)_{NaI} = -165.4$

Ans. Put these values in the following equation :

$$(\Delta H_{for})_{NaI} = (\Delta H_{sub})_{Na} + \frac{1}{2}(\Delta Hdiss)I_2 + (IP)_{Na} + (EA)_{Na} + (EA)_I + (U)_{NaI}$$

$$\text{or, } -68.8 = 25.9 + 25.5 + 118.4 + (EA)_I + (-165.4)$$

$$\text{or, } (EA)_I = -68.8 - 25.9 - 25.5 - 118.4 + 165.4 = -73.2 \text{ kcal/mole}$$

Q 4. Write the uses of Born-Haber cycle.

Ans. Born-Haber cycel can be used in the following way

a. It can be used for the determination of electron affinities of elements which are difficult to determine by other methods.

b. It is useful in analyzing and correcting the stability of various ionic compound.

c. *It also helps to understand why most fail to form stable ionic compounds in low axidation states wuch as MnCl, CaCl AlO.* By comparing the Born-Haber cycle for MCl and MCl_2 (M = Ca, Mg) it can be shown that the formation of MCl_2 is favoured over that of MCl although the energy need for formation of M^+ (*g*) and Cl^- (*g*) ions is lower than that needed for the formation of M^{2+} (*g*) and $2Cl^{-1}$ (*g*) from M (*s*) and Cl_2 (*g*). The much higher lattice energy of MCl_2 over that of MCl more than balances the advantage which MCl has over MCl_2.

3.6 Polarizing power and polarizability

Polarizing Power

Polarizing power refers to the ability of an ion to distort the electron cloud of a nearby atom or molecule. This concept is crucial in understanding how ions interact with their surroundings, especially in ionic compounds.

- Factors Affecting Polarizing Power:

1. Charge of the Ion: Higher charges on an ion increase its polarizing power. For example, a Al^{3+} ion will have a greater polarizing power than a Na^{+} ion because the Al^{3+} ion has a higher charge density.
2. Size of the Ion: Smaller ions have greater polarizing power. A smaller ion with the same charge as a larger ion will have a higher charge density and thus a stronger ability to polarize nearby electron clouds.

Applications and Implications:

- Ionic Character: In ionic compounds, the degree of polarization affects the ionic character. Greater polarizing power leads to greater covalent character because the ion distorts the electron cloud of the anion more, leading to a more shared electron density rather than a purely ionic bond.
- Lattice Energy: The polarizing power of an ion can influence the lattice energy of ionic solids. Higher polarizing power generally leads to a higher lattice energy, which means more energy is required to break the ionic lattice.

Polarizability

Polarizability is the measure of how easily the electron cloud around an atom or molecule can be distorted by an external electric field. In essence, it indicates how flexible or easily deformable the electron cloud is.

- Factors Affecting Polarizability:
    1. Size of the Atom or Molecule: Larger atoms or molecules generally have more polarizable electron clouds because the electrons are further from the nucleus and less tightly held. For example, iodine is more polarizable than fluorine.
    2. Number of Electrons: More electrons in an atom or molecule generally lead to greater polarizability since there are more electrons that can be displaced.
    3. Nuclear Charge: Atoms with higher nuclear charges (more protons) generally have less polarizable electron clouds because the electrons are held more tightly. However, this effect is often outweighed by the size effect in larger atoms.

Applications and Implications:

- Intermolecular Forces: Polarizability influences the strength of London dispersion forces (or induced dipole forces). Larger and more polarizable molecules tend to have stronger dispersion forces.

- Chemical Reactivity: Polarizability can affect a molecule's reactivity. For example, molecules with high polarizability may be more easily polarized and can participate in more reactions where polarization plays a role.

3.7 Fajan’s rules

When a cation approaches an anion closely. The positive ion attracts the electrons on the negative ion and the same time it repels the nucleus. The combined effect of these two forces is that the electron cloud of the anion no longer remains symmetrical but is elongated towards the cation. This is called distortion, deformation i.e., polarization of the anion by cation and the anion is said to be polarized. (The negative ion will also polarize the positive ion, but since anions are usually large in size and cations are small in size the effect of a large ion on a small one will be much less pronounced.) If the degree of polarization is quite small, then the bond remains largely ionic. If the degree of polarization is large, electrons are drawn from negative ions towards the positive ion, resulting in high concentration of electron between two nuclei and a large degree of covalent character arises. Higher the polarization of anion higher the covalent character of covalent compound.

(a) No polarisation (b) Polarised anion

Factor effecting the polarization of an ion: Fajan’s Rule

1. Smaller the size of cation, higher the (+) ve charge density of cation, higher the polarization power of cation i.e., higher the probability of covalent character of compound. 2. Larger the size of anion, higher the polarizability of anion, i.e., higher the probability of covalent character of compound and lower the melting point of compound.

3. Larger charges on either ion, or both ions, favors covalence. With the increase of covalence i.e., the increase of polarization, solubility of the salt in polar solvent decreases 4. A cation with 18 electrons in its outermost shell (non -inert gas or pseudo inert gas configuration, $ns^2np^6d^{10}$) has greater polarizing power (due to low shielding effect of inner orbital) to polarize an anion than a cation with 8-electron in its outermost shell (inert gas configuration ns^2p^6), even if both the cations have the size and charge. (e.g. Na+ and Cu+). From Fajans Rule it is summarized that the molecule containing high positive charge on the cation, high negative charge on anion i.e., small cation or large anion are covalent in character. While those containing low positive on the cation, low negative charge on the anion and large cation or small anion show ionic character.

5. In case of noble gas type anions with electronic configuration (n – 1) s^2np^6 the polarising effect is insignificant as s- and p- electrons are tightly bound and not easily polarised (perturbed) by electrical field of the cation. Because of the increased no of d- and f- electrons in the descending a group (in 4d- series cations, there are ten d-electrons in excess compared to the corresponding congener cations in the 3d-series. In coming to the 5d-series, in addition to the ten 3d-electrons and ten 4d-electrons there are fourteen 4f-electrons which are still more ineffective in shielding) polarising power of the cations of transition series in the order 5d > 4d > 3d to the anion. In these transition metal compounds mutual polarisation (both cation and anions) favour covalency. Thus, the degree of covalency increase in descending a group (though the ionic radii of metal ion increase from 3d to 5d) in the transition metal ions for a particular oxidation state. i.e., covalency order $ZnCl_2 < CdCl_2 < HgCl_2$

3.8 Ionic character in covalent compounds, bond moment, dipole moment and percentage ionic character

Ionic Character in Covalent Compounds

Ionic character in covalent compounds refers to the extent to which a covalent bond exhibits properties typical of an ionic bond. Even though a bond is classified as covalent, it can have some degree of ionic character if the electrons in the bond are not shared equally between the two atoms.

- Electronegativity Difference: The ionic character of a covalent bond increases with the difference in electronegativity between the two bonded atoms. A greater difference means that one atom attracts the bonding electrons more strongly, resulting in a partial positive charge on one atom and a partial negative charge on the other, thus introducing ionic character into the covalent bond.
- Example: In the molecule hydrogen chloride (HCl), chlorine is much more electronegative than hydrogen. This causes the shared electrons to spend more time closer to the chlorine atom, giving it a partial negative charge ($\delta-$) and the hydrogen a partial positive charge ($\delta+$). Although HCl is primarily a covalent compound, the bond has ionic character due to this uneven distribution of electron density.

Bond Moment and Dipole Moment

Bond moment is a measure of the polarity of a bond within a molecule. It arises due to the difference in electronegativity between the two bonded atoms, causing a shift in electron density and resulting in a dipole moment.

- Dipole Moment: The dipole moment (μ) is a vector quantity that measures the overall polarity of a bond or a molecule. It is defined as the product of the charge difference and the distance between the charges:

  $$\mu = Q \times d$$

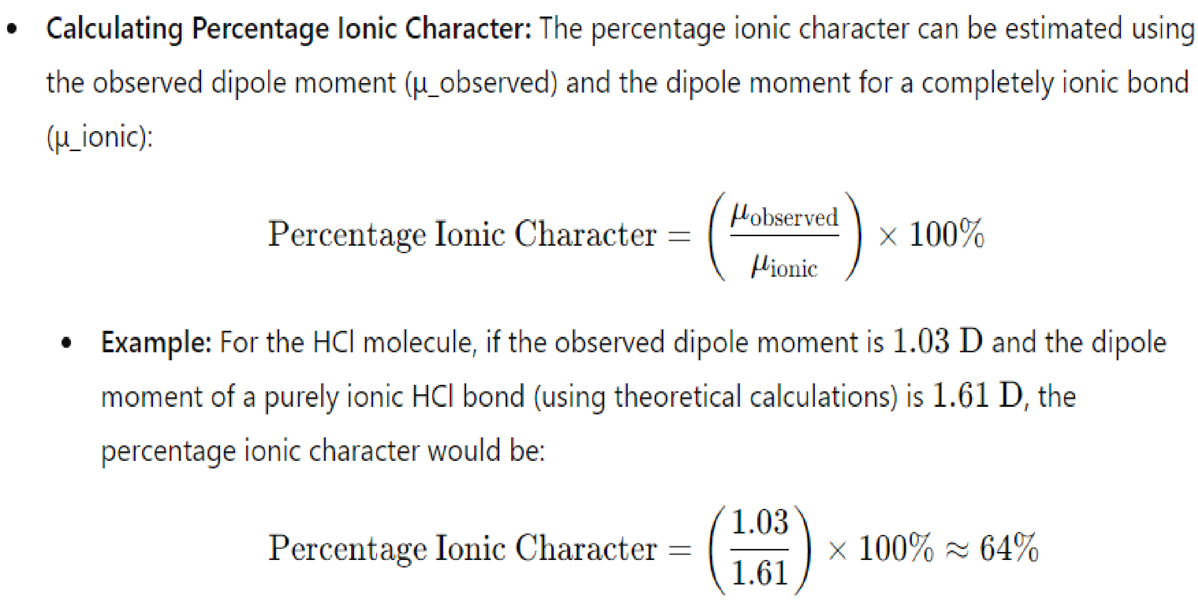
  where Q is the magnitude of the charge and d is the distance between the charges. The dipole moment is usually expressed in Debye units (D), where $1\ \text{D} = 3.336 - \times 10^{29}$ coulomb-meters.

  - Bond Dipole Moment: For a diatomic molecule, the dipole moment is simply the bond moment. For example, in HF, the dipole moment points from the hydrogen atom (partially positive) to the fluorine atom (partially negative).
  - Molecular Dipole Moment: For polyatomic molecules, the dipole moment is the vector sum of all individual bond dipole moments. It takes into account the shape of the molecule and the orientation of the dipoles.

Percentage Ionic Character

Percentage ionic character quantifies how much of an ionic nature a covalent bond possesses. It compares the actual dipole moment of a bond to the dipole moment it would have if the bond were purely ionic.

- Calculating Percentage Ionic Character: The percentage ionic character can be estimated using the observed dipole moment (μ-observed) and the dipole moment for a completely ionic bond (μ-ionic):



- **Calculating Percentage Ionic Character:** The percentage ionic character can be estimated using the observed dipole moment (μ_observed) and the dipole moment for a completely ionic bond (μ_ionic):

$$\text{Percentage Ionic Character} = \left(\frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}}\right) \times 100\%$$

  - **Example:** For the HCl molecule, if the observed dipole moment is $1.03\ \mathrm{D}$ and the dipole moment of a purely ionic HCl bond (using theoretical calculations) is $1.61\ \mathrm{D}$, the percentage ionic character would be:

$$\text{Percentage Ionic Character} = \left(\frac{1.03}{1.61}\right) \times 100\% \approx 64\%$$

3.9 Summary

General Characteristics of Ionic Bonding

1. Ionic Bond: An ionic bond is formed when atoms transfer electrons from one to another, creating positively charged cations and negatively charged anions. This electrostatic attraction between oppositely charged ions holds them together in an ionic compound.

2. Conditions for Formation of an Ionic Compound:

- High Electronegativity Difference: A significant difference in electronegativity between the two atoms involved is necessary. Typically, this occurs between metals (which lose electrons) and nonmetals (which gain electrons).
- Small Size of Cation and Large Size of Anion: A small cation with a high charge density and a large anion helps in stabilizing the ionic bond due to strong electrostatic interactions.

3. Characteristics of Ionic Compounds:

- High Melting and Boiling Points: Due to the strong electrostatic forces between ions.
- Solubility in Water: Many ionic compounds dissolve in water, where they dissociate into their constituent ions.
- Electrical Conductivity: In molten or aqueous form, ionic compounds conduct electricity due to the mobility of ions.
- Hard and Brittle: They are generally hard but can be brittle, as applying force can shift the ions, causing repulsive forces that lead to fracture.

Energy Considerations in Ionic Bonding

1. Lattice Energy: Lattice energy is the energy released when gaseous ions form a solid ionic lattice. It is crucial for the stability of the ionic compound. Higher lattice energy corresponds to a more stable ionic compound.

2. Solvation Energy: Solvation energy (or hydration energy) is the energy released when ions interact with a solvent, such as water. This energy helps to dissolve ionic compounds by stabilizing the ions in solution.

3. Importance:

- Stability: High lattice energy contributes to the stability of ionic compounds.
- Solubility: Solvation energy affects how well an ionic compound dissolves in a solvent. For a compound to dissolve, the solvation energy must be sufficiently high to overcome lattice energy.

Born-Haber Cycle and Its Applications

The Born-Haber cycle is a thermodynamic cycle used to analyze the energy changes involved in the formation of an ionic compound from its elements. It includes the following steps:

- Sublimation of the solid metal.
- Ionization of the metal atoms.
- Dissociation of nonmetal molecules (if applicable).
- Formation of anions.
- Formation of the ionic lattice.

Applications:

- Determining Lattice Energy: The cycle helps calculate lattice energy indirectly.
- Predicting Stability: It provides insights into the relative stability of different ionic compounds.

Polarizing Power and Polarizability

1. Polarizing Power: The ability of a cation to distort the electron cloud of an anion. It is higher for small, highly charged cations.

2. Polarizability: The ease with which an anion's electron cloud can be distorted by a cation. Larger anions with more electrons are generally more polarizable.

Fajan's Rules

Fajan's rules predict the degree of covalent character in an ionic bond based on:

- Charge Density of Cation: Higher charge density increases polarizing power.
- Size of Anion: Larger anions are more polarizable.
- Polarity: A greater difference in electronegativity and a higher charge on the cation enhance covalent character.

Ionic Character in Covalent Compounds

1. Bond Moment and Dipole Moment:

- Bond Moment: The dipole moment associated with a specific bond in a molecule.

- Dipole Moment: A measure of the overall polarity of a molecule or bond, reflecting the separation of charge.

2. Percentage Ionic Character: Indicates the extent to which a covalent bond exhibits ionic characteristics. Calculated by comparing the observed dipole moment with the dipole moment of a hypothetical purely ionic bond.

3.10 Sample questions

A. Multiple Choice Type Questions

1. **What is the primary characteristic of ionic bonding?**

   A) Sharing of electrons

   B) Transfer of electrons

   C) Formation of covalent bonds

   D) None of the above

   Answer: B) Transfer of electrons

2. **Which condition is necessary for the formation of an ionic compound?**

   A) Similar electronegativities

   B) Large difference in electronegativities

   C) Low ionization energy

   D) High lattice energy

   Answer: B) Large difference in electronegativities

3. **Which of the following is a characteristic of ionic compounds?**

   A) Low melting and boiling points

   B) Good electrical conductors in solid state

   C) High solubility in water

   D) All of the above

   Answer: C) High solubility in water

4. **What is lattice energy?**

   A) Energy required to vaporize an ionic compound

   B) Energy released when ions are combined to form a solid

   C) Energy associated with ionization

   D) Energy needed to break a covalent bond

   Answer: B) Energy released when ions are combined to form a solid

5. **In the context of ionic compounds, solvation energy refers to:**

   A) Energy released when ionic compounds dissolve in water

   B) Energy required to remove an electron from an ion

C) Energy needed to create an ionic bond

D) None of the above

Answer: A) Energy released when ionic compounds dissolve in water

6. **The Born-Haber cycle is primarily used to calculate:**

   A) Lattice energy

   B) Ionization energy

   C) Atomic radius

   D) Electronegativity

   Answer: A) Lattice energy

7. **Fajan's rules indicate that ionic character increases when:**

   A) The cation is large and the anion is small

   B) The cation has a high charge and the anion is highly polarizable

   C) Both ions are nonpolar

   D) There is no charge on the ions

   Answer: B) The cation has a high charge and the anion is highly polarizable

8. **What does the dipole moment of a bond indicate?**

   A) The bond length

   B) The degree of ionic character

   C) The energy of the bond

   D) The type of bond (ionic or covalent)

   Answer: B) The degree of ionic character

9. **Which of the following factors affects the polarizing power of a cation?**

   A) Size and charge of the cation

   B) Size of the anion only

   C) Molecular weight of the compound

   D) Temperature of the solution

   Answer: A) Size and charge of the cation

10. **Which statement best describes percentage ionic character in a covalent bond?**

    A) It is always zero

    B) It indicates the degree to which a bond exhibits ionic characteristics

    C) It is equal to the bond length

    D) It does not affect bond strength

    Answer: B) It indicates the degree to which a bond exhibits ionic characteristics

B. Short Type Questions

Q 1. Why covalent character of anhydrous chloride of Cu^+, Ag^+, Au^+ is higher than anhydrous chloride of Na^+, K^+, Rb^+.

Ans. Cu^+ cation has outer most electronic configuration $3s^2p^6d^{10}$. The ten *d*-electrons of the shell shield the nuclear charge of the cation less effectively than *s* and *p*- shell electrons. Thus in anhydrous chloride Cu^+ has greater polarizing power to polarize Cl^- anion. In case of NaCl, Na^+ has outer most electronic configuration $2s^22p^6$, there is no *d*-electron. As shielding constant of inner *s* orbital >> inner *d* orbital, so Cu^+ ion polarize Cl^- ion more than Na^+ ion, though both the cations have the same charge and size. So covalent character of Cu^+ ion chloride is higher than Na^+ ion chloride.

Q 2. Why m.p order of $NaCl > MgCl_2 > AlCl_3 > SiCl_4$ Explain?

Ans. In above metalic chlorides the metals are present in the following oxidation states Na^{+1}, Mg^{+2}, Al^{+3}, Si^{+4}. Radius of the cations in the order $r_{Na}{}^{+1} > r_{Mg}{}^{+2} > r_{Al}{}^{+3} > r_{Si}{}^{+4}$. i.e., charge density $\left(\frac{e}{r}\right)$ of the cations in the order $Si^{+4} > Al^{+3} > Mg^{+2} > Na^{+1}$. Due to higher charge density of the Si^{+4} ions it has greater polorizing power to polorize Cl^- anion than other metal ions. So $SiCl_4$ shows higher covalent character and less ionic character i.e., its m.p. becomes lower. As charge density of the ion is in the order $Si^{+4} > Al^{+3} > Mg^{+2} > Na^{+1}$ so polorising power of the ions is in the same order i.e., covalent character of the compounds decreases in the same order and ionic character increases from $SiCl_4$ to NaCl. As a result NaCl has higher ionic character and m.p. is is higher.

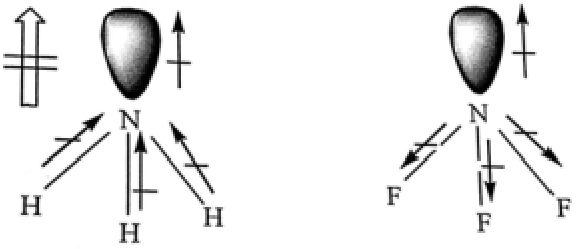
Q 3. Explain why LiCl is soluble in alchol as well as in pyridine, other alkali metal chlorides are insoluble.

Hints : Li is smaller in size. High charge density $\left(\frac{e}{r}\right)$, high polorising power, shows covalent character in nature. LiCl is souble in alcohol and pyridine (covalent). As charge density is higher, other alkalimetal chlorides are ionic in nature, other alkalimetal chlorides are insoluble in covalent solvents.

Q. 4 Arrange the following bonds in an expected order of increasing ionic character: B – O, Cl – O, F – O, N – O

Ans. According to Hannay-Smith equation % of ionic character of A–B bond = $16(\chi A - \chi B) + 3.5(\chi A - \chi B)$ 2 In the above case $\Delta\chi = \chi O - \chi B$ becomes higher among them. So % of ionic character of B—O bond becomes higher. Others have same $\Delta\chi$ value. Again, higher the μ(obs) of bond (A—B) higher its % of ionic character. Bond distance order Cl—O > N—O > F—O so dipole moment order is the same i.e., ionic character order in the same. i.e., ionic character order B—O > Cl—O > N—O > F—O.

Q.5 Why magnitude of dipole moment of NH_3 is higher than dipole moment of NF_3?



The electrogenativity difference between nitrogen and fluorine is almost the same as that between nitrogen and hydrogen. But in NH_3 the bond polarity is such that nitrogen is negative and hydrogen is (+ve) while in NF_3. Fluorines are negative but nitrogen is (+ve). The direction of bond polarity in N—F bond is opposite to that in N—H but in both cases the contribution of the lone pairs is in the same direction. So in NF_3 the bond polarity of N—F is opposite direction to bond polarity of *lpe* of N. So bond polarity is reduced. But in NH_3 the two type bond polarity direction is in a same direction. So the resultant dipole moment increases.

Try yourselves:

1. Explain why $FeCl_3$ is soluble in ether but $AlCl_3$ is not?

2. Explain why $ZnCl_2$ is more volatile than $MgCl_2$ and more soluble in organic solvents due to increased covalence?

3. KI is soluble in alcohol (covalent) but KCl is insoluble?

4. M.P. order of NaF > NaCl > NaBr > NaI

5. M.P. order of CF_4 (–183.7°C) < CCl_4 (–22.9°C) < CBr_4 (90°C) < Cl_4(171°C)

Hints: Here C in +4 oxidation state, the charge on the cation is large and as a consequence low melting covalent compounds are formed. For predominantly covalent compounds the m.p. and b.p. are roughly function s of their molecular weight.

C. Assay Type Questions

1. Explain the formation of ionic bonds, focusing on the transfer of electrons from one atom to another. Include the role of electronegativity in the formation of ionic compounds and provide examples of common ionic compounds.

2. Describe the key factors that contribute to the formation of ionic compounds. Discuss the importance of ionization energy, electron affinity, and the role of the octet rule in this process.
3. Explore the physical and chemical properties of ionic compounds, including their melting and boiling points, solubility in water, electrical conductivity, and crystalline structure. Provide specific examples to illustrate these characteristics.
4. Discuss the concepts of lattice energy and solvation energy, explaining how these energies affect the stability and solubility of ionic compounds. Include a discussion on how energy changes during the formation and dissolution of ionic compounds.
5. Outline the steps involved in the Born-Haber cycle and describe how it can be used to calculate lattice energy. Discuss the importance of this cycle in predicting the stability of ionic compounds and its applications in real-world scenarios.
6. Define polarizing power and polarizability, explaining their significance in the context of ionic bonding. Discuss how these properties influence the ionic character of compounds and the stability of ionic versus covalent bonds.
7. Explain Fajan's rules and how they relate to the polarizing power of cations and the polarizability of anions. Discuss how these rules help in predicting the ionic character of a compound and provide examples to support your explanation.
8. Analyze how ionic character can be present in covalent bonds, focusing on concepts such as bond moment, dipole moment, and percentage ionic character. Discuss how these factors can affect the properties of covalent compounds and their behavior in different environments.
9. Discuss how lattice energy influences the solubility of ionic compounds in various solvents. Include a discussion on how the balance between lattice energy and solvation energy determines whether an ionic compound will dissolve in a given solvent.
10. Discuss how ionic bonding contributes to the unique physical properties of ionic compounds. Include considerations of melting points, boiling points, hardness, and electrical conductivity, comparing these properties to those of covalent compounds.

3.11 References

1. Das, A. K. *Textbook of Inorganic Chemistry*.
2. Das, A. K. *Concepts of Inorganic Chemistry*
3. Das, A. K. *Materials Chemistry*. Publisher.

4. Das, A. K. *Chemistry of Transition Elements*. Publisher.

5. Inorganic Chemistry by R.L. Dutta

6. Essentials of Physical Chemistry by B.S. Bahl

7. Concise Inorganic Chemistry (4th Edition) by J.D. Lee

8. General and Inorganic Chemistry by P.K. Dutta

9. General and Inorganic Chemistry by R. Sarkar

Unit - 4 ❑ Covalent bonding

Structure

4.0 Objectives

1. **Understand Molecular Geometry**: Describe the molecular shapes of inorganic molecules and ions using VSEPR theory, identifying key factors that influence shapes such as electron pair repulsion.
2. **Explore Hybridization**: Explain the concept of hybridization and its role in determining molecular geometry.
3. **Analyze Coordination Geometries**: Examine the geometries of various coordination compounds. Discuss how hybridization influences these shapes.
4. **Evaluate Resonance Concepts**: Define resonance and its significance in stabilizing molecules
5. **Compare Resonating Structures**: Identify and compare different resonating structures.
6. **Application of VSEPR and Hybridization**: Apply VSEPR theory and hybridization concepts to predict the shape and bonding properties of complex molecules.

4.1Introduction

The Valence Bond (VB) approach is a foundational concept in chemistry that helps explain the shapes and bonding characteristics of molecules through two key principles: VSEPR (Valence Shell Electron Pair Repulsion) theory and hybridization. VSEPR theory postulates that the geometric arrangement of electron pairs around a central atom minimizes repulsion, leading to distinct molecular shapes, such as linear, trigonal planar, tetrahedral, square planar, and octahedral arrangements. Hybridization, on the other hand, describes the mixing of atomic orbitals to form new, hybrid orbitals that facilitate bonding.

Additionally, the concept of resonance is vital in understanding the stability and reactivity of both inorganic and organic compounds. Resonance explains how certain molecules can be represented by multiple structures, reflecting the delocalization of electrons and providing insight into molecular stability. By exploring these concepts, students can gain a deeper understanding of molecular geometry, bonding, and the behavior of a wide range of compounds in chemistry.

4.2 VB Approach

This theory leads to idea of bond formation through spin pairing of electrons between the participating atoms. A σ-bond may also be formed by overlap of other orbitals in proper orientation. A σ-bond always possesses an axis of symmetry along the internuclear axis. When the orbital overlap occurs in perpendicular to the internuclear axis, this forms π-bond. The main point of valence bond approach is as following:

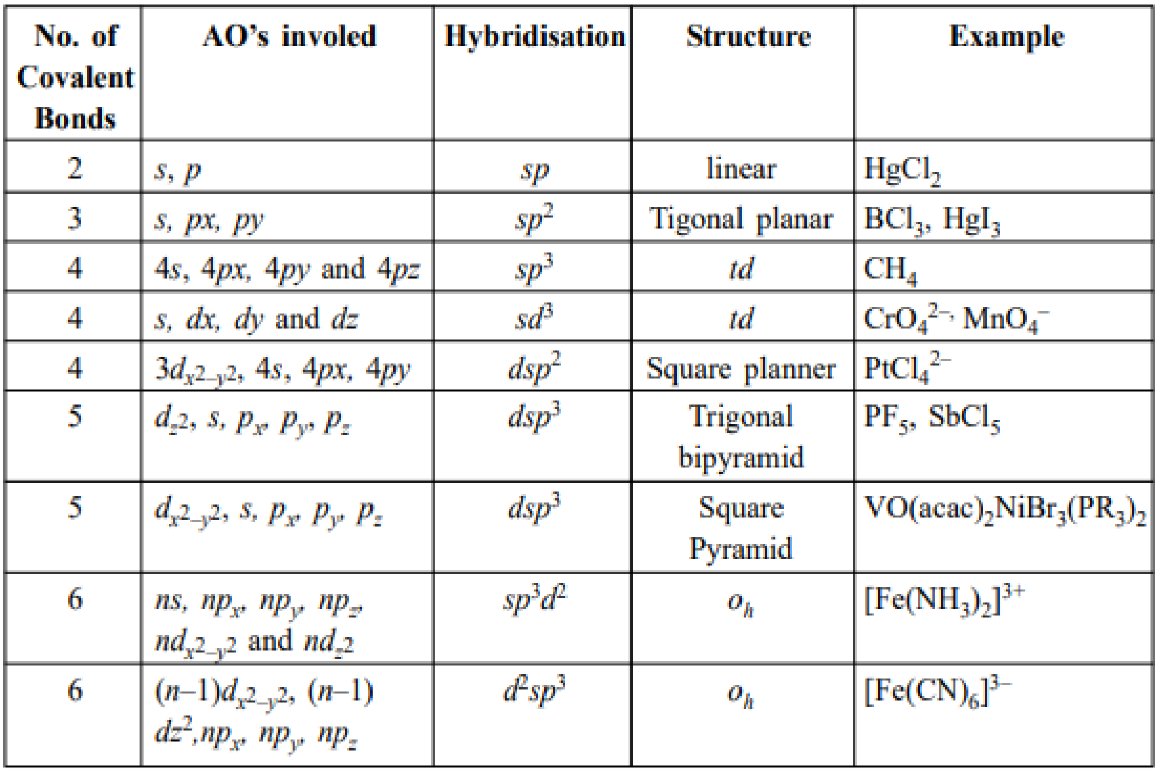
a. Atoms retain their individuality in the molecule

b. The bond is formed due to the interaction of valence electrons as the atoms approach each other i.e., the inner atomic orbits from each other forming the bond are undisturbed.

c. When they form a bond, only valence electrons from each bonded atom lose their identity

d. The stability of the bond is explained by the fact that electrons forming the bond between two atoms undergo exchange between them.

e. Important types of hybridization on metal ion of metal complexes are shown below



No. of Covalent Bonds	AO's involed	Hybridisation	Structure	Example
2	s, p	sp	linear	$HgCl_2$
3	s, px, py	sp^2	Tigonal planar	BCl_3, HgI_3
4	$4s, 4px, 4py$ and $4pz$	sp^3	td	CH_4
4	s, dx, dy and dz	sd^3	td	CrO_4^{2-}, MnO_4^-
4	$3d_{x^2-y^2}, 4s, 4px, 4py$	dsp^2	Square planner	$PtCl_4^{2-}$
5	$d_{z^2}, s, p_x, p_y, p_z$	dsp^3	Trigonal bipyramid	PF_5, $SbCl_5$
5	$d_{x^2-y^2}, s, p_x, p_y, p_z$	dsp^3	Square Pyramid	$VO(acac)_2NiBr_3(PR_3)_2$
6	ns, np_x, np_y, np_z, $nd_{x^2-y^2}$ and nd_{z^2}	sp^3d^2	o_h	$[Fe(NH_3)_2]^{3+}$
6	$(n-1)d_{x^2-y^2}, (n-1)$ dz^2, np_x, np_y, np_z	d^2sp^3	o_h	$[Fe(CN)_6]^{3-}$

4.2.1 Major points regarding VB

a. VBT cannot predict distortion of Oh complex of Cu (II) i.e., d^9 system and Ti (III) i.e., d^1 system.

b. VBT neglects the excited state complexes and hence no thermodynamics properties can be predicted.

c. VBT cannot explain spectra (colours) of the complexes.

d. VBT cannot explain in details about the magnetic properties of the complexes.

4.3 Shapes of some inorganic molecules and ions on the basis of VSEPR and hybridization with suitable examples of linear, trigonal planar, square planar, tetrahedral, and octahedral arrangements.

[1940 Sidgwick and Powell reviewed the shape of molecules later in 1957 Gillepspic and Nyholm improve this theory, explain molecular shape and bonding]

In all chemical combinations there occurs an interaction between outer orbital electrons of the reactants. The electrons belonging to the outermost quantum shell of the central reactant atom plus the additional electrons acquired as a result of bonding are called valence shell electrons. The main point of Valence shell electrons pair repulsion (V-S-E-P-R) approach is as following:

1. To know the central atom of a covalent molecule or ion and also to know no of valence electron on the central atom.

2. Each atom bonded through single bond (with central atom) will contribute one electron to the central. However double atom or triple bonded atom will not contribute any electron to the central atom.

3. Count the total “electron” of the valency shell (valence electron of central atom plus electron coming from another atom due to sigma bonding) and hence obtain no of electron pair (e.p) from which shape can be predicted. i. If e.p is 2, shape is linear, bond angle 180° ii. If e.p is 3, shape is plane triangle, bond angle 120° iii. If e.p is 4, shape is tetrahedral, bond angle 109°28′ iv. If e.p is 5, shape is trigonal by pyramidal bond angle 90° and 120° v. If e.p is 6, shape is octahedral, bond angle 90° vi. If e.p is 7, shape pentagonal bipyramid, XeF_6, XeF_5. vii. If e.p is 8, shape is square antiprism.

4. Each single bond is consisting of bond pair (bp). No. of lone pair of electrons (lp) = ep – pb. 5. Order of different repulsion is lp—lp > lp—bp > bp—bp. It is due to this repulsion covalent molecule may be distorted.

6. Shorter bond length makes the bp – bp repulsion more serve for widen the bond angle. If A—X > A—Y then bond angle of X—A—X < Y—A—Y. More steric crowding widens the bond angle more (ef. PBr_3 vs PCl_3)

7. For AB_x molecule with increasing electronegativity of B the average position of the bonding pair moves farther from the central element A. Therefore, the repulsive effect of the bonding pair on the electron pairs on A decreases with increasing electronegativity of B. Thus, the B—A—B bond angle decreases with increasingelectronegativity of B. Decreasing size of the B (of the same group) will also have the same effect. Such as bond angle order.

F—O—F (103°) < H—O—H (104.5°) < Cl—O—Cl (111°)

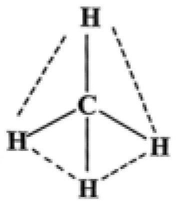
8. Space occupation of double bonded electron pair is equivalent to lp electron. Multiple bonds fatter and exert greater repulsive effect on other orbitals than is shown by single bonds. As a result, the angle between multiple bond and other single bonds in molecule will be greater than the angle between two single bonds of the molecule. Multiple bonds (i.e. pi bonds) do not grossly affect the stereochemistry or shape of a molecule. 9. Real structure will have minimum repulsion; for TBP geometry first considers repulsion at shortest angle obtain str with min repulsion. If problem is not solved, then consider repulsion at next higher angle.

N.B. With the help of VSEPR str of a covalent molecule or ion can be established and also it is possible to predict if there will be any distortion or not. For this theory assumes that the inner shells of electrons are spherical and have no influence on the geometry of valance shell electron pairs and this is valid for main group chemistry and is not useful to transition metal complexes.

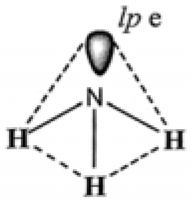
- **Give the shapes of the following form VSEPR CH_4, NH_3, H_2O, SF_4, BrF_3, ICl_2, ICl_4, CO_2, SO_2, COF_2, SOF_4, $PO4^{3-}$, XeF_2, XeF_4, XeF_6, $XeOF_4$, XeO_3**

- **CH_4 :** Here central atom is C having four electrons in its valence shell. Each H is connected with carbon through single bond. So each H will comtribute one electron to the valence shell of carbon. Total electrons in the valence shell of carbon C = 4 + 4 = 8, *ep* = 8/2 = 4, as *ep* = 4, so shape of CH_4 is tetrahedral (*td*). *bp* = 4, *lp* = 4 – 4 = 0.

  There is no distortion in the molecule and so H—C—H = 109°28′



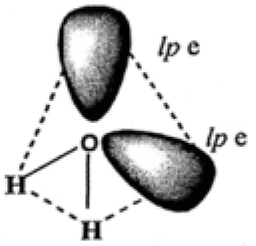
- **NH_3 :** N = 5 + 3 = 8, *ep* = 8/2 = 4, *bp* = 3, *lp* = 4 – 3 = 1, As *ep* = 4, str is *id* in which three corners are occupied by three H and 4th corner by " *lpe*". This str can also represented as *ψ-td*, the actual shape is trigonal pyramid and *lpe* protrusion from top of the pyramid. So the shape of NH_3 is pyramidal.



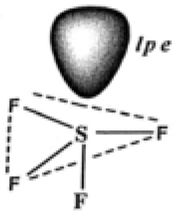
  lp-bp repulsion > *bp-bp* repulsion, so molecule will be distorted and H–N–H < 109°28′

- **H_2O :** O = 6 + 2 = 8, *ep* = 4, *bp* = 2, *lp* = 2. As *ep* = 4, so str is *td,* two corners are occupied by two H and other two corners are occupied by *lp* electron. So shape can be represented as V shaped.

  H_2O is angular molecule as *lp–lp* repulsion is greater than *lp–bp* repulsion. So molecule is distorted and H–O–H less than 109°28′ (actually this bond angle is lower than the bond angle in NH_3 as only one *lpe* is present).

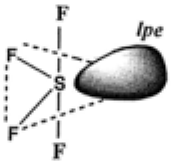


- **SF_4 :** S = 6 + 4 = 10, *ep* = 5, *bp* = 4, *lp* = 5 – 4 = 1. Since *ep* = 5, so shape is *tbp*. Now possible arrangement of *lp* and *bp* in *tbp* geometry are shown together with number of different repulsion at shortest angle 90°.



Shape-I

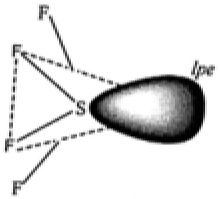
No. of *lp–lp* repulsion = 0
No. of *lp–bp* repulsion = 3
No. of *bp–bp* repulsion = 3



Shape-II

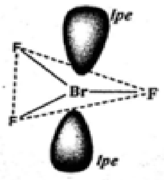
No. of *lp–lp* repulsion = 0
No. of *lp–bp* repulsion = 2
No. of *bp–bp* repulsion = 0

Due to min repulsion shape II is correct. due to *lp–bp* repulsion > *bp–bp* repulsion, so F(a)–S–F(a) < 180°. SF_4 is distorted *tbp* shape can be represented as



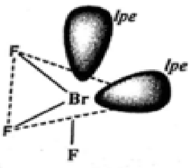
Actually this shape is *ψ-tbp*.

- **BrF_3 : Br** = 7 + 3 = 10, *ep* =5, *bp* = 3, *lp* = 2, shape is *tbp*. Now possible arrangement of *bp* and *lp* are shown below with no of different repulsion at shortest angle 90°.



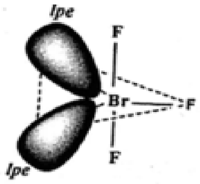
Shape-I

No. of *lp–lp* repulsion = 0
No. of *lp–bp* repulsion = 6
No. of *bp–bp* repulsion = 0



Shape-II

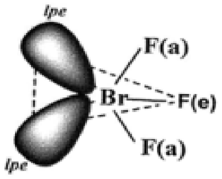
No. of *lp–lp* repulsion = 1
No. of *lp–bp* repulsion = 3
No. of *bp–bp* repulsion = 2



Shape-III

No. of *lp–lp* repulsion = 0
No. of *lp–bp* repulsion = 4
No. of *bp–bp* repulsion = 2

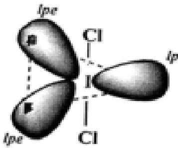
Now due to min repulsion Shape III is correct. The molecule will be distorted having T shape.



$F(a)\text{-}\hat{Br}\text{-}F(e) < 90$

$F(a)\text{-}\hat{Br}\text{-}F(a) < 180$

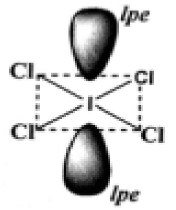
- **ICl_2 : I** = 7 + 2 + 1 = 10, *ep* = 5, *bp* = 2, *lp* = 3. Str is *tbp*. For min repulsion three *lp* electron will be present at equatorial position and so shape of ICl_2 is linear without any distribution.



$Cl\text{-}\hat{I}\text{-}Cl = 180$

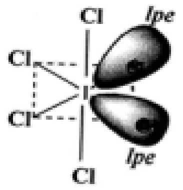
lp–lp repulsion = 0, *lp–lp* = repulsion = 6, *bp–bp* repulsion = 0

- **ICl_4^- : I** = 7 + 4 + 1 = 12, *ep* = 6, *bp* = 4, *lp* = 6 – 4 = 2 str is octahedral (Oh). Possible arrangement of *lp* and *bp* are shown below with different repulsion at 90°.



Shape-I

No. of *lp–lp* repulsion = 0
No. of *lp–bp* repulsion = 8
No. of *bp–bp* repulsion = 0



Shape-II

No. of *lp–lp* repulsion = 1
No. of *lp–bp* repulsion = 4
No. of *bp–bp* repulsion = 4

Due to min repulsion shape I is correct and this is square planer in shape without any distortion.

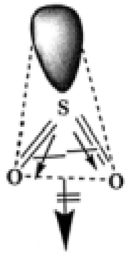
[**N.B.** In a sigma bond the electron density is concentrated in between the two atoms and on a line joining the two atoms. Double and triple bond occur by sidewise overlap of orbitals, giving *pi* bonds. The shape of molecules is determined by the sigma bond (and lone pairs) but not by the *pi* bond. *pi* bonds merely shorten the bond lengths. In CO_2, C is tetra valent, O is divalent. We do not calculate the O contribution in CO_2]

- **CO_2 :** C = 4 + 0 = 4, *ep* = 2, Shape is linear.

$$O \overset{\leftarrow\!+}{=} C \overset{+\!\rightarrow}{=} O$$

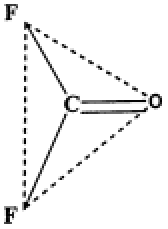
Due to higher E.N of O than C each C–O has bond polarity (→). Now two such equal bond polarities are acting in opposite direction and so there will be no resultant polarity. So CO_2 is non polar molecule.

- **SO_2 :** S = 6 + 0 = 6, *ep* = 3, shape is plane triangle. Two corners will be occupied by two oxygen and third corner by "*lp e*"

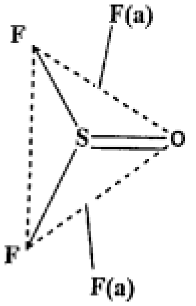


Due to difference in E.N each S–O bond has bond polarity (→). Now due to angular shape of molecule there will be resultent polarity (→) of the molecule so SO_2 is polar molecule.

- **COF_2 :** C = 4 + 0 + 2 = 6, *ep* = 3. Shape is triangular planar. Since double bonded electron pair is equvalent to '*lp*' electron so repulsion between double bonded electron pair and *bp* (single bonded eletron pair) > *bp–bp* repulsion. So the molecule will be distorted with F–C–F < 120° and F–C–O > 120°



- **SOF_4 :** S = 6 + 0 + 4 = 10, *ep* = 5, shape is of *tbp* geometry. Four corners will be occupied by four F and fifth corner will be occupied by double bonded oxygen.



$F(a) - \hat{S} - O > 90$

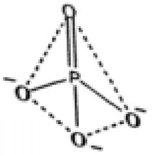
$F(a) - \hat{S} - F > 180$

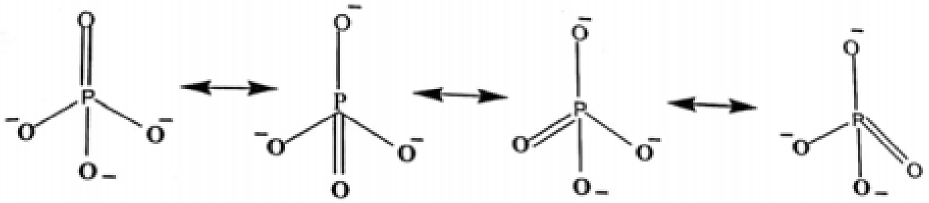
$F(e) - \hat{S} - F(e) < 120$

$F(a) - \hat{S} - O > 120$

- **PO_4^{3-} :** P = 5 + 0 + 3 = 8, *ep* = 4. Shape is *td*

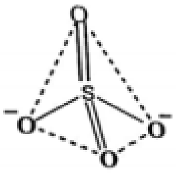
  PO_4^{3-} ion has undistorted tetrahedral shape due to resonance hybrid str of PO_4^{3-} due to resonance hybrid shape of PO_4^{3-}

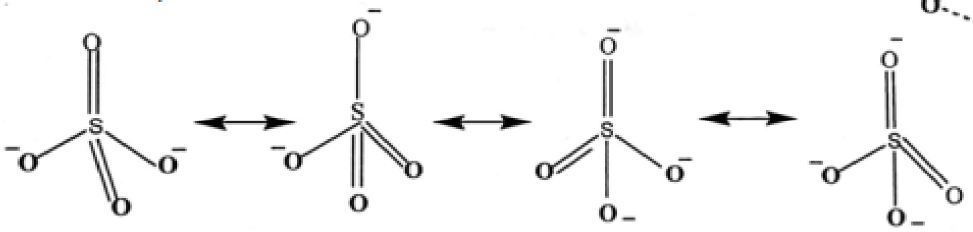




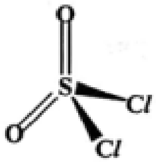
- **SO_4^{2-} :** S = 6 + 2 = 0 = 8, *ep* = 4, shape is *td*

  The SO_4^{2-} ion has undistorted *td* shape due to resonance hybrid str of SO_4^{2-}



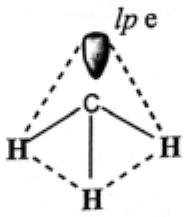


- **SO_2Cl_2 :** S = 6 + 0 + 2 = 8 *ep* = 4, *bp* = 4, *lp* = 0 shape is *td*.

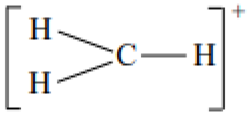


- **Methyl carbanion (CH_3) :** C = 4 + 3 + 1 8, *ep* = 8/2 = 4, *bp* = 3, *lp* = 1

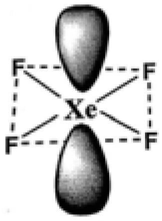
  The shape is *td* in which three corners are occupied by three H and 4th corner by "*lp e*". This shape can also represented as *ψ-td*, the actual shape is trigonal pyramid and *lpe* protrusion from top of the pyramid. So the shape of CH_3 is pyramidal.



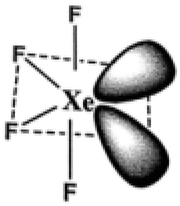
- **Methyl carbocation ($^{+}CH_3$)/($(CH_3)_3C^{+}$) :** C = 4 + 3 – 1 = 6, *ep* = 3, *bp* = 3, *lp* = 0 shape is plane triangle.



- **XeF_4 :** Xe = 8 + 4 = 12, *ep* = 6, Shape is *octahedral. bp* = 4, *lp* = 6 – 4 = 2. For minimum repulsion two *lp e* will be at trans position and actual shape will be square planer.



I



II

In XeF_4 shape II is more favourable than shape I, but practically shape I is stable as two lone pair electrons present in trans direction and it leading to a planer geometry. In shape II, two "*lpe*" present in neighbouring position in the plane. So some extent *lp–lp* repulsion occurs in shape II. So it is unstable in nature. The preferable shape of XeF_4 is I.

N.B. : *same matters happen in case of* ICL_4^{-}, BrF_4^{-}.

N.B. : *In tbp geometry whatever may be the no. of lpe, they will be present at equatorial position only.*

Limitation of VSEPR theory

a. The effect of the stereochemcially inactive lone pairs cannot be predicted (e.g. TeX_6^{-2}, X = Cl, Br) b. The theory does not work for the transition metal compounds where the crystal field stabilization energy (CFSE) plays an important role to determine the shape.

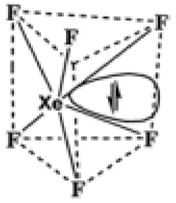
c. A large deviation in bond angle as in case like PH_3 compared to NH_3, H_2S compared to H_2O etc can be explained better in terms of cost of Hybridization.

d. It cannot yield any quantitative result. e. The system having extensively delocalized π electron cloud cannot be tackled well in the light of VSEPR theory.

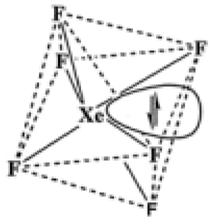
☐ One of the example of limitation of VSEPR theory XeF_6

XeF_6 : Xe = 8 + 6 = 14, *ep* = 7, *bp* = 6, *lp* = 1. Str should be distorted pentagonal bipyramid through sp^3d^3 hybridization. But in fact the problem is very much complicated. The str of XeF_6 depends on the sample phase. In solid state it exists as terameric and trimeric rings of $XeF_5^+F^-$ ion pairs XeF_5^+ having five bond pairs and one stereochemically active lone pairs bears a distorted *Oh* geometry. i.e., square pyramid as expected from VSEPR theory.

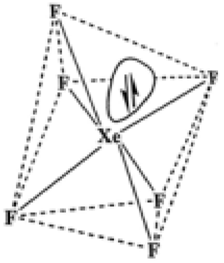
In vapour phase, it exists as a monomer, XeF_6 with a stereochemically active lone pair, it has got three possibility i.e., (**1**) 1, 4 2 capped trigonal prism (**2**) pentagonal bi pyramid (**3**) 1, 3, 3 capped Oh. Thus in no way it can have a regular goemetry.



(1, 4, 2 capped triognal prism)



(pentagonal bipyramid)



1, 3, 3 capped Oh)

3, 3 capped Oh. Thus in no way it can have a regular geometry.

Prediction of the simple molecular orbital theory involving 3c-4e MOS it is suggested that it to have a regular Oh geometry. Thus the problem is not settled theoretically. Experimentally, the molecule is found to be dynamic to fluctuate with the time this leads to intramolecular rearrangement of the fluorine positions. Thus this shows a fluxional behaviour i.e., stereochemically non rigidity.

☐ The bond angle in H_2O is 104.5° and that in H_2S is 92.2°—explain

In case of H_2O, Oxygen is 2nd period element. According to VSEPR *lp–lp* > *lp–bp* > *bp–bp* repulsion. So the normal bond angle of 109°28′ decreases to 104.5°.

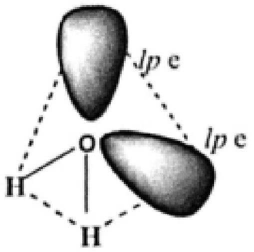
But in H_2S, S is a 3rd period element. Electronegativity of O is greater than S.

According to VSEPR theory, it is believed that the bonding pair goes away from the central atom with the decrease of electronegativity of the central atom and as a result, the repulsion among the bonding and non-bonding pairs gets automatically reduced for the heavier members (acting as the central atoms which are relatively less electronegative).

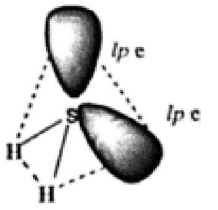
(***Hybridization concept*** : *The larger size of the heavier members and the repulsion among the bonding and nonbonding pairs of itself less pronounced which reduces the bond energies and as a result it becomes difficult to meet the hybridisation cost for* sp^3 *hybridisation. As effective hybridization does not occur so when heavier members combine with the less electronegative H prefer pure p- orbitals for bonding keepings* *the lone pair in the s- orbital. We know that introduction of more p- character by the central atom in M-X bonding will make the molecule more angular)*

In other way, the lone pair (which is more diffused for the less electronegative central atom) on the central atom causes more distortion to contract bond angles.

As a result we can conclude that the X–H (X = O, S) bond energy and cost of hybridisation, steric factors, electronegativy of the central atom are some extent responsible for gradually decreases of bond angle with increases of atomic no among the hydrides of Gr. 15 and Gr. 16



H_2O $H\text{–}\hat{O}\text{–}H = 104^\circ 28'$



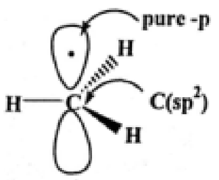
H_2S $H\text{–}\hat{S}\text{–}H = 92^\circ 15'$

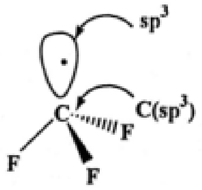
N.B. : *Bond angle order of* **1.** $NH_3 > PH_3 > AsH_3 > SbH_3$ **2.** $H_2O > H_2S > H_2Se > H_2Te$

☐ **Write down the shape of $^{\cdot}CH_3$ and $^{\cdot}CF_3$ (using VSEPR theory) :**

The electronegativity sequence is $\chi_F >> \chi_C >> \chi_H$ as a result bond pair of the C–F bond is attracted more towards the F and bond of C–H bgond is slightly attacted towards Carbon. Thus the *bp–bp* repulsion in CH_3 is much higher than that in CF_3. In fact, in CH_3, the repulsions are : *bp–bp* >> odd electron –*bp*, while in CF_3, the odd electron –*bp* repulsion is slightly larger than the *bp–bp* repulsion. Thus to minimise the *bp–bp* repulsion in CH_3, it adopts the sp^2 hybridisation of planar geometry, where bond angle is higher (120°) than that in the pyramidal str (109°) having sp^3 hybridisation. In CH_3 odd electron (in a pure *p*- orbital) –*bp* repulsion is less operate at 90°.

In CF_3, *bp–bp* repulsion are less and it adopts the sp^3 hybridisation of pyramidal str and all these repulsions occur at 109.5°. In fact, in CF_3, the bond angle is slightly decreased due to the odd electron –*bp* repulsion.





4.4 Concept of resonance and resonating structures in various inorganic and organic compounds.

The stability or wave function of the mulecule is obtained by the suitable combination of the wave functions of different structures, each weighted according to its stability or energy. None of the structures represents properties of the actual molecule. In such case, large number of alternative structures are to be considered to explain all the properties of molecule. The phenomenon is called resonance and the individual structures are called the canonical form.

The difference of energy between the lowest energy canonical form and the actual molecule is the stabilization gained through resonance known as the resonance energy or sometime as the exchange energy. Let us consider HF molecule.

$$\text{H—F (I)} \longleftrightarrow \text{H+F– (II)} \longleftrightarrow \text{H–F+ (III)}$$

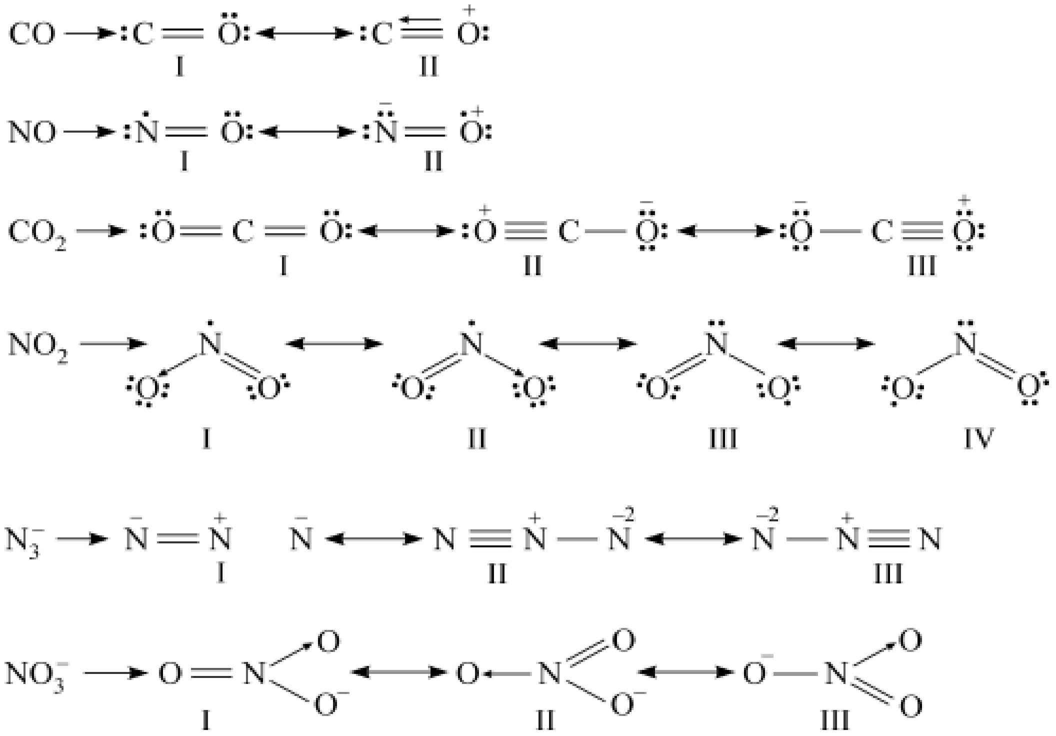
Each of them can explain some of the properties of the molecule. None of them can explain all the properties of the molecule. For e.g., canonical form (I) can explain volatile nature of HF, Form (II) can explain solubility of HF in water. Actual molecule is hybrid form of all the canonical forms. Hybrid form is more stable than any of the canonical forms. Energy by which hybrid form lowers the most stable canonical form is called resonance energy. Resonance energy of benzene is 150.6 joule per mol. All the canonical forms do not contribute equally to the hybrid form. That canonical form which contains (+ve) charge on more electropositive atom and (-ve) charge on more electronegative atom will contribute to a greater extent than the canonical form containing (+ve) charge on more electronegative atom and (-ve) charge on more electropositive atom. So canonical form (III) has negligible contribution. In all the canonical form no. of unpaired electron will be same. Relative position of all the atoms in all the canonical forms will be the same.

Condition for resonance

1. The relative position of all the atoms in each of the canonical form must be the same only the arrangements of electrons may differ.
2. The number of unpaired electrons should be the same in all the canonical forms.
3. The positive charge should reside as far as possible, on the less electronegative element and vice versa.
4. Greater no of covalent bonds add to the stability of the canonical form.
5. Like charges should not reside on adjacent atoms.
6. For atoms of second period involved in resonance, planarity is common with sp or sp^2 hybridization so as to permit good p–p overlap.
7. The larger the number of the contributing strs. the greater is the stability of the molecule.

N.B. Localization of the charge on an atom is an unstable situation which is stabilized by the delocalization of the charge. Hence the resonance is generally more important for the ions than for the molecule.

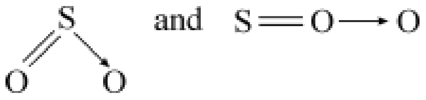
Resonance structure of some molecules



Q 1. State givine reason whether the following

(i)

(ii)



Ans. Hints : (ii) pair does not show resonance due to point 1. and 6. in the condition for resonance.

4.5 Summary

- **Fundamentals**: VB theory explains bonding by the overlap of atomic orbitals, where electrons are shared between atoms. The strength of the bond depends on the extent of this overlap.
- **Hybridization**: To explain molecular shapes, atomic orbitals can mix to form hybrid orbitals, leading to different geometrical arrangements. Common types include sp, sp^2, and sp^3 hybridization.
- **Directional Nature of Bonds**: The theory emphasizes that bonds are directional, which helps explain the specific angles observed in molecules.
- **Linear**: Molecules like CO_2 and $BeCl_2$ exhibit a linear shape with bond angles of 180° due to sp hybridization.

- **Trigonal Planar**: Molecules such as BF_3 and SO_3 have a trigonal planar shape with bond angles of 120°, resulting from sp^2 hybridization.
- **Tetrahedral**: CH_4 (methane) exemplifies a tetrahedral arrangement, with bond angles of 109.5° due to sp^3 hybridization.
- **Square Planar**: Molecules like XeF_4 exhibit a square planar shape with bond angles of 90°, formed by dsp^2 hybridization.
- **Octahedral**: Compounds such as SF_6 are octahedral, featuring bond angles of 90° and resulting from d^2sp^3 hybridization.
- **Resonance**: This concept refers to the delocalization of electrons in molecules where multiple valid Lewis structures can be drawn. These structures, known as resonance forms, contribute to the overall hybrid structure.
- **Examples**:
  - **Benzene (C_6H_6)** : Exhibits resonance with alternating double bonds, leading to equal bond lengths.
  - **Nitrate Ion (NO_3^-)** : Displays resonance through multiple arrangements of double and single bonds between nitrogen and oxygen.
- **Importance**: Resonance stabilizes molecules by spreading electron density over several atoms, lowering overall energy.

4.6 Sample Questions

A. Multiple Choice Type Questions

•What is the main principle of Valence Bond Theory (VB)?

- A) Electrons are shared equally between atoms.
- B) Atoms form bonds by overlapping atomic orbitals.
- C) Molecules are rigid structures.
- D) Electrons are transferred from one atom to another.
- **Answer: B) Atoms form bonds by overlapping atomic orbitals.**

• Which **hybridization corresponds to a linear molecular shape?**

- A) sp
- B) sp^2
- C) sp^3
- D) dsp^2
- **Answer: A) sp**

- What **is the bond angle in a trigonal planar molecule?**

  - A) 90°
  - B) 120°
  - C) 109.5°
  - D) 180°
  - **Answer: B) 120°**

- Which **of the following molecules has a tetrahedral shape?**

  - A) CO_2
  - B) NH_3
  - C) CH_4
  - D) BF_3
  - **Answer: C) CH_4**

- Which **hybridization is associated with a square planar molecular geometry?**

  - A) sp^2
  - B) sp^3
  - C) dsp^2
  - D) d^2sp^3
  - **Answer: C) dsp^2**

- What **bond angle is typical for an octahedral arrangement?**

  - A) 90°
  - B) 120°
  - C) 109.5°
  - D) 180°
  - **Answer: A) 90°**

- What **is resonance in the context of molecular structure?**

  - A) The permanent arrangement of electrons.
  - B) The equal sharing of electrons.
  - C) The delocalization of electrons across multiple structures.
  - D) The vibration of atoms in a molecule.
  - **Answer: C) The delocalization of electrons across multiple structures.**

- Which **of the following is an example of a molecule that exhibits resonance?**

  - A) CH_4
  - B) H_2O
  - C) NO_3^-
  - D) CO_2
  - **Answer: C) NO_3^-**

- Which **hybridization results in a molecule with bond angles of approximately 109.5°?**

  - A) sp
  - B) sp^2
  - C) sp^3
  - D) dsp^3
  - **Answer: C) sp^3**

- In **benzene (C_6H_6)**, what does resonance contribute to the molecule?

  - A) Unequal bond lengths
  - B) Delocalized π-electrons
  - C) Fixed double bonds
  - D) Ionic character
  - **Answer: B) Delocalized π-electrons**

- **Which of the following statements correctly describes the hybridization of the central atom in the phosphate ion (PO_4^{3-})?**

  - A) sp
  - B) sp^2
  - C) sp^3
  - D) dsp^2
  - **Answer: C) sp^3**

- **In the context of resonance structures, which of the following statements is true?**

  - A) All resonance forms contribute equally to the hybrid.
  - B) The most stable resonance form has the least formal charges.
  - C) Resonance structures can differ only in the position of the nuclei.
  - D) Resonance does not affect molecular stability.
  - **Answer: B) The most stable resonance form has the least formal charges.**

- **Which of the following molecules or ions is expected to exhibit a non-linear shape due to lone pair repulsion?**

  - A) CO_2
  - B) H_2O
  - C) BF_3
  - D) SF_6
  - **Answer: B) H_2O**

- **For the molecule SO_2, which of the following hybridization and geometry combinations is correct?**

  - A) sp^2, bent
  - B) sp^3, trigonal pyramidal
  - C) sp, linear
  - D) dsp^2, square planar
  - **Answer: A) sp^2, bent**

•Which of the following pairs of molecules are structural isomers?

- A) C_2H_6 and C_2H_4
- B) CH_3OH and C_2H_6O
- C) C_3H_8 and C_3H_6
- D) CH_3COOH and $C_2H_4O_2$
- **Answer: B) CH_3OH and C_2H_6O**

•Which molecule exhibits sp³d hybridization and what is its molecular geometry?

- A) ClF_3, T-shaped
- B) PCl_5, trigonal bipyramidal
- C) SF_6, octahedral
- D) NH_3, trigonal pyramidal
- **Answer: B) PCl_5, trigonal bipyramidal**

•Consider the nitrate ion (NO_3^-). How many resonance structures can be drawn for it?

- A) 1
- B) 2
- C) 3
- D) 4
- **Answer: C) 3**

•Which of the following statements is false regarding the concept of hybridization?

- A) Hybrid orbitals are degenerate.
- B) Hybridization can explain molecular geometries.
- C) Hybridization always involves s and p orbitals.
- D) Hybridization results in orbitals with different shapes than the parent orbitals.
- **Answer: C) Hybridization always involves s and p orbitals.** (It can also involve d orbitals.)

•In an octahedral molecule, if two of the six positions are occupied by lone pairs, what is the resulting molecular geometry?

- A) Octahedral
- B) Square pyramidal
- C) T-shaped
- D) Square planar
- **Answer: B) Square pyramidal**

•Which of the following molecular species has a bond order greater than 1 and is a resonance hybrid?

- A) O_3 (ozone)
- B) CO_2 (carbon dioxide)
- C) NO (nitric oxide)
- D) N_2 (nitrogen)

- **Answer: A) O_3** (ozone)

B. Short Type Questions

Definition of Resonance

Q.1 Define resonance. Enumerate the conditions for this concept. Draw the possible resonating structures of O_3 and NO^{2-} indicating with justification the most probable one in each case. Identify a special relationship between the molecule O_3 and the molecular ion NO^{2-}.

Resonance is a concept in chemistry that describes the delocalization of electrons within molecules that can be represented by two or more valid Lewis structures (resonance structures). These structures differ only in the arrangement of electrons, not in the positions of the atoms. The true structure of the molecule is a hybrid of these resonance forms, which stabilizes the molecule.

Conditions for Resonance

1. **Multiple Lewis Structures**: The molecule must have at least two valid Lewis structures that can be drawn.
2. **Delocalized Electrons**: There must be p-orbitals or π-bonds that allow for the movement of electrons between different atoms or bonds.
3. **Same Atomic Connectivity**: The arrangement of atoms (connectivity) must remain unchanged between the resonance structures.
4. **Similar Energy Levels**: The resonance structures should have comparable energy levels, with the most stable structures contributing more to the resonance hybrid.

Resonance Structures of Ozone (O_3)

1. **Structure 1**:
   - O=O–O (with a double bond between the first two oxygen atoms)
2. **Structure 2**:
   - O–O=O (with a double bond between the last two oxygen atoms)

Most Probable Structure: Both structures are equivalent due to the symmetry of the ozone molecule. However, the bond lengths are equal, indicating that the actual structure is a resonance hybrid of both forms. Thus, both contribute significantly to the overall resonance.

Resonance Structures of Nitrite Ion (NO_2^-)

1. **Structure 1**:
   - O=N–O (with a double bond between nitrogen and one oxygen)
2. **Structure 2**:
   - O–N=O (with a double bond between nitrogen and the other oxygen)

Most Probable Structure: The resonance structures are equivalent, but the formal charge distribution must be considered. The most stable structure minimizes formal charges; thus, both forms have similar stability, but the one with a formal charge of 0 on nitrogen is generally favored.

Special Relationship Between O_3 and NO_2^-

Ozone (O_3) and the nitrite ion (NO_2^-) are related through their resonance structures. Both species involve delocalized π-bonds and can be represented by multiple resonance forms. Additionally, the structure of NO_2^- can be viewed as a nitrogen atom bonded to two oxygen atoms, similar to the bonding observed in ozone, highlighting the shared feature of resonance and electron delocalization in their structures.

Q.2 Applying the VSEPR concept to determine the str and shape of the following molecules ClF_3, Methyl carbanion, SO_2Cl_2, $(CH_3)_3C^+$, NH_3, BCl_3, BrF_3, ICl^{2-}, PCl_2F_3, XeF_6, IF_3, $XeOF_4$,CH_4, SF_4, XeF_4.

Hints:

ClF_3

- **Steric Number**: 5 (3 bonding pairs, 2 lone pairs)
- **Geometry**: Trigonal bipyramidal
- **Shape**: T-shaped

Methyl Carbanion (CH_3^-)

- **Steric Number**: 4 (4 bonding pairs)
- **Geometry**: Tetrahedral
- **Shape**: Tetrahedral

SO_2Cl_2

- **Steric Number**: 4 (2 bonding pairs of O, 2 bonding pairs of Cl)
- **Geometry**: Tetrahedral
- **Shape**: Bent (due to the presence of the lone pairs on S)

$(CH_3)_3C^+$

- **Steric Number**: 4 (4 bonding pairs)
- **Geometry**: Tetrahedral
- **Shape**: Tetrahedral

NH_3

- **Steric Number**: 4 (3 bonding pairs, 1 lone pair)
- **Geometry**: Tetrahedral
- **Shape**: Trigonal pyramidal

BCl_3

- **Steric Number**: 3 (3 bonding pairs)
- **Geometry**: Trigonal planar
- **Shape**: Trigonal planar

BrF_3

- **Steric Number**: 5 (3 bonding pairs, 2 lone pairs)
- **Geometry**: Trigonal bipyramidal
- **Shape**: T-shaped

ICl_2^-

- **Steric Number**: 4 (2 bonding pairs, 2 lone pairs)
- **Geometry**: Tetrahedral
- **Shape**: Bent

PCl_2F_3

- **Steric Number**: 5 (2 bonding pairs, 3 bonding pairs)
- **Geometry**: Trigonal bipyramidal
- **Shape**: Seesaw (due to lone pairs)

XeF_6

- **Steric Number**: 6 (6 bonding pairs)
- **Geometry**: Octahedral
- **Shape**: Distorted octahedral (due to lone pairs)

IF_3

- **Steric Number**: 5 (3 bonding pairs, 2 lone pairs)
- **Geometry**: Trigonal bipyramidal
- **Shape**: T-shaped

$XeOF_4$

- **Steric Number**: 6 (4 bonding pairs, 1 lone pair)
- **Geometry**: Octahedral
- **Shape**: Square planar

CH_4

- **Steric Number**: 4 (4 bonding pairs)
- **Geometry**: Tetrahedral
- **Shape**: Tetrahedral

SF_4

- **Steric Number**: 5 (4 bonding pairs, 1 lone pair)
- **Geometry**: Trigonal bipyramidal
- **Shape**: Seesaw

XeF_4

- **Steric Number**: 6 (4 bonding pairs, 2 lone pairs)
- **Geometry**: Octahedral
- **Shape**: Square planar

c. Assay Type Questions

1. Discuss the Valence Bond Theory and its significance in understanding molecular bonding.

2. Explain the VSEPR theory and its application in predicting molecular geometry.

3. Describe the significance of lone pairs in determining molecular shape using VSEPR theory.

4. Examine the concept of resonance in molecular chemistry and its relationship to Valence Bond Theory.

4.7 References

- Das, A. K. *Textbook of Inorganic Chemistry*.
- Das, A. K. *Concepts of Inorganic Chemistry*
- Das, A. K. *Materials Chemistry*. Publisher.
- Das, A. K. *Chemistry of Transition Elements*. Publisher.

5. Inorganic Chemistry by R.L. Dutta

6. Essentials of Physical Chemistry by B.S. Bahl

7. Concise Inorganic Chemistry (4th Edition) by J.D. Lee

8. General and Inorganic Chemistry by P.K. Dutta

9. General and Inorganic Chemistry by R. Sarkar

Unit - 5 ❑ Molecular Orbital

Structure

5.0 Objectives

- Define the fundamental principles of Molecular Orbital Theory and its significance in molecular chemistry.
- Explain the concept of molecular orbitals formed by the linear combination of atomic orbitals (LCAO).
- List and elaborate on the key rules governing the LCAO method in constructing molecular orbitals from atomic orbitals.
- Describe the characteristics of bonding and antibonding molecular orbitals formed from s-s, s-p, and p-p combinations of atomic orbitals.
- Analyze the molecular orbital diagrams for homonuclear diatomic molecules, including diatomic hydrogen (H2), nitrogen (N2), and oxygen (O2).
- Assess the electronic configurations, stability, and magnetic properties of these molecules based on MO theory.
- Explore the application of MO theory to heteronuclear diatomic molecules, specifically carbon monoxide (CO), nitrogen monoxide (NO), and the ion NO+.
- Compare and contrast the Valence Bond (VB) theory with Molecular Orbital (MO) theory, highlighting strengths and limitations of each approach.
- Discuss how VB and MO theories provide different insights into molecular bonding and behavior, including resonance, hybridization, and electron delocalization.

5.1 Introduction

Molecular Orbital (MO) Theory provides a comprehensive framework for understanding the electronic structure of molecules. Unlike Valence Bond Theory, which emphasizes localized bonding interactions between pairs of atoms, MO Theory focuses on the formation of molecular orbitals that are delocalized over the entire molecule. This approach allows for a more nuanced understanding of molecular properties, including bonding, stability, and reactivity.

At the heart of MO Theory is the Linear Combination of Atomic Orbitals (LCAO) method, which combines atomic orbitals to create molecular orbitals that can be classified as bonding, antibonding, or nonbonding. This classification reveals key insights into the energy levels and electron density distributions within a molecule.

As we delve into the characteristics of bonding and antibonding molecular orbitals, as well as the differences between homonuclear and heteronuclear diatomic molecules, we will highlight the utility of MO Theory in predicting molecular behavior. Additionally, a comparative analysis with Valence Bond Theory will underscore the strengths and limitations of each approach, enriching our understanding of molecular interactions in chemistry.

5.2 Theory MO Approach

Molecular Orbital (MO) Theory is a vital concept in quantum chemistry that describes how atomic orbitals combine to form molecular orbitals, which are spread over the entire molecule rather than localized between individual atoms. This theory provides a deeper understanding of molecular bonding, structure, and properties.

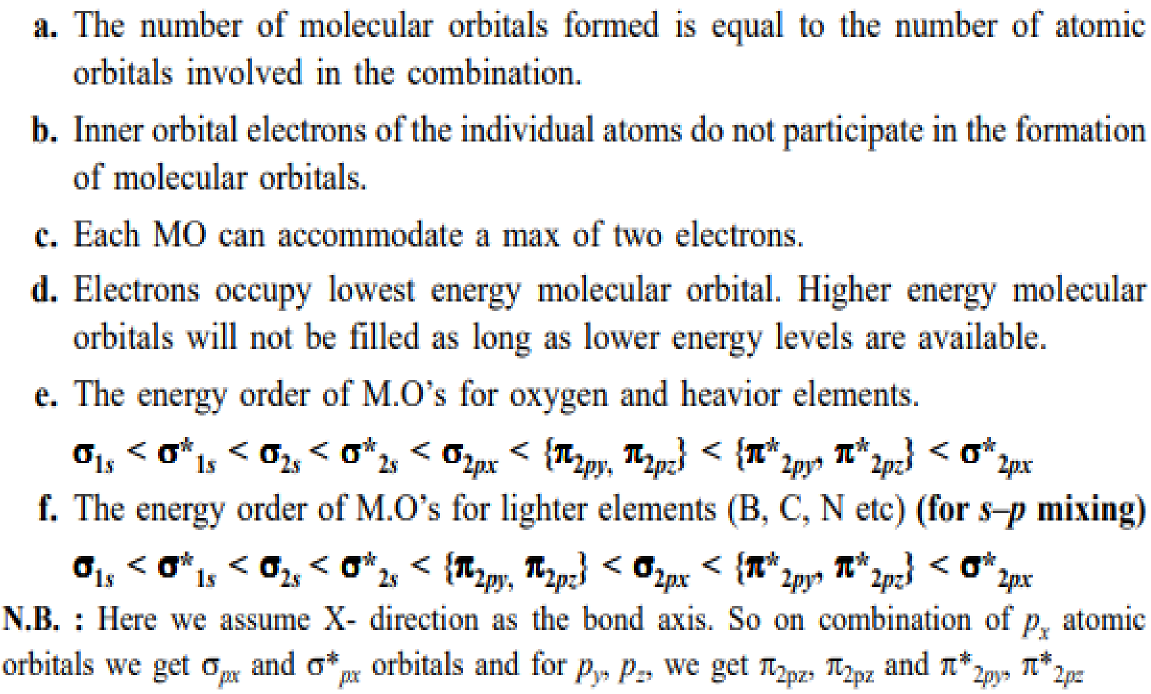
Key Principles of MO Theory

1. **Linear Combination of Atomic Orbitals (LCAO)**:
   - MO Theory employs the LCAO method, where atomic orbitals from contributing atoms are mathematically combined to form molecular orbitals.
   - The resulting molecular orbitals can be classified as bonding, antibonding, or nonbonding based on their energy and electron density distribution.
2. **Bonding and Antibonding Molecular Orbitals**:
   - **Bonding Orbitals**: Formed when atomic orbitals combine constructively, resulting in a lower energy state and increased electron density between the nuclei, which stabilizes the molecule.
   - **Antibonding Orbitals**: Formed through destructive interference of atomic orbitals, leading to higher energy states and reduced electron density between the nuclei, which destabilizes the molecule.
3. **Types of Combinations**:
   - **s-s, s-p, and p-p Combinations**: Each combination has distinct characteristics. For example:
     - **s-s combinations** yield a symmetric bonding orbital and an antisymmetric antibonding orbital.

        - **s-p combinations** involve mixing s and p orbitals, creating a bonding orbital with significant electron density along the internuclear axis.
        - **p-p combinations** can lead to π bonding and antibonding orbitals, crucial for multiple bonds.

4. **Nonbonding Molecular Orbitals**:
    - Nonbonding orbitals are derived from atomic orbitals that do not significantly contribute to bonding. They can affect molecular properties, such as polarity and reactivity, without stabilizing or destabilizing the bond.
5. **Homonuclear and Heteronuclear Diatomic Molecules**:
    - MO Theory effectively describes both homonuclear diatomic molecules (like O_2 and N_2) and heteronuclear diatomic molecules (like CO and NO). The energy levels and electron configurations provide insights into their bond strengths, magnetism, and chemical behavior.
6. **Comparison with Valence Bond Theory**:
    - While MO Theory emphasizes the delocalization of electrons and molecular orbitals, Valence Bond Theory focuses on localized bonds. Understanding both theories provides a holistic view of molecular structure and bonding.

5.3 Rules for the LCAO method



a. The number of molecular orbitals formed is equal to the number of atomic orbitals involved in the combination.

b. Inner orbital electrons of the individual atoms do not participate in the formation of molecular orbitals.

c. Each MO can accommodate a max of two electrons.

d. Electrons occupy lowest energy molecular orbital. Higher energy molecular orbitals will not be filled as long as lower energy levels are available.

e. The energy order of M.O's for oxygen and heavior elements.

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2px} < \{\pi_{2py}, \pi_{2pz}\} < \{\pi^*_{2py}, \pi^*_{2pz}\} < \sigma^*_{2px}$$

f. The energy order of M.O's for lighter elements (B, C, N etc) **(for *s–p* mixing)**

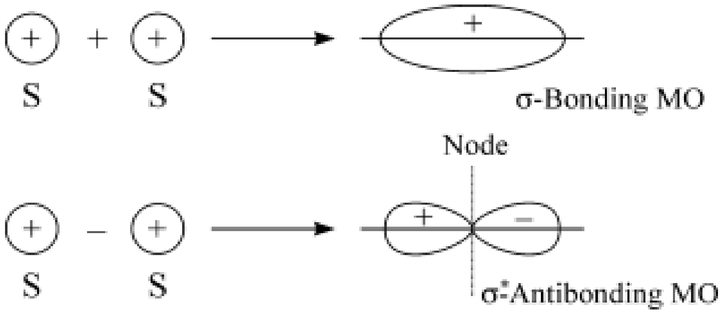
$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \{\pi_{2py}, \pi_{2pz}\} < \sigma_{2px} < \{\pi^*_{2py}, \pi^*_{2pz}\} < \sigma^*_{2px}$$

N.B. : Here we assume X- direction as the bond axis. So on combination of p_x atomic orbitals we get σ_{px} and σ^*_{px} orbitals and for p_y, p_z, we get π_{2pz}, π_{2pz} and π^*_{2py}, π^*_{2pz}

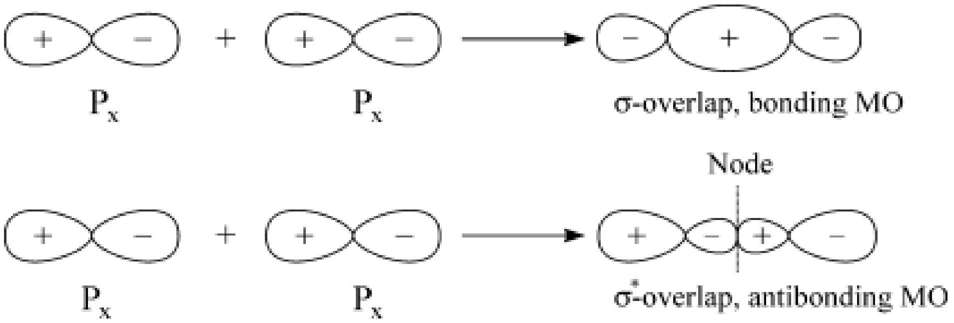
5.4 Bonding and antibonding MOs and their characteristics for s-s, s-p and p-p combinations of atomic orbitals, nonbonding combination of orbitals

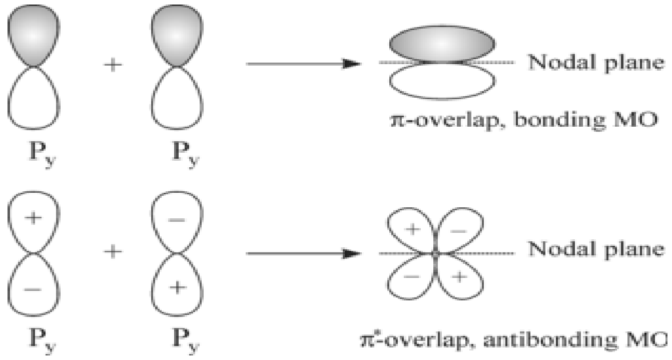
Molecular orbitals (MOs) are formed from the combination of atomic orbitals. They can be categorized into bonding, antibonding, and nonbonding orbitals based on their energy levels and electron density distributions. Below, we discuss the characteristics of bonding and antibonding MOs for different combinations of atomic orbitals: s-s, s-p, and p-p, as well as nonbonding orbitals.

s-s Combination of orbital:

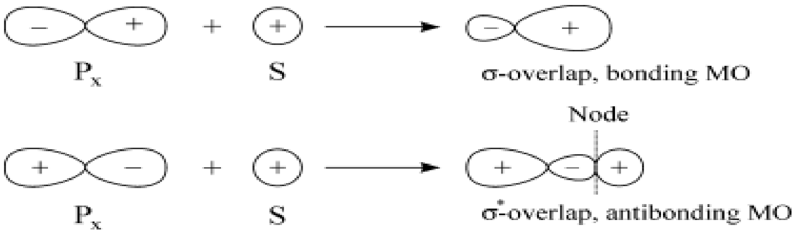


P–P combination of ortbial :





S–P combination of orbitals :



Bond order :

$$B.O = \frac{\text{No. of electrons in bonding MO} - \text{No of electrons in antibonding M.O}}{2}$$

Higher the B.O stronger will be the covalent bond, shorter will be the covalent bond length, higher the stretching frequency. when B.O value of a compound is zero, the compound does not exist.

For $He_2 \rightarrow \sigma_{1s}2\sigma^{*}{}_{1s}2$ B.O $= \frac{2-2}{2} = 0$, So He_2 does not exist.

Electronic distribution in the M.O of He_2* ion is $\sigma_{1s}2\sigma^{*}{}_{1s}0$.

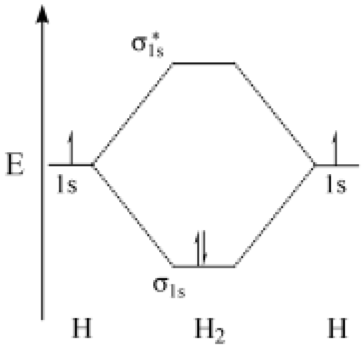
B.O $= \frac{2-1}{2} = \frac{1}{2}$, so He_2^+ exist.

5.4 MO treatment of homonuclear diatomic molecules of and heteronuclear diatomic molecules such as CO, NO and NO$^+$.

Molecular Orbital (MO) Theory provides a systematic way to understand the electronic structure of diatomic molecules, both homonuclear (consisting of two identical atoms) and heteronuclear (composed of different atoms). Below is an overview of how MO Theory applies to these types of molecules.

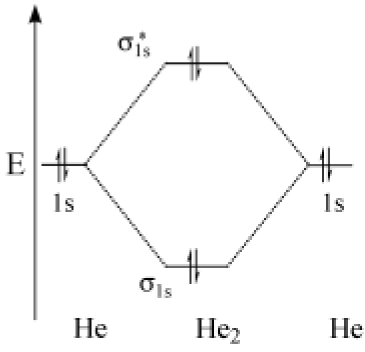
❑ *Examples for molecular orbitals for Homo nuclear diatomic molecules :*

H_2 molecule



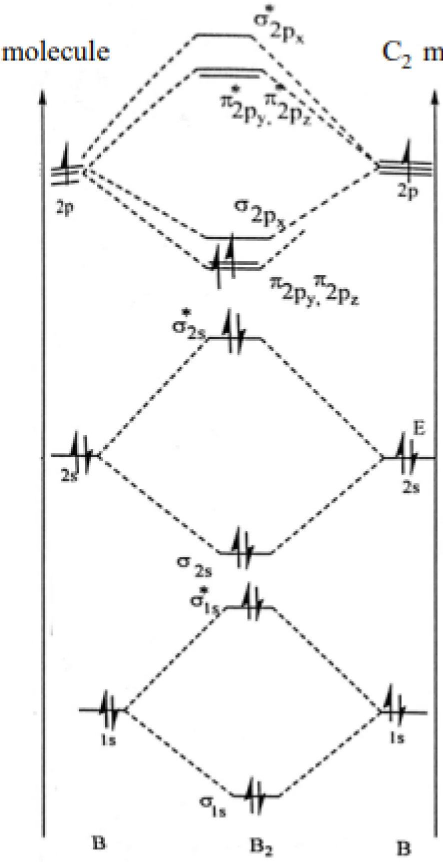
H_2 (2) $\longrightarrow$ $\sigma_{1s}^2\ \sigma_{1s}^{*0}$

He_2 molecule



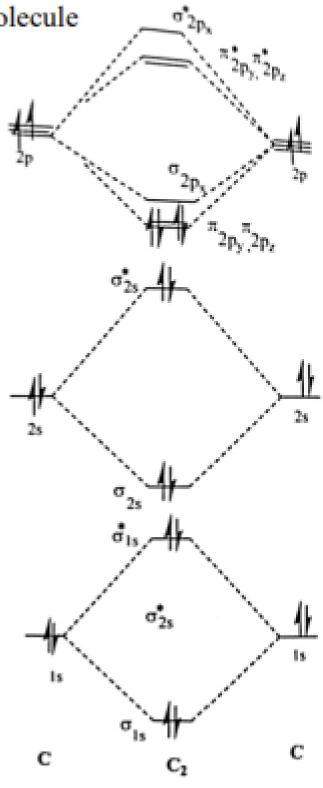
He_2 (4) $\longrightarrow$ $\sigma_{1s}^2\ \sigma_{1s}^{*2}$

B_2 molecule



$B_2(10) \rightarrow \sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\{\pi_{2p_y}^1, \pi_{2p_z}^1\}$

C_2 molecule



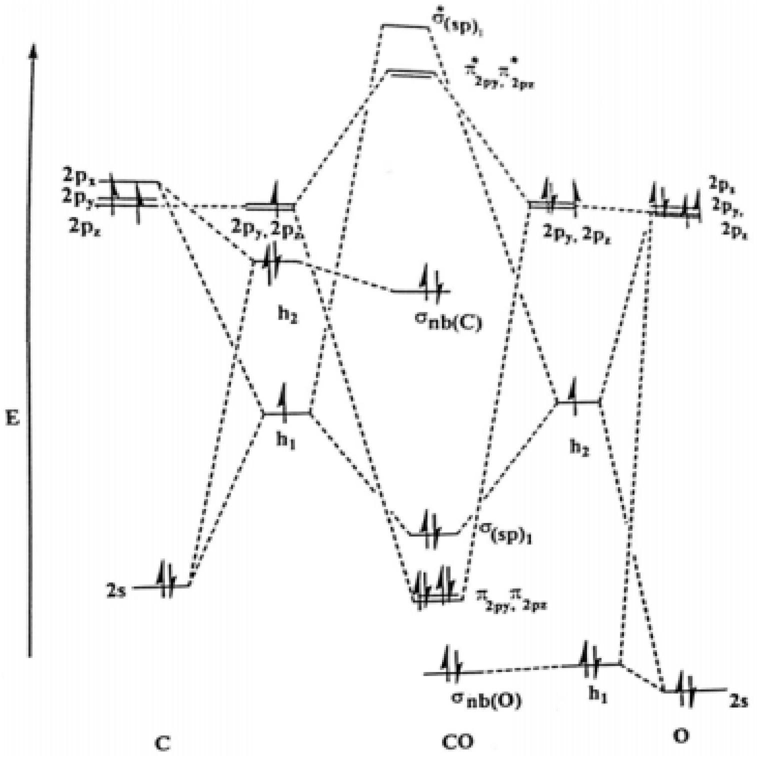
$C_2(12) \rightarrow \sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\{\pi_{2p_y}^2, \pi_{2p_z}^2\}$

- ***B_2 molecule is paramagnetic while C_2 molecule is diamagnetic Explain?***

  According to above M.O diagram due to presence of unpaired electron in the π–MO of B_2 so it is paramagnetic in nature. But due to absence of unpaired electron in the π–MO of C_2, C_2 molecule is diamagnetic in nature.

- ***Draw the M.O diagramme of CO molecule and indicate the bond order and magnetic nature.***

  CO is hetero nuclear diatomic molecule, the two atom of which differ in atomic number by two units. $C(6) = 1s^2 2s^2 2p^2$, $O(8) = 1s^2 2s^2 2p^4$. So the corresponding atomic orbitals in the valency shell in two atoms differ in energy appreciably. According to Coulson $2s$ and $2p_x$ mixsing occurs in the valency shell both the atom and then the linear combination of atomic orbitals give following M.O diagrame for CO molecule.



Modified M.O electron distribution of CO molecule is

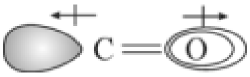
$$CO = KK\ \sigma^2_{(nb)O} \{\pi^2_{2py}, \pi^2_{2pz}\} \sigma^2_{(sp)1} \sigma^2_{(nb)C} \{\pi^{*}{}_{2py}^{0}, \pi^{*}{}_{2pz}^{0}\} \sigma^*_{(sp)1}$$

$$B.O = \frac{6-0}{2} = 3$$

Since all the electrons in the MOS are paired CO molecule is diamagnetic. There are two nonbonding electron pairs i.e., one lone pair is lower energy, greater s-character lying towards highly electronegative O atom and the other is greater p-character, higher energy lying towards less electronegative C atom. So CO can act as a ligand by donating the electron pairs through carbon.

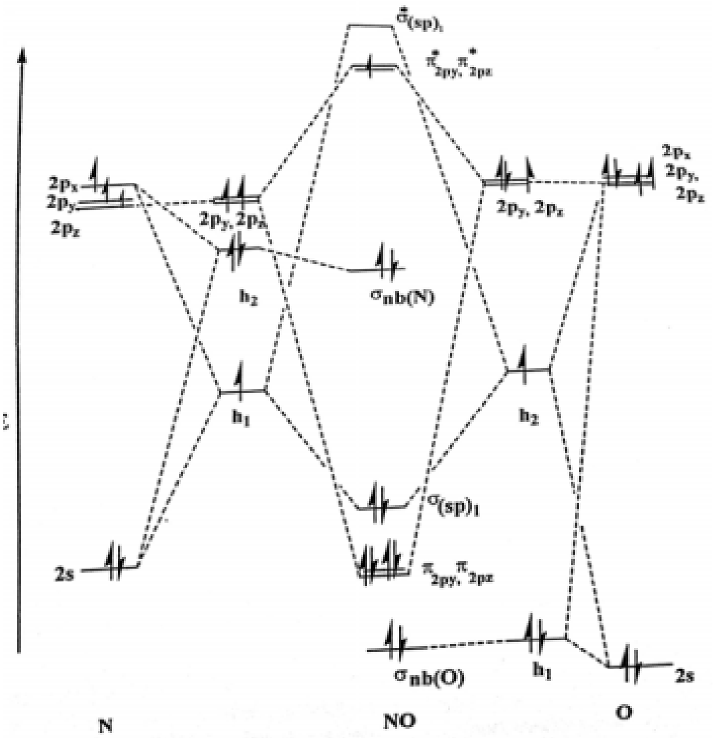
But CO molecule has low laying emtpy π^*_{2py} and π^*_{2pz} M.O which are suitable for acceptance of electron pair. For this reason CO can act as π- acidic ligand by simultaneous donation and acceptance of electron pair.

The CO bond moment acts in a direction opposite to the lone pair moment of carbon, being almost equal in magnitude. They almost completely cancelled each other and so the dipole moment of CO is almost Zero i.e., CO is almost nonpolar.



- ***Draw the M.O diagramme of NO molecule***

NO is hetero—nuclear diatomic molecule, the two atom of which differ in atomic number by one unit. N(7) = $1s^2 2s^2 2p^3$, O(8) = $1s^2 2s^2 2p^4$. So the corresponding atomic orbitals in the valency shell in two atoms differ in energy appreciably. According to Coulson $2s$ and $2p_x$ mixsing occurs in the valency shell both the atom and then the linear combination of atomic orbitals give following M.O diagrame for NO molecule.



Modified M.O electron distribution of NO molecule is

NO (15) = KK $\sigma^2_{(nb)O}\{\pi^2_{2py},\pi^2_{2pz}\}\ \sigma^2_{(sp)1}\ \sigma^2_{(nb)C}\{\pi^{*}{}_{2py}^{1},\ \pi^{*}{}_{2pz}^{0}\}\sigma^{*}{}_{(sp)1}^{0}$

$$\text{B.O} = \frac{6-1}{2} = 2.5$$

Modified M.O electron distribution of NO^+ molecule is

NO^+ (14) = KK $\sigma^2_{(nb)O}\{\pi^2_{2py},\pi^2_{2pz}\}\ \sigma^2_{(sp)1}\ \sigma^2_{(nb)C}\{\pi^{*}{}_{2py},\ \pi^{*}{}_{2pz}^{0}\}\sigma^{*}{}_{(sp)1}^{0}$

$$\text{B.O} = \frac{6-0}{2} = 3$$

5.5 Comparison of VB and MO approaches

Valence Bond (VB) Theory and Molecular Orbital (MO) Theory are two foundational approaches to understanding molecular bonding and electronic structure. While both aim to explain how atoms combine to form molecules, they differ significantly in their methodologies and insights. Here's a comparison of the two**:**

Aspect	**Valence Bond Theory (VB)**	**Molecular Orbital Theory (MO)**
Basic Concept	Emphasizes localized bonds formed by overlapping atomic orbitals between pairs of atoms.	Focuses on delocalized electrons spread over the entire molecule, forming molecular orbitals.
Bond Formation	Bonds are formed through the overlap of atomic orbitals. Each bond is between a pair of electrons.	Bonds are formed by the combination of atomic orbitals to create molecular orbitals, which can accommodate more than two electrons.
Orbital Hybridization	Requires hybridization of atomic orbitals (e.g., sp^3, sp^2, sp) to explain bond angles and shapes.	Does not require hybridization; molecular orbitals are formed directly from the linear combination of atomic orbitals.
Bonding Description	Bonds are described as localized interactions between two atoms, with individual bond strengths being easily identified.	Bonds are described as delocalized interactions, making it more challenging to assign bond strengths to individual interactions.
Multiple Bonds	Explains multiple bonds (e.g., double and triple bonds) through hybridized orbitals and overlapping p orbitals.	Accounts for multiple bonds through the formation of π and σ molecular orbitals, providing a clearer view of electron delocalization.
Resonance	Uses resonance structures to describe molecules with delocalized electrons, treating them as hybrid structures.	Naturally incorporates electron delocalization in the description of molecular orbitals, eliminating the need for resonance structures.
Magnetic Properties	Predicts magnetic properties based on the presence of unpaired electrons in individual atomic orbitals.	Provides a clearer picture of paramagnetism and diamagnetism through the analysis of molecular orbital configurations.
Applicability	More effective for simple molecules and certain complex organic compounds, where localized bonding is prominent.	More effective for describing large, complex molecules, resonance-stabilized species, and transition metal complexes.
Visualization	Easier for visualizing individual bonds and interactions, as it focuses on specific atomic orbitals and bond formation.	Provides a broader view of the entire molecule's electronic structure, emphasizing the overall energy levels and electron distribution.

5.6 Summary

Both Valence Bond and Molecular Orbital theories provide valuable insights into molecular bonding, each with its strengths and limitations. VB Theory excels in explaining simple molecules and localized bonding interactions, while MO Theory offers a more comprehensive view of electron delocalization and molecular properties, especially in complex systems. MO Theory focuses on the formation of delocalized molecular orbitals that extend over the entire molecule, allowing for a clearer description of electron distribution and resonance without needing separate resonance structures. Both theories is crucial for a complete picture of molecular chemistry.

5.7 Sample Questions

A. Multiple Choice Questions

1) **Which of the following correctly describes a bonding molecular orbital?**
A) Higher energy than the original atomic orbitals
B) Forms between two nuclei with increased electron density
C) Has a nodal plane between the nuclei
D) None of the above
Answer: B) Forms between two nuclei with increased electron density

2) **What is the bond order of a diatomic molecule with 8 bonding electrons and 2 antibonding electrons?**
A) 3
B) 4
C) 2
D) 5
Answer: A) 3

3) **In which type of molecular orbital is the electron density concentrated above and below the internuclear axis?**
A) σ (sigma) orbital
B) π (pi) orbital
C) δ (delta) orbital
D) Nonbonding orbital
Answer: B) π (pi) orbital

4) **Which molecular orbital theory concept best explains the paramagnetism of O_2 ?**
A) All electrons are paired.
B) There are unpaired electrons in the molecular orbitals.
C) Bonding orbitals are completely filled.
D) The molecule is linear.
Answer: B) There are unpaired electrons in the molecular orbitals.

5) **Which of the following statements about antibonding molecular orbitals is true?**
A) They are formed by constructive interference of atomic orbitals.
B) They stabilize the molecule.
C) They have a higher energy than bonding molecular orbitals.
D) They contain more electron density between the nuclei.
Answer: C) They have a higher energy than bonding molecular orbitals.

6) **For the homonuclear diatomic molecule N_2, how many unpaired electrons are present in its molecular orbital configuration?**
A) 0
B) 1
C) 2
D) 3
Answer: A) 0

7) **What is the general trend in energy levels for molecular orbitals formed from the combination of atomic orbitals?**
A) Bonding orbitals < Nonbonding orbitals < Antibonding orbitals
B) Antibonding orbitals < Bonding orbitals < Nonbonding orbitals
C) Nonbonding orbitals < Bonding orbitals < Antibonding orbitals
D) Bonding orbitals < Antibonding orbitals < Nonbonding orbitals
Answer: A) Bonding orbitals < Nonbonding orbitals < Antibonding orbitals

8) **Which of the following molecules would be expected to have a bond order of 2?**
A) N_2
B) O_2
C) CO
D) NO
Answer:B) O_2

9) **In MO Theory, which type of molecular orbital is created by the lateral overlap of p orbitals?**
A) σ (sigma) orbital
B) π (pi) orbital
C) ρ (rho) orbital
D) Nonbonding orbital
Answer: B) π (pi) orbital

10) **How does MO Theory describe resonance in molecules?**
A) By using multiple structures with varying bond types
B) By incorporating the delocalization of electrons across molecular orbitals
C) By indicating localized electron pairs
D) By focusing only on single bonds
Answer: B) By incorporating the delocalization of electrons across molecular orbitals

B. Short Type Questions

Q.1 Justify: He_2 molecule does not exist.

Answer: For He_2 , both helium atoms contribute two electrons, leading to a total of four electrons in the molecular orbitals:

$$(\sigma(1s))^2\ (\sigma^*(1s))^2$$

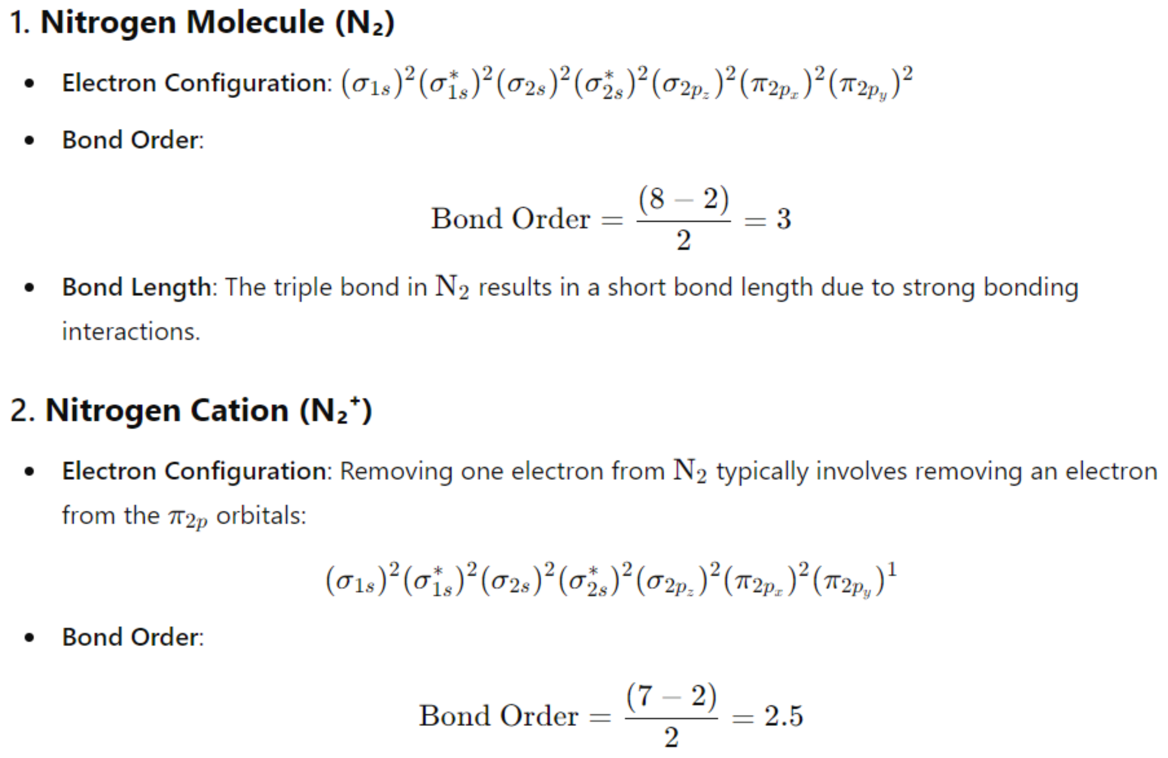
This configuration results in two bonding electrons and two antibonding electrons.
The bond order is calculated using the formula:
Bond Order=(Number of bonding electrons−Number of antibonding electrons) /2

For He_2 : BondOrder=(2−2) / 2=0

A bond order of 0 indicates that there is no net bonding interaction between the two helium atoms. With no bonding interactions (bond order of 0), He_2 lacks stability and cannot exist as a bound molecular species. The repulsion between the electrons in the antibonding orbital cancels out any potential bonding.

Q.2 "The bond length in N_2^+ is greater than that in N_2 while bond length in NO^+ is less than that in NO". Explain the observation using MO theory.

Answer:



1. Nitrogen Molecule (N_2)

- **Electron Configuration**: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_x})^2(\pi_{2p_y})^2$
- **Bond Order**:

$$\text{Bond Order} = \frac{(8-2)}{2} = 3$$

- **Bond Length**: The triple bond in N_2 results in a short bond length due to strong bonding interactions.

2. Nitrogen Cation (N_2^+)

- **Electron Configuration**: Removing one electron from N_2 typically involves removing an electron from the π_{2p} orbitals:

$$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_x})^2(\pi_{2p_y})^1$$

- **Bond Order**:

$$\text{Bond Order} = \frac{(7-2)}{2} = 2.5$$

- **Bond Length**: The bond order decreases from 3 to 2.5, leading to a longer bond length compared to $\mathrm{N_2}$ because there are fewer bonding interactions and greater repulsion from the unpaired electron in the π_{2p} orbital.

3. Nitric Oxide (NO)

- **Electron Configuration**: For NO, the configuration can be written as:

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p_x})^2(\pi_{2p_y})^1$$

- **Bond Order**:

$$\text{Bond Order} = \frac{(8-2)}{2} = 3$$

- **Bond Length**: The triple bond results in a shorter bond length due to strong bonding interactions.

4. Nitric Oxide Cation (NO^+)

- **Electron Configuration**: Removing an electron from NO typically removes an electron from the π_{2p} orbital:

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p_x})^1(\pi_{2p_y})^1$$

- **Bond Order**:

$$\text{Bond Order} = \frac{(7-2)}{2} = 2.5$$

- **Bond Length**: The bond order decreases from 3 to 2.5, but the bond length in $\mathrm{NO^+}$ is shorter than in NO because the remaining electrons in the bonding π orbitals are held closer to the nuclei, resulting in a stronger bond.

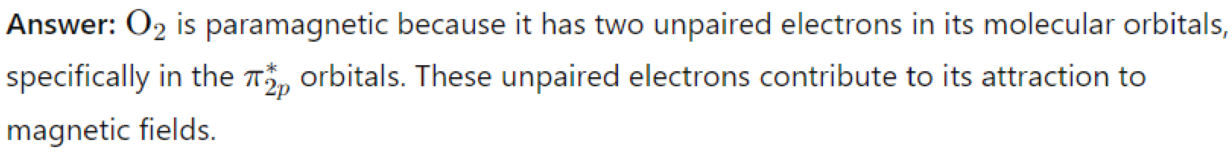
N_2 vs. N_2^+: $\mathrm{N_2^+}$ has a longer bond length than $\mathrm{N_2}$ due to the reduction in bond order from 3 to 2.5, leading to weaker bonding interactions.

NO vs. NO^+: $\mathrm{NO^+}$ has a shorter bond length than NO because, despite the decrease in bond order, the remaining bonding interactions are stronger, resulting in a tighter bond.

Q. 3 Explain why O_2 molecule is paramagnetic but O_2^{2-} is diamagnetic.

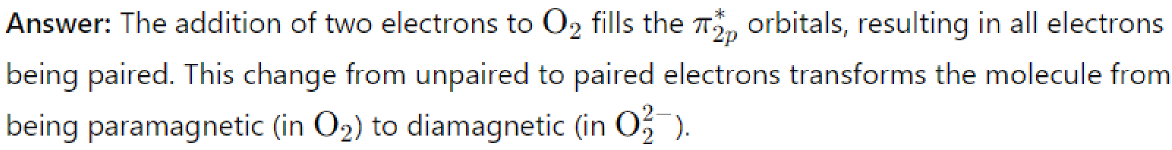
- **Hints:** Draw the MO.
- O_2: Paramagnetic due to two unpaired electrons in the π∗ orbitals.
- **O_2^{2-}**: Diamagnetic because all electrons are paired after filling the π∗ orbitals.

Q.4 Why O_2 paramagnetic in nature?



Answer: O_2 is paramagnetic because it has two unpaired electrons in its molecular orbitals, specifically in the π^*_{2p} orbitals. These unpaired electrons contribute to its attraction to magnetic fields.

Q.5 How does the addition of two electrons affect the magnetic properties of O_2 when forming O_2^{2-}?



Answer: The addition of two electrons to O_2 fills the π^*_{2p} orbitals, resulting in all electrons being paired. This change from unpaired to paired electrons transforms the molecule from being paramagnetic (in O_2) to diamagnetic (in O_2^{2-}).

Q.6 What is the basic principle of Molecular Orbital (MO) Theory?

Answer: MO Theory describes how atomic orbitals combine to form molecular orbitals that can be occupied by electrons. These molecular orbitals can be bonding, antibonding, or nonbonding, depending on how atomic orbitals overlap.

Q.7 How do bond molecular orbitals differ from antibonding molecular orbitals?

Answer: Bonding molecular orbitals result from the constructive interference of atomic orbitals, leading to increased electron density between the nuclei, which stabilizes the molecule. Antibonding molecular orbitals result from destructive interference and have a nodal plane between the nuclei, leading to decreased electron density between them and destabilizing the molecule.

C. Assay Type Questions

1. Define Molecular Orbital Theory (MO Theory). Explain the concept of molecular orbitals and their formation from atomic orbitals. Differentiate between bonding, antibonding, and nonbonding molecular orbitals.

2. Discuss how MO Theory explains bond order, stability, and the magnetic properties of molecules.

3. Highlight the advantages of MO Theory over Valence Bond Theory in explaining certain molecular phenomena.

4. Describe the molecular orbital filling for homonuclear diatomic molecules such as N_2, O_2, and F_2.

5. Compare and contrast the bond orders of these molecules and their relationship to bond strength and length.

6. Discuss the implications of unpaired electrons in terms of paramagnetism and diamagnetism. Provide examples to illustrate how changes in electron count (e.g., in ions like O_2^{2-}) affect stability and magnetic properties.

5.8 References

1. R.L. Dutta, Inorganic Chemistry Pt-I and II. The New book Stall, 5th Edn. 2006. 2. A.S. Das, Fundamental Concepts of Inorganic Chemistry, Vol.-1, 2 & 3, 2nd Edn. CBS Publisher, 2012. 3. G. Wulfsberg, Inorganic Chemistry, Viva Books Private Ltd. New Delhi, 2001. 4. D.F. Shriver, P.W. Atkins and C.H. Langford, Inorganic Chemistry, Oxford University Press, New York, 1990. 5. B. Douglas, D. McDaniel and J. Alexander, Concepts and Models of Inorganic Chemistry, 3rd Edn. John Wiley and Sons, Inc. New York, 2001. 6. J.E. Huheey, E.A. Keiter and R.L. Keiter, Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edn. Harper Collins College Publishers, New York, 1993. 7. N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, 2nd Edn, Pergamon, New York, 1997. 8. A.G. Sharpe: Inorganic Chemistry. 9. J.D. Lee, Concise Inorganic Chemistry, Chapman and Hall, London, 1991. 10. F.A. Cotton, G. Wilkinson, C.M. Murillo and M. Bochmann, Advanced Inorganic Chemistry, 6th Edn. John Wiley and Sons, Inc., New York, 1999. 11. J.J. Katz, G.T. Seaborg and L.R. Morss (Eds). The Chemistry of the Actinide Elements, Vols I and II, 2nd Edn, Capman and Hall, London, 1986. 12. D.M. Adams, Inorganic Solids, Wiley, New York, 1992

Unit - 6 ❑ s-and p-Block Elements

Structure

6.0 Objectives

After reading this unit, we will be able to know:

- The general periodic properties of s-block elements
- Definition of ionisation enthalpy, electron affinity, and electronegativity.
- Study on the allotropes of carbon, sulphur, and phosphorous.
- Diagonal relationships of IA, IIA, IIIA, and IVA group elements.
- Anomalous behaviour of first member of each group

6.1 Introduction

s-block elements

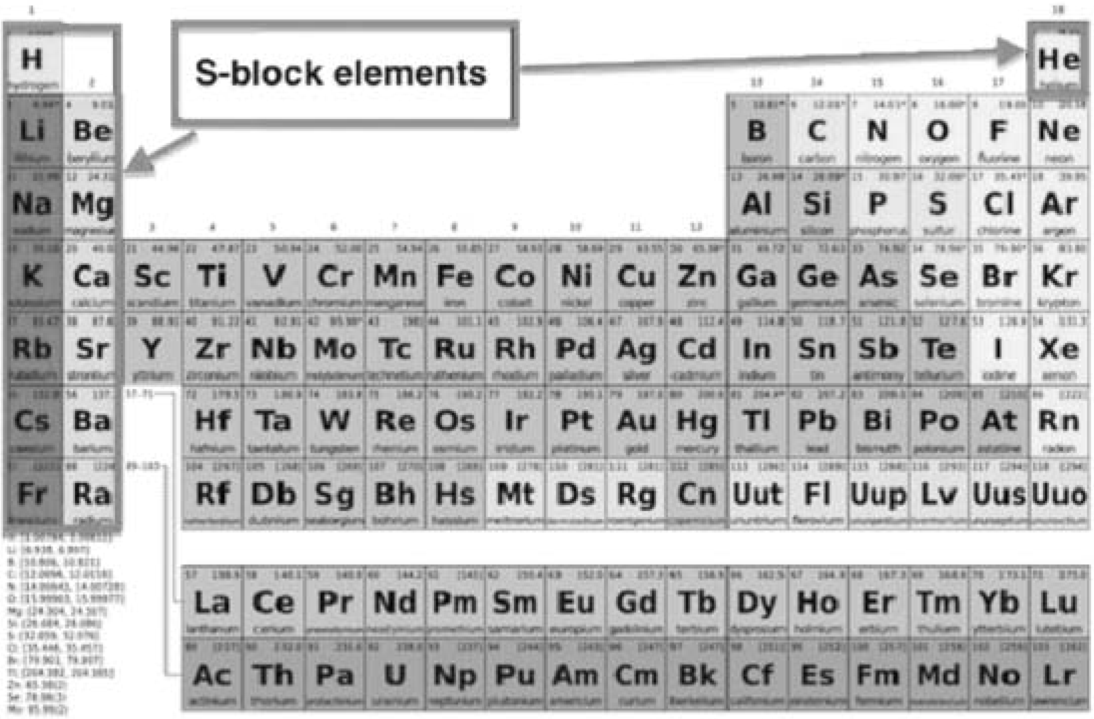
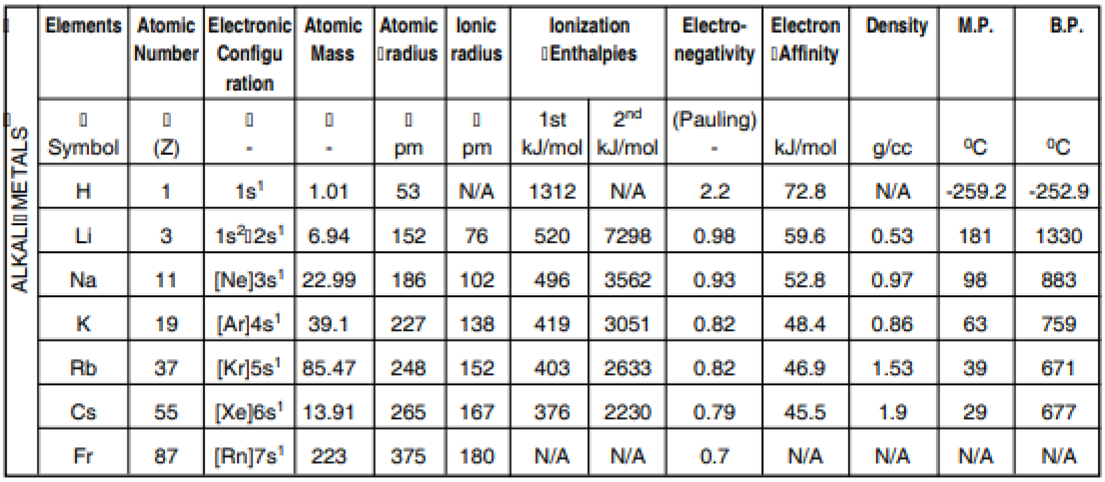
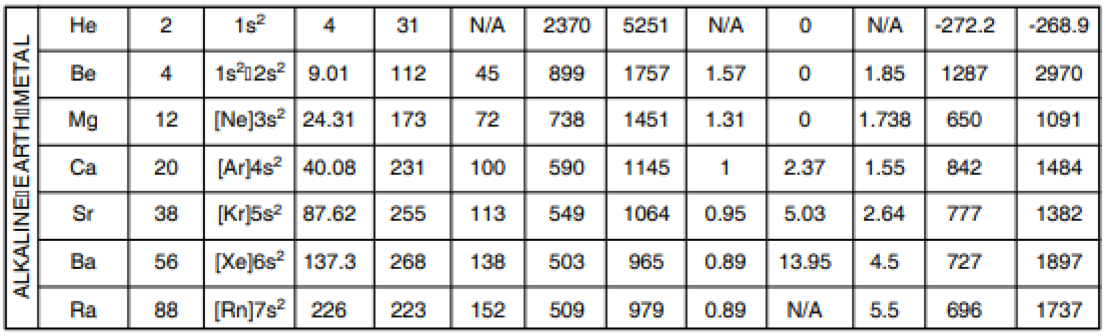


Table: Details of elements belong to *s*-block of the periodic table



	Elements	Atomic Number	Electronic Configuration	Atomic Mass	Atomic radius	Ionic radius	Ionization Enthalpies		Electro-negativity	Electron Affinity	Density	M.P.	B.P.
ALKALI METALS	Symbol	(Z)	-	-	pm	pm	1st kJ/mol	2nd kJ/mol	(Pauling) -	kJ/mol	g/cc	°C	°C
	H	1	$1s^1$	1.01	53	N/A	1312	N/A	2.2	72.8	N/A	-259.2	-252.9
	Li	3	$1s^2 2s^1$	6.94	152	76	520	7298	0.98	59.6	0.53	181	1330
	Na	11	$[Ne]3s^1$	22.99	186	102	496	3562	0.93	52.8	0.97	98	883
	K	19	$[Ar]4s^1$	39.1	227	138	419	3051	0.82	48.4	0.86	63	759
	Rb	37	$[Kr]5s^1$	85.47	248	152	403	2633	0.82	46.9	1.53	39	671
	Cs	55	$[Xe]6s^1$	13.91	265	167	376	2230	0.79	45.5	1.9	29	677
	Fr	87	$[Rn]7s^1$	223	375	180	N/A	N/A	0.7	N/A	N/A	N/A	N/A



ALKALINE EARTH METAL	He	2	$1s^2$	4	31	N/A	2370	5251	N/A	0	N/A	-272.2	-268.9
	Be	4	$1s^2 2s^2$	9.01	112	45	899	1757	1.57	0	1.85	1287	2970
	Mg	12	$[Ne]3s^2$	24.31	173	72	738	1451	1.31	0	1.738	650	1091
	Ca	20	$[Ar]4s^2$	40.08	231	100	590	1145	1	2.37	1.55	842	1484
	Sr	38	$[Kr]5s^2$	87.62	255	113	549	1064	0.95	5.03	2.64	777	1382
	Ba	56	$[Xe]6s^2$	137.3	268	138	503	965	0.89	13.95	4.5	727	1897
	Ra	88	$[Rn]7s^2$	226	223	152	509	979	0.89	N/A	5.5	696	1737

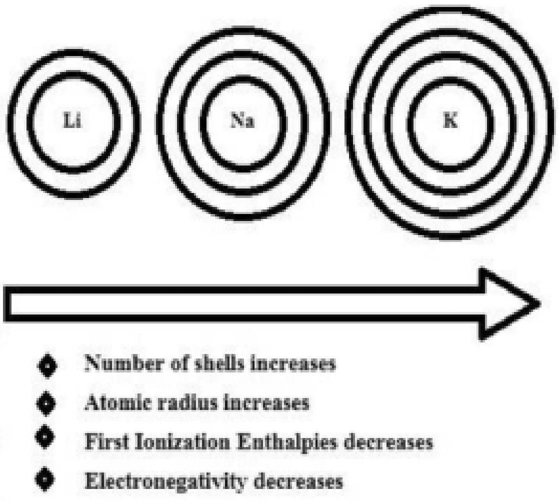
H and He are exceptional, not behaving like the other elements of this block. Fr and Ra are radioactive elements.

The general electronic configuration of the outermost shell of s-block elements: ns^1 or ns^2. There are 14 elements in the S block. S block elements with ns^1 configuration are known as alkali metals and those with ns^2 configuration are known as alkaline earth metals. They belong to the Group 1 and Group 2 in the modern periodic table (with 18 Groups).

6.2 General Periodic Properties of s and p-block elements

The periodic table is organized in a way that reflects the periodicity of elements, especially in the s- and p-blocks, based on their electronic configurations.

Atomic radius and ionic radius: Atomic and ionic radii of the elements increase down the group as new shells are added. Ionic radii are lower than the corresponding atomic radii due to formation of cation, i.e., radius of M-atom is greater than the M^+ (for group 1) or M^{++} ion (for group 2).



Ionization enthalpy: It is the amount of energy required to remove an electron from the outermost shell of a gaseous atom. According to the general electronic configuration they possess one (for group 1) or two (for group 2) electrons in the outer most shell as compared to the nearest inert gas. Therefore the electron in the last orbital is loosely held by the nucleus. If a group 1 element loses the outermost electron then it will get the stable electronic configuration like the nearest inert gas. As a result the first ionisation enthalpies are lower as compared to the other blocks. But the second ionisation enthalpies of the group 1 elements are extremely high because removal of another electron from the stable filled shell is very difficult.

Again for group 2 elements second ionisation enthalpies are higher than the first ionisation enthalpies. Since, loosing of one electron will make the atom positively charged ion so the 2nd electron can be removed by overcoming the strong force of nucleus of the positively charged ion. But the values are relatively less than the 2nd ionisation enthalpies of the group 1 elements as they are getting the electronic configuration of the nearest inert gas after removal of the second electron.

Now down the group ionisation enthalpies decreases in both group 1 and 2.

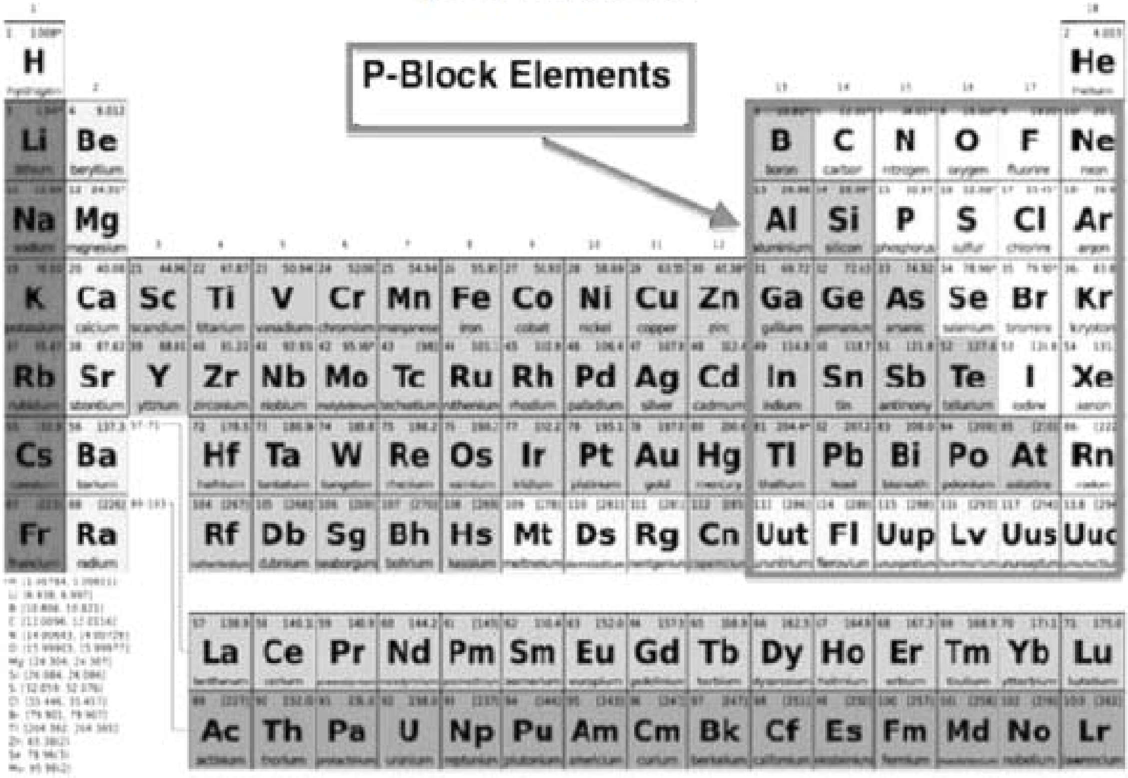
Electron affinity: Electron affinity is the energy released due addition of one extra electron to the atom in gaseous state. Down the group electron affinity decreases as the outer most shell is going far away from the nucleus down the group.

Metal non metal character: Metallic character down the group increases.

Electronegativity: Electronegativity of an element is the power of the atom of that element in a covalent compound to attract the shared bonded pair of electrons towards itself.

Electronegativity down the group decreases as the effective nuclear charge (as well as the power of attraction of the nucleus to the shared bond pair) decreases.

p-Block Elements



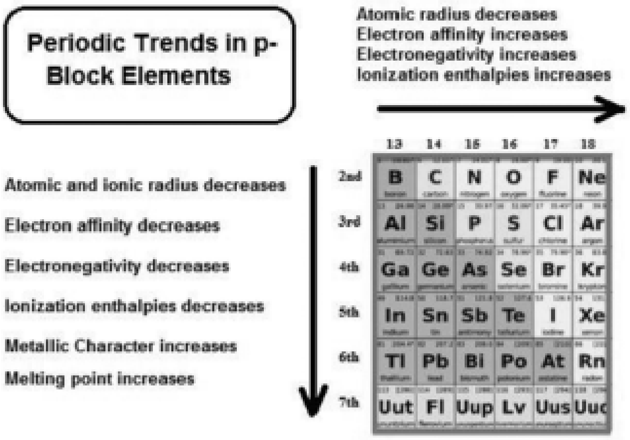
The elements with incomplete or complete *p*-orbital as their outermost orbital are known as p-block elements. General electronic configuration of the p-block elements is : ns^2, np^{1-6}. Six groups from group 13 to group 18 of the periodic table constitute the p-block elements.

The elements with general electronic configuration

General electronic configuration	First member of the group	Name of the family	Position in the periodic table
ns^2, np^1	Boron	Boron Family	Group 13 elements
ns^2, np^2	Carbon	Carbon Family	Group 14 elements
ns^2, np^3	Nitrogen	Nitrogen Family	Group 15 elements
ns^2, np^4	Oxygen	Oxygen Family	Group 16 elements
ns^2, np^5	Fluorine	Halogens	Group 17 elements
ns^2, np^6	Helium	Noble gases	Group 18 elements

For the 4th period elements ($n = 4$), add $3d^{10}$; 5th period element ($n = 5$), add $4d^{10}$; finally for the 6th period elements ($n = 6$), add $4f^{14}\ 5d^{10}$ after the electronic configuration of the last inert gas.

By putting the value of n as number of periods then we can get the electronic configuration of each element of these families. As for example, electronic configuration of Ga (4th period of boron family so $n = 4$) [Ar] $3d^{10}\ 4s^2\ 4p^1$. In this way we can write the electronic configuration of each element of *p*-block elements.



Atomic radius: In the same period from left to right electrons are added to the same energy level (*p*-orbital) and number of protons increases in the nucleus (Z_{eff} increases) as a result, atomic radius decreases due to increase of attraction force. But down the group electrons are added to the next shell, therefore, atomic radius increases.

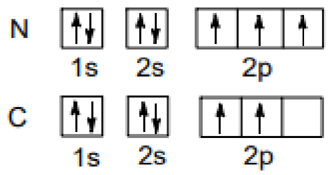
Ionic radius: For cation ionic radius decreases compared to the neutral atom and for anion ionic radius increases compared to the neutral atom.

Electron affinity: Along the period from left to right electron affinity generally increases. Down the group electron affinity generally decreases. For the noble gases electron affinity tends to zero as they have the most stable electronic configuration.

Exceptional cases :

Exception to this is also observed in case of F and Cl. As the gain of electron is easy for the larger Cl-atom compared to the small size fluorine atom. Because the addition of extra electron to the small sized F-atom leads to high electronic repulsion compared to the larger Cl-atom.

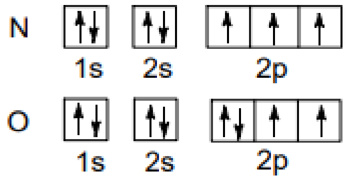
Electron affinity of carbon is greater than nitrogen.



Since half filled or fulfilled shells are more stable than incompletely filled shells. Here gaining of one electron will make the p-orbital half filled for the carbon atom hence it has greater electron affinity than that of nitrogen.

Ionization enthalpies: Along the group from left to right ionization enthalpies increase because size of the atom decreases and effective nuclear charge increases therefore over all attraction of outer electron by the nucleus increases. Whereas down the group ionisation enthalpies decreased as the size of the atom increases control of nucleus over the outermost electron decreases. So, energy required to remove the outermost electron will be low.

Exceptional cases:



Oxygen has lower ionization enthalpy than nitrogen. This is due to stable half filled p-orbitals of nitrogen. Removal of electron from nitrogen atom requires to break the stable half filled p-subshells where as removal of electron from oxygen atom makes to achieve the stable half filled electronic configuration.

Due to poor shielding of *d* and *f* orbitals the ionization enthalpies of boron family increases as follows: B>Tl>Ga>Al>In [shielding order of the orbitals $4f > 5d > 3d$]

B: [He] $2s^22p^1$

Al: [Ne] $3s^23p^1$

Ga: [Ar] $\mathbf{3d^{10}}4s^24p^1$

In: [Kr] $\mathbf{4d^{10}}5s^25p^1$

Tl: [Xe] $\mathbf{4f^{14}5d^{10}}6s^26p^1$

Metallic properties: Along the period from left to right metallic character decreases as tendency to accept electron to form negative ion (to achieve the electronic configuration of nearest inert gas) increases. Down the group as the atomic masses increases the metallic character increases. If we move diagonally then we will get both metallic and non-metallic character i.e., metalloids. In this *p*-block there are metals, non-metals and metalloids (they are indicated by different colours in above diagram).

Electronegativity: In a period left to right electronegativity increases. This is because of increase of effective nuclear charge. But down the group electronegativity decreases as the size of the atom down the group increases.

6.3 Atomic and ionic size

s-block Elements: Atomic size increases down the group due to the addition of electron shells. For example, lithium is smaller than cesium.

p-block Elements: Atomic size generally increases down a group as well, but there is a more complex trend across periods. Across a period from left to right, atomic size decreases due to increased nuclear charge pulling electrons closer.

Ionic Size:

Cations: When s and p block elements lose electrons to form cations, their ionic size decreases compared to their atomic size because of the reduced electron-electron repulsion and increased effective nuclear charge.

Anions: Conversely, when these elements gain electrons to form anions, their ionic size increases due to added electron-electron repulsion.

6.4 Electronegativity (Pauling, Mulliken, and Alfred-Rochow scales)

Electronegativity is a chemical property that describes an atom's ability to attract and hold onto electrons within a chemical bond. It is a dimensionless quantity, and the most common scale for measuring electronegativity is the **Pauling scale**, developed by Linus Pauling.

Key Points About Electronegativity:

Trends in the Periodic Table:

- Across a Period: Electronegativity increases from left to right across a period because atoms become smaller, and the effective nuclear charge increases, which strengthens the atom’s ability to attract electrons.
- Down a Group: Electronegativity decreases as you move down a group because atomic size increases, and the outer electrons are farther from the nucleus, reducing the atom's ability to attract electrons.

Most Electronegative Element: Fluorine (F) is the most electronegative element, with a value of 3.98 on the Pauling scale.

Influence on Bond Type:

- Nonpolar Covalent Bonds: When two atoms with similar electronegativities bond, they share electrons more equally.

- Polar Covalent Bonds: If the difference in electronegativity between two bonded atoms is moderate, the bond becomes polar, where one atom attracts the shared electrons more strongly.
- Ionic Bonds: A large difference in electronegativity typically results in ionic bonding, where one atom fully transfers electrons to the other.

Electronegativity Scale:

Linus Pauling in 1832 first proposed a method to measure the electronegativity of an element. This scale of measurement of electronegativity is known as Pauling Scale. According to Pauling absolute value of electronegativity is a non-measurable quantity. Therefore, he proposed a formula to measure the difference of electronegativity of two elements. If A and B are two elements (which can form AB compound) then the difference of electronegativity of A and B will be as follows:

$$|X_A - X_B| = 0.102\sqrt{E_{A-B} - (E_{A-A} - E_{B-B})^{1/2}}$$

E_d(AA), E_d(BB) and E_d(AB) are the bond dissociation energies of A-A, B-B and A-B bonds in eV respectively. To make the electronegativity dimensionless quantity RHS of the equation is multiplied by $(eV)^{-1//2}$. [where 1eV = 1.602×10^{-19} Coulomb × 1 Volt = 1.602×10^{-19} J]

Now to get the actual value of the electronegativity of any element the electronegativity of the other element should be assigned a certain value. Pauling arbitrarily assigned the electronegativity value of fluorine atom as 4.0. Now if we apply the above formula for HF molecule and use the electronegativity value of F atom as 4.0 then electronegativity of H atom can be determined easily. In this way electronegativity of all the elements were calculated.

Mulliken Scale:

Robert S. Mulliken measured the electronegativity of an element as the arithmetic mean of the ionisation energy and electron affinity of that element.

$$\chi = \frac{E_i + E_{ea}}{2} \text{ (Both in eV).}$$

As Pauling scale of electronegativity is the most popular scale of electronegativity hence the value of electronegativity obtained from Mulliken scale should be fitted with Pauling scale. The conversion equation is as follows:

$$\chi_{\text{Pauling}} = 0.374\, \chi_{\text{Mulliken}} + 0.17$$

Limitations of Mulliken's method: For most of the elements electron affinity and values are not known hence electronegativity can not be determined for most of the elements.

Alfred-Rochow Scale:

A Louise Alfred and Eugene G. Rochow proposed that electronegativity of an element is proportional to the effective nuclear charge of its atom and inversely proportional to the square of the covalent radius (i.e, distance).

$$\chi \propto \frac{Z_{eff}.e^2}{r^2_{\text{cov}}}$$

Equation to convert the electronegativity value into Pauling's scale is given below:

$$\chi_{\text{Pauling}} = 3590\,\chi \propto \frac{Z_{eff}}{r^2_{\text{cov}}} + 0.744$$

[Calculation of effective nuclear charge is done with help of Slater's rule:

Effective nuclear charge (Z_{eff}) = Atomic number(Z) - screening constant(ó)

To find out the screening constant, write down the electronic configuration of the element in following order and grouping:

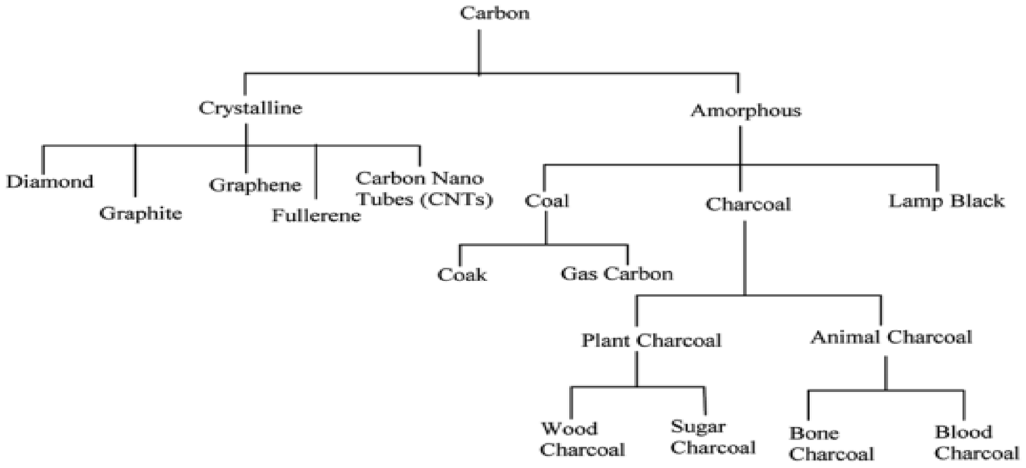
(1*s*) (2*s* 2p) (3s 3p) (3d) (4s 4p) (4d) (4f) (5s 5p) (5d) (6s)

	(*n*-2) or lower orbital (*s*, *p*)	(*n*-1)s, (*n*-1)*p*, (*n*-1)*d* orbital	(*n*)*s* or (*n*)*p* orbital	(*n*)*d* orbital or (*n*)*f* orbital
Last electron residing in *s* or *p* orbital	1	0.85	0.35	-
Last electron residing in *d* or *f* orbital	1	1	1	0.35

6.5 Allotropy in C, S, and P

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.

$Na_2CO_3 + C = Na_2O + 2CO$ $\qquad$ $2C + O_2 + 2F_2 = CO_2 + CF_4$

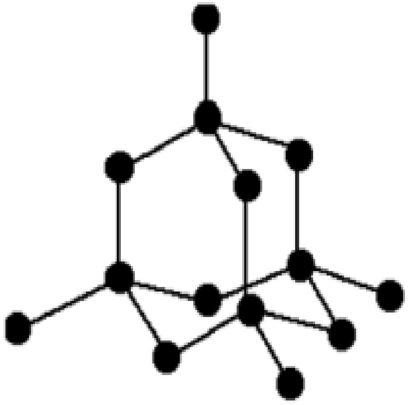
Structure of diamond: Structural information of the diamond was obtained from the X-ray diffraction studies of its single crystal. It forms a cubic crystal where each carbon atom is sp^3 hybridized and is attached to four other carbon atoms with a single bond to form the entire three dimensional networks. C-C bond distance is 1.54Å.

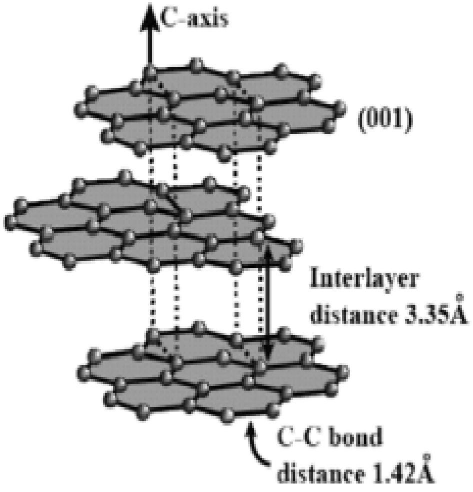
The melting point and boiling point of diamond is very high because of this sigma bonding network. Melting and boiling requires breaking of these strong sigma bonds which require huge energy.

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.

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.





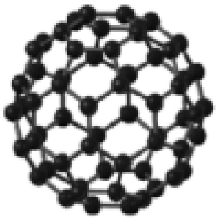
Graphene: Graphene is a super thin, super strong and transparent crystalline allotrope of carbon with. Its carbon atoms are densely packed in a regular hexagonal honeycomb pattern like graphite. It is conductive and self-repairing material. Each atom has four bonds, one σ-bond with each of its three neighbours and one π-bond that is oriented out of plane.

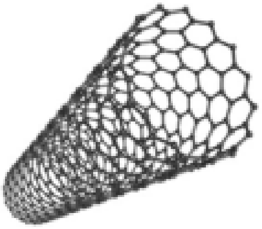
Fullerene: This is the spherical shaped allotrope of carbon characterized first in 1985. The molecular formula of the first reported fullerene is C_{60}, where 60 carbon atoms are arranged in 20 six-memebered and 12 five-memebered rings to from a football or a bucky ball like shape. Buckminster used 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.

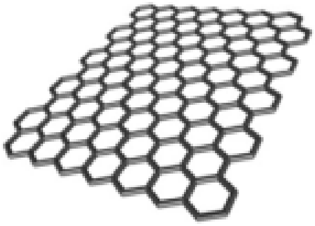
Thin films of C_{60} are mustard-coloured but in bulk it appears dark brown. Films of C_{70} are red-brown and grey-black in bulk. Solution of C_{60} is magenta coloured where as the C_{70} solution is dull-red. Both the solids have very high melting points they dissolve slowly in organic solvent only. 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.

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. In1991 a Japanese scientist Sumio Iijima first discovered the carbon nanotubes. The outer radius of the carbon nanotubes may vary from 1-30 nm.







Allotropes of Phosphorous:

Several allotropic forms of solid phosphorous exist. White, red and black phosphorous are most common of them.

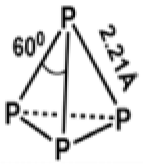
White phosphrous: The most common form of solid phosphorous is white phosphorous. It is waxy solid with melting point 44°C and boiling point 287°C; density 1.82 g/cc. It becomes yellow on exposure to light. White phosphrous is insoluble in water but soluble in organic and non-aqueous solvents like CS_2, benzene, liquid NH_3, SO_2, PCl_3 and $POCl_3$. It is highly poisonous. It is the most reactive form of phosphorous. It emits greenish glow on exposure to air. It ignites spontaneously in above 50°C.

Structure of white phosphorous: Four P-atoms are bonded together symmetrically to form a tetrahedral P_4 unit. The P-P bond distances are 2.21Å and interbond angles are 60°.

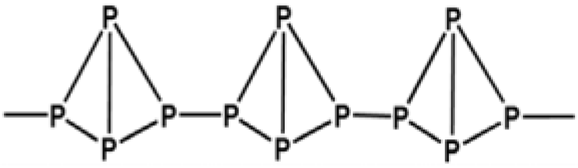
Red phosphrous: It less reactive than white phosphorous, non-poisonous and insoluble in organic solvents. Its density is higher than the white phosphorous (~2.16 g/cc).

Red phosphorous is obtained by heating (270-300^{0}C) white phosphorous in absence of air. It ignites in air only at above 250^{0}C.

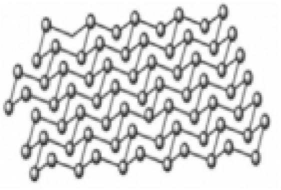
Its structure is a polymeric chain of tetrahedrally structured P_4 molecules in which one of the P-P bonds are broken to enable the linking of these tetrahedrons.



White phosphorous



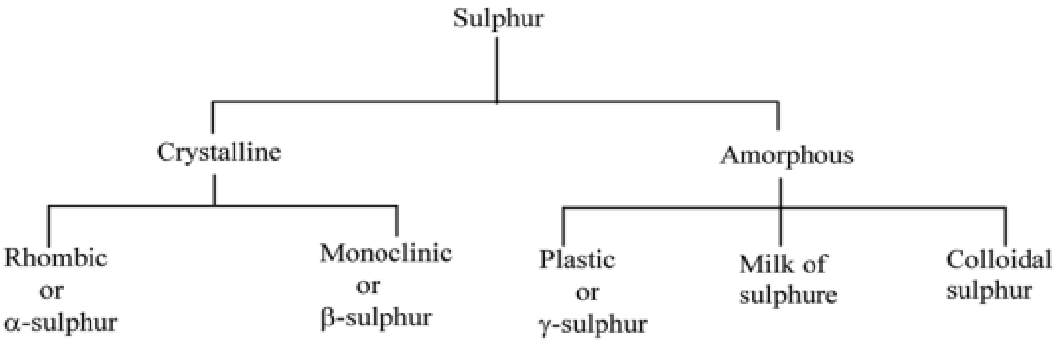
Red phosphorous



Black phosphorous

Black phosphrous: This is the least reactive allotrope of phosphrous. It forms by heating the white phosphorous above 200°C under high pressure. The structure of the black phosphorous resembles with the structure of graphite and it has semiconducting properties. The shortest distance between the layers is 3.9Å and the bond angles are about 100°. Black phosphorous does not ignite in air even above 400°C.

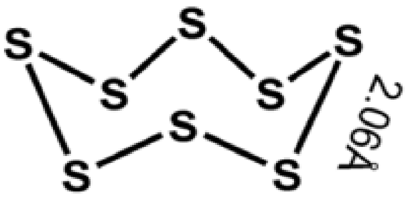
Allotropes of Sulphur:

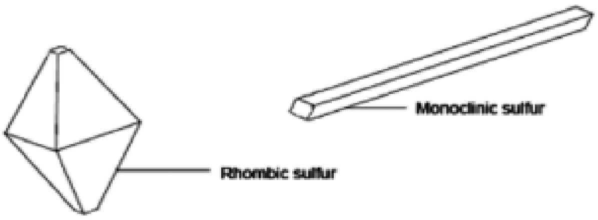


Rhombic sulphur: It is the most stable form of sulphur with melting point 112.8°C. Its density is 2.06 g/cc and it is highly soluble in CS_2.

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.





Oxidation states with reference to elements in unusual and rare oxidation states like carbides and nitrides

Period	Gr.IA	Gr.IIA	Gr.IIIA	Gr.IVA	Gr.VA	Gr.VIA	Gr.VIIA
1	**+1**, -1						
2	**+1**	**+2**	**+3**	**+4** to **-4**	**+5**, +4, **+3**, +2, +1, -3	**-2**, -1, -0.5, +1, +2	**-1**
3	**+1**	**+2**	**+3**, +2, +1	**+4** to **-4**	**+5**, **+3**, -3	+6, +4, **-2**	+7, +5, +3, +1, **-1**
4	**+1**	**+2**	**+3**, +1	**+4**, +2	**+5**, **+3**	+6, +4, **-2**	+7, +5, +4, +3, +1, **-1**
5	**+1**	**+2**	**+3**, +1	**+4**, +2	**+5**, **+3**	+6, +4, **-2**	+7, +5, +3, +1, **-1**

Table: Showing the common and other possible oxidation states of the elements

6.6 Oxidation states with reference to elements in unusual and rare oxidation states like carbides and nitrides)

Oxidation states of elements can vary significantly, especially in compounds like carbides and nitrides, where elements exhibit unusual or rare oxidation states that don't align with typical valency rules. Here's a breakdown of some notable examples:

Carbides:

Carbides are compounds of carbon with a more electropositive element. Carbon exhibits unusual oxidation states in various types of carbides:

1. Ionic Carbides (e.g., Calcium Carbide – CaC_2):
   - In CaC_2 , calcium is in the +2-oxidation state, and carbon in the carbide ion $C_2{}^{2-}$ has an oxidation state of -1.
   - The $C_2{}^{2-}$ ion resembles the acetylide anion, where the two carbon atoms are triple-bonded.
2. Covalent Carbides (e.g., Silicon Carbide – SiC):

   Silicon carbide (SiC) has a more covalent nature. Silicon typically has an oxidation state of +4, while carbon in this compound is considered to be -4, an unusually low oxidation state for carbon.
3. Metallic Carbides (e.g., Tungsten Carbide – WC):

   In WC, tungsten is in a +4 state, and carbon is in -4, though the bonding is more metallic and covalent in nature rather than purely ionic.

Nitrides:

Nitrides are compounds of nitrogen with less electronegative elements. Nitrogen typically has a wide range of oxidation states in these compounds, including rare states like -3 and +5.

1. Ionic Nitrides (e.g., Lithium Nitride – Li_3N):

   In Li_3N, lithium is in the +1-oxidation state, and nitrogen is in the unusual -3 oxidation state. The nitride ion (N^{3-}) indicates nitrogen's ability to gain three electrons, forming a stable ionic compound.
2. Covalent Nitrides (e.g., Boron Nitride – BN):

   Boron nitride (BN) is isoelectronic with carbon and resembles graphite in structure. Boron has a +3-oxidation state, while nitrogen is -3, although the bonding here is covalent.
3. Metallic Nitrides (e.g., Titanium Nitride – TiN):

In TiN, titanium is typically considered to be in a +3-oxidation state, while nitrogen is again in the -3-oxidation state. These nitrides have metallic conductivity due to delocalized electrons.

Rare Oxidation States:

1. Carbides with Zero Oxidation State for Carbon:

   In some metal carbides like $_4$AC_3 , carbon appears to be in a -4 state. However, considering resonance or delocalization, the formal oxidation state may not fully describe the bonding, which often includes contributions from metallic bonding.

2. Nitrides with High Oxidation States for Metals:

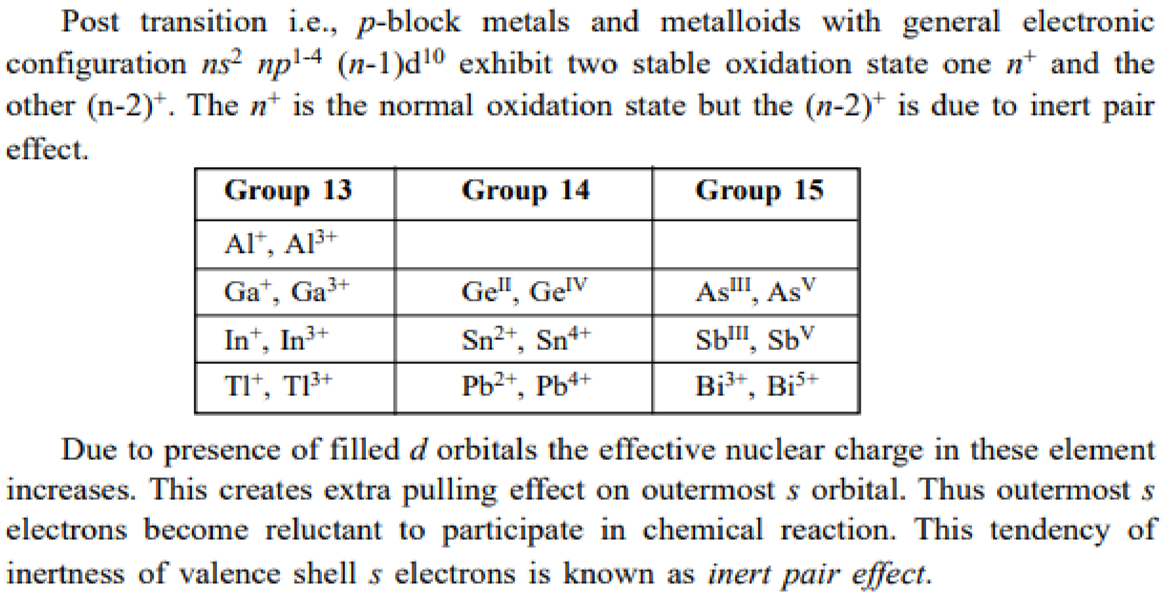
   In transition metal nitrides, the metals can show unusual oxidation states. For instance, in Vanadium Nitride (VN), vanadium can be considered as having a +3 or even higher oxidation states due to its ability to form multi-bonded interactions with nitrogen.

Applications and Stability:

Carbides: Carbides are often extremely hard materials with high melting points. Tungsten carbide (WC), for instance, is used in cutting tools due to its hardness.

Nitrides: Nitrides are used in ceramics and semiconductors. Gallium Nitride (GaN) is used in LEDs, while Aluminum Nitride (AlN) is important for its high thermal conductivity.

6.7 Inert pair effect



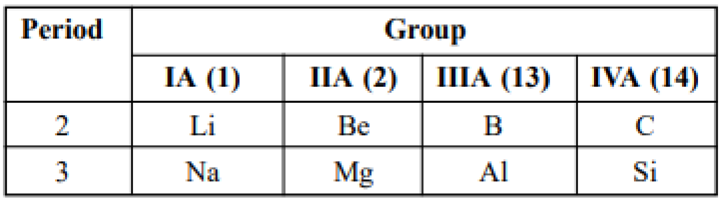
Post transition i.e., *p*-block metals and metalloids with general electronic configuration ns^2 np^{1-4} $(n\text{-}1)d^{10}$ exhibit two stable oxidation state one n^+ and the other $(n\text{-}2)^+$. The n^+ is the normal oxidation state but the $(n\text{-}2)^+$ is due to inert pair effect.

Group 13	Group 14	Group 15
Al^+, Al^{3+}		
Ga^+, Ga^{3+}	Ge^{II}, Ge^{IV}	As^{III}, As^V
In^+, In^{3+}	Sn^{2+}, Sn^{4+}	Sb^{III}, Sb^V
Tl^+, Tl^{3+}	Pb^{2+}, Pb^{4+}	Bi^{3+}, Bi^{5+}

Due to presence of filled *d* orbitals the effective nuclear charge in these element increases. This creates extra pulling effect on outermost *s* orbital. Thus outermost *s* electrons become reluctant to participate in chemical reaction. This tendency of inertness of valence shell *s* electrons is known as *inert pair effect*.

6.8 Diagonal relationship

Diagonal relationship is the similarities of properties observed between the pairs of diagonally placed elements in the second and third periods of the periodic table. Following pairs, Li & Mg, Be & Al, B & Si exhibit similar properties. Chemical properties of elements are guided by the ratio of effective nuclear charge to atomic radius. In a period, from left to right effective nuclear charge increases and down a group, atomic/ionic radius increases. Now, if we move diagonally, the ratio of effective nuclear charge to atomic radius is almost constant. Thus, they exhibit similar properties. This similarity of properties observed between the pairs of diagonally placed elements in the second and third periods of the periodic table is known as diagonal relationship.



Period	Group			
	IA (1)	IIA (2)	IIIA (13)	IVA (14)
2	Li	Be	B	C
3	Na	Mg	Al	Si

Similarities between Li and Mg:

i) Both lithium and magnesium are lighter and harder than other elements in their groups. ii) Both react slowly with water. iii) The carbonates of both the elements decompose easily on heating to form carbon di-oxide along with their corresponding oxides. iv) Both forms nitrides while heating in air. v) The hydroxides of both the elements decompose on heating. vi) Both forms only oxides not peroxide or superoxide.

Similarities between Be and Al:

i) Both have tendency to form covalent compounds. ii) Chloride of both the element i.e., BeC_{l2} and $AlCl_3$ acts a Lewis acid and acts as catalyst in Friedel-Crafts reaction. iii) Both $BeCl_2$ and $AlCl_3$ have chlorine bridged structure in the vapour phase. iv) Both the elements are resistant to acids and form a protective layer of their oxides. v) Both the metals dissolve in strong alkalies to form soluble complexes. vi) Oxides and hydroxides of both the elements are amphoteric in nature. vii) Carbides of both the metals produce methane on reaction with water.

Similarities between B and Si:

i) Both have very high melting and boiling points. ii) Both are non-conductor of electricity iii) Both acts as semiconductor iv) Both exist amorphous and crystalline forms. v) Both do not form cations. vi) Both form weak acids (H_3BO_3& H_4SiO_4).

6.9 Anomalous behaviour of first member of each group

The anomalous behavior of every first element in a group is due to following reasons: i) The non-availability of d-orbital in their valence shell ii) Exceptional small size iii) High ionization energy iv) High electronegativity v) Large value of ratio of effective nuclear charge to atomic radius. As for example, carbon is the first member of group IV elements, it doesn't have d-orbital like the other members of the group, so it can't expand its valency more than 4.

6.10 Summary

In this chapter the periodic variations of general properties s-block elements are shown with numerical data. The variations of the properties with suitable reasons are presented here. The allotropies of carbon, sulphur and phosphorous are discussed with proper structures and properties. The diagonal relationships show by the elements Li & Mg; Be & Al; and B & Si are explained in this unit. The reasons behind the anomalous behaviours of first member of each group are specified in this chapter.

Atomic and Ionic Size

Atomic and ionic sizes generally increase down a group due to the addition of electron shells. However, they decrease across a period due to increased nuclear charge, which pulls electrons closer to the nucleus.

Electronegativity

Electronegativity measures an atom's ability to attract electrons. Various scales exist:

Pauling Scale: Based on bond energies; values are dimensionless.

Mulliken Scale: Average of ionization energy and electron affinity.

Alfred-Rochow Scale: Considers atomic radii and charge, providing a different perspective on electronegativity.

Allotropy in C, S, and P

Elements like carbon, sulfur, and phosphorus exhibit allotropy, meaning they can exist in different structural forms. For example, carbon has diamond and graphite forms, while sulfur has several crystalline forms (e.g., rhombic and monoclinic). Phosphorus has white, red, and black allotropes.

Oxidation States

Elements in the s and p blocks can exhibit various oxidation states. Uncommon oxidation states, such as those found in carbides (C^{4-}) and nitrides (N^{3-}), highlight the versatility of these elements in forming compounds.

Inert Pair Effect

The inert pair effect refers to the tendency of the s-electrons in the heavier p-block elements to remain unshared, resulting in lower oxidation states than expected. This effect becomes more pronounced down a group.

Diagonal Relationship

Diagonal relationships occur between certain pairs of elements in different groups but the same periods (e.g., Li and Mg, Be and Al). These pairs often display similar chemical properties due to comparable ionic sizes and charges.

Anomalous Behaviour of First Member of Each Group

The first element of each group (e.g., Li, Be, B, C, N) often shows distinct properties compared to heavier members. This anomaly is due to smaller atomic size, higher electronegativity, and unique bonding characteristics, resulting in behavior that deviates from periodic trends.

6.11 Sample Questions

A. Multiple Choice Type Questions

1. Which of the following statements about atomic size is true?

A) Atomic size decreases across a period due to increased shielding.
B) Atomic size increases down a group due to increased nuclear charge.
C) Atomic size increases down a group due to added electron shells.
D) Atomic size remains constant across a period.
Answer: C

2. What does the Pauling scale measure?

A) Atomic radius
B) Electronegativity
C) Ionization energy
D) Electron affinity
Answer: B

3. Which of the following elements exhibits allotropy?

A) Sodium
B) Chlorine

C) Carbon
D) Argon
Answer: C

4. Which oxidation state is typically found in carbides?

A) +4
B) -4
C) +2
D) -2
Answer: B

5. The inert pair effect is most prominent in which group of elements?

A) Group 1
B) Group 2
C) Group 13
D) Group 14
Answer: B

6. Which of the following pairs of elements demonstrates a diagonal relationship?

A) Li and Na
B) Be and Al
C) N and O
D) C and Si
Answer: B

7. Which of the following statements is true regarding the first member of a group?

A) They exhibit higher oxidation states than heavier members.
B) They show similar properties to their heavier counterparts.
C) They often have unique bonding characteristics.
D) They have larger atomic radii than the second member.
Answer: C

8. What is the common allotrope of sulfur?

A) Graphite
B) Diamond
C) Rhombic
D) Amorphous
Answer: C

9. Which scale for electronegativity considers both ionization energy and electron affinity?

A) Pauling Scale
B) Mulliken Scale
C) Alfred-Rochow Scale

D) Lewis Scale
Answer: B

10. In which oxidation state is nitrogen typically found in nitrides?

A) +3
B) -3
C) +5
D) -2
Answer: B

B. Short Type Questions

1. Explain the following:

a) First ionization energy of N-atom is higher than the O-atom.

b) First ionization energy of P-atom is higher than the S-atom.

c) Electron affinity of chlorine is greater than the fluorine.

d) Give the general electronic configuration of s and p block elements.

2. What do you mean by diagonal relationship? Give example.

3. Why Li is as strong a reducing agent as Cs?

4. List the different scales of electronegativity and briefly describe the theoretical basis behind each.

5. Why are the Group I metal soft low melting and of low density?

6. Why and in what ways does lithium resemble magnesium?

7. Define effective nuclear charge.

8. Using Slater's rules, calculate the effective nuclear charge on an electron in each of the orbitals in an atom of potassium.

9. Using Slater's rules, calculate the relative effective nuclear charge on one of the 3d electrons compared to that on one of the 4s electrons for an atom of manganese.

10. Using Slater's rules, calculate the effective nuclear charge on a 3p electron in (a) aluminum and (b) chlorine.

11. Which element should have the higher ionization energy, silicon or phosphorus? Give reason.

12. Which element should have the higher ionization energy, arsenic or phosphorus? Give reason.

13. What is the reason for lithium having a greater tendency to form covalent compounds than the other elements in the group?

14. Which one, in each pair of elements-boron and carbon and carbon and nitrogenwill have the higher second ionization energy? Give your reasoning in each case.

15. Discuss the similarities of chemistry of boron and silicon.

Ans. Similarities between B and Si: i) Both have very high melting and boiling points. ii) Both are non-conductor of electricity iii) Both acts as semiconductor iv) Both exist amorphous and crystalline forms v) Both do not form cations. vi) Both form weak acids (H_3BO_3& H_4SiO_4).

16. Explain the diagonal relationship between beryllium and aluminium.

Ans. Be and Al are diagonally place in the periodic table hence they have following similarities: i) Both have tendency to form covalent compounds. ii) Chloride of both the element i.e., $BeCl_2$ and $AlCl_3$ acts a Lewis acid and acts as catalyst in Friedel-Crafts reaction. iii) Both $BeCl_2$ and $AlCl_3$ have chlorine bridged structure in the vapour phase. iv) Both the elements are resistant to acids and form a protective layer of their oxides. v) Both the metals dissolve in strong alkalies to form soluble complexes. vi) Oxides and hydroxides of both the elements are amphoteric in nature. vii) Carbides of both the metals produce methane on reaction with water.

17. Contrast the properties of the three main allotropes of carbon-diamond, graphite, and C60. 18. What are the factors that distinguish the chemistry of nitrogen from that of the other members of Group 15?

18. What trend is observed in atomic size as you move down a group in the periodic table?

19. Define electronegativity. Why is the Pauling scale significant?

20. Name two allotropes of carbon.

21. What oxidation state is commonly associated with carbides?

22. Explain the inert pair effect in heavier p-block elements.

23. Which two elements demonstrate a diagonal relationship, and what characteristic do they share?

24. List one anomalous behavior of the first member of Group 14.

25. What is the common allotrope of sulfur and how does it differ from its other forms?

26. How does the Mulliken scale differ from the Pauling scale in measuring electronegativity?

27. What is the typical oxidation state of nitrogen in nitrides?

C. Assay Type Questions

1. Discuss the trends in atomic and ionic size across periods and down groups in the periodic table. What factors contribute to these trends, and how do they affect chemical reactivity?
2. Explain the concept of electronegativity and describe the differences between the Pauling, Mulliken, and Alfred-Rochow scales. How do these scales help in understanding chemical bonding?
3. Analyze the phenomenon of allotropy in elements such as carbon, sulfur, and phosphorus. Discuss the significance of different allotropes in terms of their properties and applications.

4. Explore the oxidation states of s and p-block elements, with particular emphasis on unusual oxidation states seen in compounds like carbides and nitrides. What implications do these states have for chemical reactions and compound formation?
5. Describe the inert pair effect and its implications for the chemistry of heavier p-block elements. How does this effect influence the oxidation states and bonding behavior of these elements?
6. Examine the diagonal relationship in the periodic table, providing examples of pairs of elements that exhibit this relationship. Discuss the reasons for their similar properties despite being in different groups.
7. Critically evaluate the anomalous behavior of the first member of each group in the s and p-blocks. What unique properties do they exhibit, and how do these properties differ from their heavier counterparts?
8. Investigate the significance of periodic trends in predicting the behavior of elements in chemical reactions. How do concepts such as atomic size, electronegativity, and oxidation states interplay in determining reactivity?
9. Discuss the various allotropes of sulfur, highlighting their structural differences and physical properties. How do these differences affect their uses in industry and science?
10. Analyze the role of the inert pair effect in the chemical behavior of lead and tin in Group 14. How does this effect contribute to the differences observed in their compounds and reactivity?

6.12 References

1. Inorganic Chemistry by R.L. Dutta 2. Essentials of Physical Chemistry by B.S. Bahl 3. Concise Inorganic Chemistry (4th Edition) by J.D. Lee 4. General and Inorganic Chemistry by P.K. Dutta 5. General and Inorganic Chemistry by R. Sarkar

Unit - 7 ❑ Compounds of s- and p-Block Elements

Structure

7.0 Objectives
7.1 Introduction
7.2 Ionic hydrides
7.3 Covalent hydrides
7.4 Interstitial hydrides
7.5 Hydrides of nitrogen
7.6 Hydroxyl Amine
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7.8 Sulfoxilic acid
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7.16 Perchloric acid
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7.18 Phosphorous Pentachloride
7.19 Thionyl chloride
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7.0 Objectives

After reading this unit learners should able to know:

- The definition of hydride and their classification
- Definition, characteristics and preparations of ionic hydride, covalent hydride and interstitial hydride.
- Synthesis of ammonia, hydrazine, hydrazoic acid and hydroxyl amine.
- Chemistry of oxyacids of phosphorous.
- Chemistry of oxyacids of sulphur acids.

7.1 Introduction

When hydrogen is combined with any other elements to form a compound then that compound is known as hydride. Hydrides are classified into three major categories namely, ionic, covalent and interstitial hydrides.

7.2 Ionic hydrides

In this type of compound hydrogen combines with more electropositive elements like, Li, Na, Ca, Sr, Ba etc. Preparation: They are mainly prepared by heating hydrogen with that element or by heating the azide salt of group IA elements (alkali and alkaline earth metals) with hydrogen. Properties: Ionic hydrides are crystalline solid and they form rock salt. They have higher melting and boiling point and conduct electricity in fused state. Hydrogen is released at the cathode on electrolysis under molten state. Thermal stability increases on increasing size of cation.

The thermal stability decreases in following order: $LiH > NaH > KH > RbH > CsH$.

MH_2 is more stable than MH. Ionic hydrides are always formed in stoichiometric ratio and their heat of formation is very high.

Density of hydride is more than their corresponding metal. Ionic hydrides are hydrolyzed in proton containing solvents and produce hydrogen gas.

Ionic hydrides are very strong reducing agent. $SiCl_4 + 4NaH = SiH_4 + 4NaCl$ Order of reactivity of the hydrides is as follows: $LiH < NaH < KH < RbH < CsH$. Ionic hydrides are Lewis base due to presence of hydride ($H^–$) ion. LiH is soluble in ether and used as reducing agent in organic reactions. Calcium hydride is also known as hydrolyth.

These hydrides react violently with water to release hydrogen gas. $MH + H_2O = MOH + H_2$ On heating they decompose readily and release hydrogen gas; hydrogen gas ignites spontaneously hence they are used as solid fuel.

7.3 Covalent hydrides

Generally, the compounds formed by the Group IVA, VA, VIA and VIIA elements (non-metals and more electronegative than hydrogen) along with boron (B) and aluminium (Al) with hydrogen are known as covalent hydrides.

Preparation:

i) By reduction of covalent chlorides using $LiAlH_4$ in ether medium.

$SiCl_4 + 4LiAlH_4 = SiH_4 + 4LiCl + 4AlH_3$

ii) By the reduction of metal alkyls with hydrogen.

$Zn(CH_3)_2 + H_2 = ZnH_2 + 2CH_4$

iii) By the reaction of Mg_3X_2 (X= N, P, As, Sb etc) with dil. HCl

$Mg_3X_2 + 6HCl = 3MgCl_2 + 2XH_3$

iv) iv) By the hydrolysis of covalent halides.

$PX_3 + 3H_2O = H_3PO_3 + 3XH$

Properties: Generally, melting and boiling points of these hydrides are less, except those participating in hydrogen bonding. Like ionic hydrides covalent hydrides are reducing agent. Down a group reducing property increases. Thermal stability decreases down a group because orbital overlap of X-H bond decreases down the group.

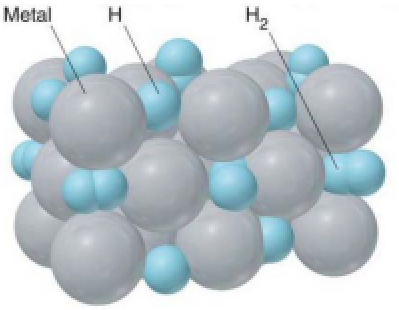
7.4 Interstitial hydrides

Transition elements (*d*- and *f*-block elements) having electronegativity between 1.2 and 1.4 form such hydrides. On heating transition metal with dihydrogen under pressure, hydrogen atoms being smaller in size occupies the gap or interstices inside metal lattice, hence they are called as interstitial hydrides. They are always formed in non-stoichiometric ratio and their general formula is MH_x (where x is always a fraction). The formula of interstitial hydride formed by palladium is $PdH_{0.7}$. The ratio of hydrogen atoms to the metal atoms in these hydrides is not fixed but changes depending on heat and pressure.

Preparation:

i) By adsorption of hydrogen gas directly

ii) By the electrolytic reduction of metal oxides using Pb cathode.



Properties: They are harder than their corresponding metals. They conduct electricity in solid state and have magnetic properties.

The density of these hydrides is less than their corresponding metals. This is because of the little expansion of lattice after inclusion of hydrogen.

Uses:

i) These hydrides are used as reducing agent in catalytic reduction or hydrogenation reactions for the synthesis of useful organic molecules.

ii) Palladium can absorb 935 times of its own volume of hydrogen gas under suitable condition. This process may be used to separate isotopes of hydrogen.

iii) These hydrides are acted as storage of hydrogen fuel.

7.5 Hydrides of nitrogen

Laboratory method of preparation of ammonia: By heating ammonium salt with any base (more basic than ammonia) like $Ca(OH)_2$.

Reaction:

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} 2NH_3 + CaCl_2 + 2H_2O$$

Other methods of preparation of ammonia:

Industrial method of preparation of ammonia:

Haber's process **:** Industrially ammonia is prepared by Haber's process. It is prepared by the reaction of nitrogen and hydrogen gas at high atmospheric pressure (~250 atm) and high temperature 550°C) in presence of a catalyst.

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta H = -12.2 \text{ kcal/mol}$$

Physico-chemical principle of Haber's process**:** Since this is a reversible reaction, probability of production of maximum ammonia is guided b Le Chatelier's Principle.

Impact of temperature: Since the reaction is exothermic it might be expected that formation of the product will be high at lower temperature but at the same time it should be kept in mind that lower temperature can decrease the rate of the reaction. Therefore, temperature should be fixed in such a way that both rate of reaction remains higher and formation of the product is also remains high. It is observed that the optimum temperature for the formation of ammonia is 550°C.

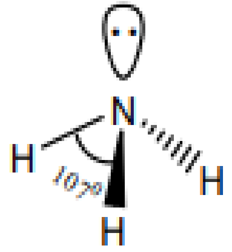
Impact of pressure: Volume is compressed in over all reaction as four molecules of reactant are converted into two molecules of products. Therefore, if pressure is increased then formation of the product will increase. It is observed that the effective pressure for the formation of ammonia is 200 atm.

Role of catalyst: Catalyst can increase or decrease the rate of reaction but it cannot change the state of equilibrium of the reaction. Therefore, role of the catalyst here is to help the reaction to reach equilibrium quickly. A compound of iron is used here as a catalyst and a mixture of Mo or K and aluminium oxide is used as a promoter of the catalyst.

Method of Preparation: Synthesis-gas is kept inside a reaction chamber of chrome-vanadium steel under 200 atm pressure (created with the help of a pump). Mixture of the catalyst and promoter are placed on a porous tray inside the reaction chamber. The reaction chamber is heated around 550° C electrically. 12% ammonia is produced on passing the mixture of gases through the porous tray.

Physical properties : Ammonia is colourless gas with a pungent smell and lighter than air. It has a very high critical temperature (32.5°C) hence can be liquefied very easily. Boiling point is –77.8°C. It is highly soluble in water. 1 ml water can dissolve 1175 ml of ammonia gas at 0°C. It forms hydrogen bond with water molecule in aqueous solution.

Structure of ammonia molecule: Ammonia is a covalent compound. The central nitrogen atom is sp^3 hybridized and each hydrogen atom is connected to the central nitrogen atom through covalent bond forming a pyramidal shape. H—N—H bond angle is about 107°.



Chemical Properties

a) Basic properties: Ammonia is basic in nature. It is a Lewis base.

b) Reducing properties:

c) Hydrogen Bonding

Liquid ammonia:

Application and uses:

Hydrazine : Hydrazine is prepared by the reaction of ammonia and sodium hypochlorite. To avoid unwanted side reactions little amount of gelatin is added.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$

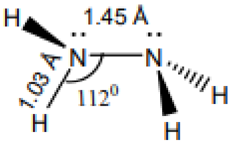
$$NH_3 + NH_2Cl + NaOH \longrightarrow H_2N.NH_2 + NaCl + H_2O$$

Unwanted side reactions :

$$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl$$

$$3NH_2Cl + 2NH_3 \longrightarrow N_2 + 3NH_4Cl$$

Structure of Hydrazine: The structure of the hydrazine can be obtained by replacing one hydrogen atom of ammonia by $-NH_2$ group. Thus the chemical formula of hydrazine becomes $NH_2–NH_2$ and the molecular formula becomes N_2H_4. Each NH_2 unit is pyramidal in nature with H–N–N bond angle of 112°. The N–N and N–H bond distances are about 1.45 Å and 1.03 Å respectively.



Bonding : Each nitrogen atom in hydrazine is sp^3 hybridized. Three single covalent bonds are formed by each nitrogen atom of hydrazine, one each with two hydrogen atoms and one with the other nitrogen atom. One loan pair exists on each nitrogen atom of hydrazine hence it acts as Lewis base.

Physical properties: Pure hydrazine is a colourless fuming hygroscopic liquid. Its b.p. is 114°C and m.p. is 2°C. It is highly soluble in water.

Chemical properties: On combustion in presence of air or oxygen it produces huge amount of heat. Hence, it is used as rocket fuel.

$$N_2H_4 + O_2 = N_2 + 2H_2O \qquad \Delta H = -148.6 \text{ kcal/mol}$$

Redox properties: Oxidation state of nitrogen in hydrazine is —2 hence it can increase its oxidation state (oxidation number) by forming the most stable molecular form of nitrogen i.e., nitrogen gas (oxidation state 0) again its oxidation state can be decreased by forming ammonia (oxidation state —3). Thus it can acts both as reducing agent and oxidizing agent.

Reducing properties: It acts as a strong reducing agent in basic medium whereas in acidic medium it's reducing ability decreases.

$$N_2H_4 + Zn + HCl = 2NH_3 + ZnCl_2$$

Oxidising properties: In acidic medium it acts as oxidising agent.

Basic nature: There are two loan pairs of electrons are present in hydrazine (one each on each nitrogen atom) molecule, hence it acts as a di-acidic base. With HCl it forms mono and di-hydrochloride salt.

$$N_2H_4 + HCl = N_2H_5Cl\,; \qquad N_2H_{5.}Cl + HCl = N_2H_6Cl_2$$

[Reaction with HCl and one complexation reaction.]

Applications in industrial, organic and environmental chemistry

Hydrazoic acid:

Also known as hydrogen azide and azoimide.

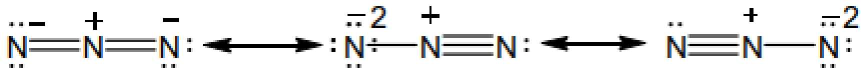
Preparation: Hydrazoic acid is prepared in two steps, in the first step, sodium azide is prepared by heating nitrous oxide with sodamide at 90°C. In step two, the mixture containing the sodium azide is refluxed with dil. H_2SO_4. The solution thus obtained is refluxed again with anhyd. $CaCl_2$.

Physical properties: Pure hydrazoic acid is colourless liquid with strong and very unpleasant smell. Its melting point is –80°C and boiling point is 36°C. Density is 1.09 g/cc. It is highly soluble in water and alcohol and ether.

Chemical properties: It is highly poisonous and explosive in nature. After explosion it produces hydrogen and nitrogen gas with huge heat. Azide salts of Pb, Ba and Hg are used as detonator.

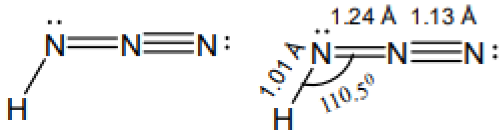
Azide ion has very close similarity with halides hence it is also known as pseudo-halide.

Acidic properties: It is a very weak acid with pK_a value 4.6. After releasing hydrogen ion (H^+) the azide ion is stabilized by resonance.



Structure: bonding and their important properties like oxidation/reduction, acidic/ basic nature

N_3H



7.6 Hydroxyl Amine (NH_2OH)

If one of the hydrogen atoms of ammonia is replaced by – OH radical then it will become the hydroxyl amine.

Preparation: Initially under suitable condition a nitrite salt is reduced by SO_2 to form nitroso di-sulphonic acid then it is hydrolysed by HCl to obtain hydroxylamine hydrochloride.

$$NO_2^- + HSO_3^- \longrightarrow HO_3SNO \xrightarrow{HSO_3^-} \underset{\text{NItroso di-sulphonicacid}}{(HO_3S)_2NOH}$$

$$(HO_3S)_2NOH \xrightarrow{HCl} \underset{\text{Hydroxyl amine hydrochloride}}{NH_2OH.HCl}$$

Physical properties: Pure hydroxyl amine is a colourless liquid. It starts dissociating above 0°C and at around 15°C it produces H_2O, NH_3, N_2O and N_2 under rapid dissociation.

Chemical properties: It is a mono acidic base.

Redox properties: As the oxidation state of nitrogen in hydroxyl amine is —1. It has both oxidizing and reducing properties.

Reduction: In acidic or neutral medium ferric and cupric salts are reduced by NH_2OH to ferrous and cuprous salts respectively.

i) $4FeCl_3 + 2NH_2OH = 4FeCl_2 + N_2O + 4HCl + H_2O$

ii) $2NH_2OH + 4CuO(\text{Fehling's solution}) = 2Cu_2O + N_2O + 2H_2O$

iii) $2NH_2OH + 4HgCl_2 = 2Hg_2Cl_2 + N_2 + 4HCl + H_2O$

iv) $2NH_2OH + 4AgNO_3 = 4Ag + N_2 + 4HNO_3 + H_2O$

Oxidation:

In basic medium:

i) $2Fe(OH)_2 + NH_2OH + H_2O = 2Fe(OH)_3 + NH_3$

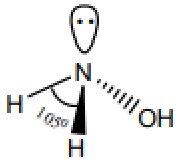
ii) $NH_2OH + H_2O_2 = NH_3 + O_2 + H_2O$

In weak acidic medium:

i) $NH_2OH + 2HI + HCl = I_2 + NH_4Cl + H_2O$

ii) $SnCl_2 + NH_2OH + 3HCl = SnCl_4 + NH_4Cl + H_2O$

Structure: The structure of hydroxyl amine is pyramidal with a lone pair of electrons on central nitrogen atom.



7.7 Oxyacids of Phosphorous

H_3PO_2, H_3PO_3, H_3PO_4, $H_4P_2O_6$, $H_4P_2O_7$, $(HPO_3)_n$

Hypo-phosphorous acid:

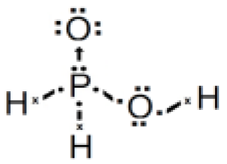
Preparation: Hypo-phosphorous acid is prepared in two steps.

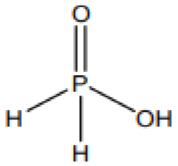
i) In the first step barium hypo-phosphite is preapared by heating red phosphorous with barium hydroxide.

$$8P + 3Ba(OH)_2 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3$$

ii) In step two aqueous solution of hypo-phosphrous acid is obtained by the quantitative addition of dil. H_2SO_4 to the barium-hyposhosphite. The bi-product $BaSO_4$ is precipitated out from the solution.

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2$$

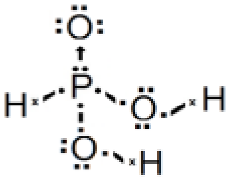


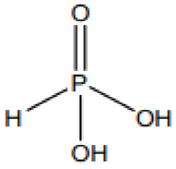


Phosphorous acid:

Preparation: Phosphorous acid is prepared by the hydrolysis of phosphorous trichloride.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$





Phosphorous acid acts as a reducing agent. It reduces sulfurous acid to sulfur.

$$2H_3PO_3 + H_2SO_3 = 2H_3PO_4 + S + H_2O$$

Hypo-phosphoric acid:

Hypo-phosphoric acid is prepared in two steps. In the first step, sodium hypophosphate is prepared by the oxidation of red phosphorous by the alkaline solution of sodiumchlorite.

$$2P + 2NaClO_2 + 2H_2O \longrightarrow Na_2H_2P_2O_6 + 2HCl$$

On heating it disproportionates to H_3PO_3 and HPO_3.

$$H_4P_2O_6 = H_3PO_3 + HPO_3$$

Phosphoric acid: Phosphoric acid is mostly known as orthophosphoric acid.

Preparation:

i) Phosphoric acid is prepared by the oxidation of hot white phosphorous by 1:1 nitric acid.

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

ii) By dissolving phosphorous pentoxide in excess hot water.

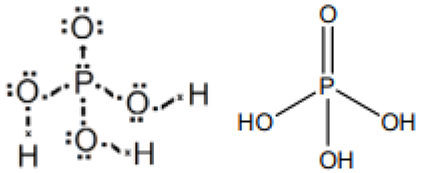
$$P_2O_5 + 3H_2O = 2H_3PO_4$$

iii) From naturally occurring calcium phosphate:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$$

Phosphoric acid is a colorless odorless viscous liquid. Its boiling point is 158°C. Fused phosphoric acid conducts electricity due to autoprotolysis (self-ionization).

$$2H_3PO_4 = H_4PO_4^+ + H_2PO_4^-$$



The oxidation state of phosphorus in phosphoric acid (H_3PO_4) is + 5. Since it cannot increase it beyond 5, it cannot act as a reducing agent. However, it can behave as oxidising agent by decreasing its oxidation state.

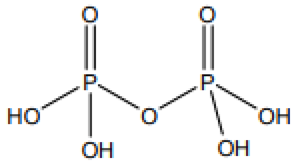
Orthophosphoric acid is used in several industries, agriculture and in our daily life products. phosphoric acid is used commonly in the removal of rust from metals like iron, steel, etc. This acid acts as an acidifying agent in beverage industry i.e., to acidify foods like jams, processed meats, cheese, etc. to keep them away from bacteria and fungi.

Pyro-phosphoric acid:

Preparation: It is prepared by heating phosphoric acid at 250°C – 260°C.

$$2H_3PO_4 = H_4P_2O_7 + H_2O$$

Pure pyro-phosphoric acid is a colorless crystalline solid. Its melting point is 61°C.



Meta-phosphoric acid: It is prepared by heating orthophosphoric acid or pyro-phosphoric acid above 300°C. nH3PO4 = $(HPO_3)_n$ + nH_2O Physical properties: It is colorless crystalline solid with density 2g/cc. The melting point is 200°C and boiling point is 600°C. It is soluble in alcohol but decomposes in water to form orthophosphoric acid.

7.8 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

7.9 Sulfurous acid

It is prepared by passing sulphur-dioxide (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.

7.10 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).

$$H_2SO_3 + Zn/Hg \rightarrow H_2S_2O_4 + ZnO + H_2O.$$

Free acid is not available it is available only in aqueous solution. It is a di-basic acid and a very strong reducing agent

7.11 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.

$$Na_2SO_3 + SO_2 = Na_2S_2O_5$$

7.12 Sulfuric acid

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.

$$SO_2 + O_2\,(air) \xrightarrow[\text{Pt or } V_2O_5]{450°C} SO_3$$

$$SO_2 + H_2O = H_2SO_4$$

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.

7.13 Hypochlorous acid (Cl—OH)

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.

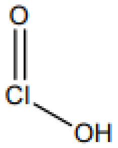
7.14 Chlorous acid

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.

$$4HClO_2 = 2ClO_2 + ClO_3^- + Cl^- + 2H^+ + H_2O$$



7.15 Chloric acid

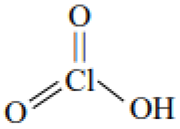
Chloric acid is prepared in similar way that of chlorous acid, barium chlorate is taken instead of barium chlorite.

$Ba(ClO)_3 + H_2SO_4 = BaSO_4 + 2HClO_3$

Its aqueous solution is colorless and odourless. 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.

$$3SO_2 + HClO_3 + 3H_2O = 3H_2SO_4 + HCl$$

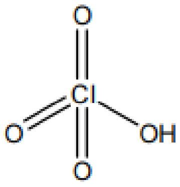


7.16 Perchloric acid

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.

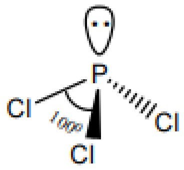


7.17 Phosphorous trichloride

Preparation: It is prepared by the reaction of red phosphorous with chlorine gas (in 1:3 ratio).

$$2P + 3Cl_2 = 2PCl_3$$

Structure of PCl_3: The hybridization of P in PCl_3 is sp^3. The shape of the molecule is pyramidal. The P-Cl bond distance is 2.04Å.



Physical properties: PCl_3 is a fuming liquid. Its boiling point is 76°C.

Chemical properties:

i) In presence of water it readily hydrolyzed to produce H_3PO_3.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

ii) On reaction with conc. H_2SO_4 it produces chlorosulfonic acid, meta-phosphoric acid and sulfur di-oxide.

$$PCl_3 + 2H_2SO_4 = ClSO_3H + HPO_3 + SO_2 + 2HCl$$

iii) On reaction with sulfur tri-oxide (SO_3) it produces phosphoryl chloride ($POCl_3$).

$$PCl_3 + SO_3 = POCl_3 + SO_2$$

iv) On reaction with thionyl chloride it produces thiophosphoryl chloride ($PSCl_3$), phosphoryl chloride ($POCl_3$) and phosphorous pentachloride (PCl_5).

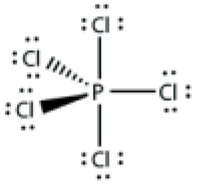
$$3PCl_3 + SOCl_2 = PSCl_3 + POCl_3 + PCl_5$$

7.18 Phosphorous Pentachloride

Preparation: PCl_5 is prepared by the direct reaction of PCl_3 with Cl_2.

$$PCl_3 + Cl_2 = PCl_5$$

Structure of PCl_5: The hybridization of P in PCl_5 is sp^3d. The geometry of the molecule is trigonal bipyramid. The axial and equatorial bond distances are 2.14 Å and 2.04 Å respectively.



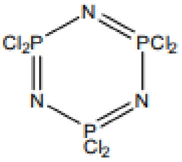
Physical properties: It is a light yellow crystalline solid. It sublimes at 160°C and it melts at 180°C by its own vapor pressure. It conducts electricity when dissolves in polar organic solvent like, acetonitrile and nitro-benzene. In solid state it exists as ionic $[(PCl_4)^+.(PCl_6)^-]$ compound. But it remains as PCl_5 in vapor state and in non-polar solvent.

Chemical properties: It is highly reactive substance. It creates fumes in air and produce $POCl_3$ on hydrolysis with quantitative amount of water.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2\ HCl$$

Phosphorus pentachloride may be used as chlorinating reagent to convert any substituted aldehyde into the corresponding vinyl chloride. It can also undergo reaction with ammonium chloride to yield linear phosphazenes and cyclophosphazenes.

$$nNH_4Cl + nPCl_5 \longrightarrow (NPCl_2)_n + 4n\ HCl$$



Structure of cyclophosphazene (n =3)

Sulfur forms mainly three types of oxy-halides, they are classified as thionyl or sulfinyl halide (SOX_2), sulfuryl or sulfonyl halide (SO_2X_2) and pyro-sulfuryl halides.

7.19 Thionyl chloride

Preparation: Thiony chloride is mainly prepared by two methods:

i) By passing anhyd. sulfur di-oxide gas slowly over phosphorous penta-chloride (PCl_5). $PCl_5 + SO_2 = SOCl_2 + POCl_3$

ii) By heating sodium sulphite and phosphorous pentachloride together at 150°C.

$$Na_2SO_3 + 2PCl_5 = SOCl_2 + POCl_3 + 2NaCl$$

Physical properties: Thionyl chloride is a colorless, pungent smelling, heavier but volatile liquid. Its boiling point is 78°C.

Chemical properties: It readily undergoes hydrolysis when comes in contact with water. Because of this property of thionyl chloride is used as dehydrating agent. The compounds that cannot be dried by heating are dried by thionyl chloride.

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl$$

Thionyl chloride is used in organic synthesis to replace hydroxyl (–OH) functional group present in various forms in organic molecule by chloro (–Cl) radical.

$$R\text{-}OH + SOCl_2 = R\text{-}Cl + SO_2 + HCl \qquad (R = \text{alky, aryl})$$

$$R\text{-}COOH + SOCl_2 = R\text{-}COCl + SO_2 + HCl \qquad (R = \text{alky, aryl})$$

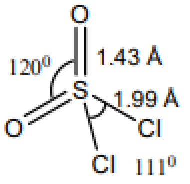
7.20 Sulfuryl chloride

It is also known as sulfony chloride and sulfuric oxychloride.

Preparation: It is prepared by the direct reaction of sulfur di-oxide and chlorine gas in presence of camphor or active charcoal as catalyst.

$$SO_2 + Cl_2 \xrightarrow{\text{Catalyst}} SO_2Cl_2$$

It is a colorless, pungent smelling highly volatile liquid (at room temperature). Its melting point and boiling point are –54°C and 69°C respectively. Its density is 1.665 g/mL at 20°C. It is highly corrosive in nature. Unlike $SOCl_2$ it is stable in water and does not undergo hydrolysis reaction easily. It forms colorless penta-hydrated crystals with molecular formula $SO_2Cl_2.5H_2O$ in ice-cold water.



It forms fumes in air which reacts with moisture to give strongly acidic mists that are heavier than air. Then it decomposes slowly in water to give hydrochloric acid and sulfuric acid. It reacts violently with bases.

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

It is widely used for chlorination of various compounds, as it dissociates into sulfur dioxide and chlorine during reaction. Thus, it acts as a source of molecular chlorine for various aromatic chlorination reactions. Sulfuryl chloride may be used as an efficient reagent for the *p*-chlorination of phenols.

7.21 Summary

In this chapter the various types of hydrides like ionic, covalent and interstitial hydrides are discussed with examples. In this unit the detail synthetic procedures of hydrides of nitrogen such as ammonia, hydrazine, and hydrazoic acid and hydroxyl amine are considered. The detail chemistry including their preparation and structures of the oxyacids of phosphorous and sulphur are presented unit.

7.22 Questions

A. Multiple Choice Type Questions

Sure! Here are 10 multiple-choice questions covering the topics you listed:

Question 1: Which of the following is an example of an ionic hydride?

A) Water
B) Lithium hydride
C) Methane
D) Ammonia

Answer: B) Lithium hydride

Question 2: Covalent hydrides are typically formed by which type of bonding?
A) Ionic bonding
B) Covalent bonding
C) Metallic bonding
D) Hydrogen bonding

Answer: B) Covalent bonding

Question 3: What is a characteristic feature of interstitial hydrides?
A) They contain hydrogen in ionic form.
B) They form covalent bonds with hydrogen.
C) They have hydrogen atoms occupying interstitial sites in metal lattices.
D) They are exclusively gaseous at room temperature.

Answer: C) They have hydrogen atoms occupying interstitial sites in metal lattices.

Question 4: Hydroxylamine is best described as:
A) A strong acid
B) A nitrogen-containing compound
C) An alkane
D) A halide

Answer: B) A nitrogen-containing compound

Question 5: Which oxyacid of phosphorus contains the highest oxidation state of phosphorus?
A) Phosphorous acid
B) Phosphoric acid

C) Hypophosphorous acid
D) Phosphinic acid

Answer: B) Phosphoric acid

Question 6: What is the chemical formula for sulfurous acid?
A) H2SO4
B) H2SO3
C) H2S
D) H2SO2

Answer: B) H2SO3

Question 7: Which of the following statements about hypo-sulfurous acid is correct?
A) It has one less oxygen than sulfurous acid.
B) It is a strong acid.
C) It has the formula H_2SO_4.
D) It is a gas at room temperature.

Answer: A) It has one less oxygen than sulfurous acid.

Question 8: Which of the following is true about sulfuric acid?
A) It is a weak acid.
B) It is the strongest mineral acid.
C) It has the formula H2S.
D) It does not form sulfate ions.

Answer: B) It is the strongest mineral acid.

Question 9: Chloric acid is characterized by which of the following properties?
A) It has a formula of HClO.
B) It is a strong oxidizing agent.
C) It contains phosphorus.
D) It is a colorless solid at room temperature.

Answer: B) It is a strong oxidizing agent.

Question 10: Which of the following elements typically forms ionic hydrides?
A) Carbon
B) Sodium
C) Phosphorus
D) Oxygen

Answer: B) Sodium

Question 11: Which of the following covalent hydrides is known for its strong hydrogen bonding?

A) SiH_4

B) NH_3

C) PH_3

D) H_2S

Answer: B) NH_3

Question 12: Which of the following metals is known to form interstitial hydrides?

A) Sodium

B) Titanium

C) Calcium

D) Potassium

Answer: B) Titanium

Question 13: Which compound is formed when nitrogen reacts with excess hydrogen?

A) Nitrogen trihydride

B) Nitrogen dihydride

C) Ammonia

D) Hydrazine

Answer: C) Ammonia

Question 14: Hydroxylamine can be used as a reagent in which type of reactions?

A) Oxidation reactions

B) Reduction reactions

C) Hydration reactions

D) Dehydration reactions

Answer: B) Reduction reactions

Question 15: What is the formula for hypophosphorous acid?

A) H_3PO_2

B) H_3PO_4

C) H_2PO_3

D) $H_4P_2O_7$

Answer: A) H_3PO_2

Question 16: Which statement is true about sulfoxilic acid?

A) It is a strong base.

B) It contains both sulfur and a hydroxyl group.

C) It has the formula $H_2C_2O_2S$.

D) It is a gaseous compound.

Answer: B) It contains both sulfur and a hydroxyl group.

Question 17: Hypochlorous acid is primarily used in which of the following applications?
A) Fertilizer
B) Disinfectant
C) Battery electrolyte
D) Food preservative

Answer: B) Disinfectant

Question 18: Chlorous acid can be represented by which of the following formulas?
A) $HClO_2$
B) $HClO_3$
C) $HClO_4$
D) HClO

Answer: A) $HClO_2$

Question 19: What is a common use for thionyl chloride?
A) As a drying agent
B) In food preservation
C) As a reducing agent
D) As a solvent

Answer: A) As a drying agent

Question 20: What is a characteristic of chloric acid?

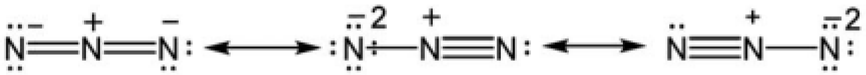
A) It is a colorless liquid.
B) It is used primarily in fertilizers.
C) It is a strong reducing agent.
D) It is not soluble in water.

Answer: A) It is a colorless liquid.

B. Short Type Questions

1. Construct a possible electron-dot structure for the azide ion.

Ans. All the three possible electron dot structures are as follows:



2. Answer the following questions:
    (a) Construct an electron-dot structure for $POCl_3$ (assume it to be similar to POF_3) and draw its molecular shape.
    (b) According to the hybridization concept, what is the likely hybridization of the central phosphorus atom?
    (c) The phosphorus-oxygen distance is very short. How would you explain this?
3. Contrast the properties of the two common allotropes of phosphorus.
4. Discuss the essential differences between oxygen and the other members of Group 16.
5. Explain why: H_3PO_2 is a monobasic acid but H_3PO_3 is a dibasic acid.
6. Between BF_3 and BCl_3 which one is stronger Lewis acid?–Explain.
7. Explain the acidity order of H_3PO_4, H_3PO_3 and H_3PO_2.
8. Describe the different types of hydrides which are formed.

C. AssayType Questions

1. Discuss the formation, structure, and properties of ionic hydrides. Explain their role in industrial applications and their reactivity with water and other compounds.

2. Explain the bonding in covalent hydrides with examples. How does the type of bonding influence their physical and chemical properties? Compare covalent hydrides of group 14 elements with those of group 15.

3. What are interstitial hydrides? Discuss their structure, formation, and significance in hydrogen storage technologies. How do they differ from ionic and covalent hydrides?

4. Provide a detailed overview of the hydrides of nitrogen, focusing on ammonia, hydrazine, and azides. Discuss their preparation, structure, and uses, with an emphasis on industrial and biological importance.

5. Describe the synthesis, structure, and reactivity of hydroxylamine. What are its uses in organic chemistry and industry? Discuss its role in biochemical processes as well.

6. Discuss the various oxyacids of phosphorus, including their structures, properties, and trends in acidity. How do their oxidation states influence their behavior in chemical reactions?

7. What is sulfoxilic acid? Describe its structure and possible modes of preparation. Discuss its role in chemical reactions and any industrial applications.

8. Explain the structure, properties, and applications of sulfurous acid. How does it act as a reducing agent, and what is its role in environmental chemistry?

9. Define hypo-sulfurous acid and discuss its structure and chemical behavior. Explain its importance in chemical synthesis and potential applications.

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10. Describe the structure and formation of pyrosulfurous acid. How does it compare with other sulfur-containing acids? Discuss its role in redox reactions.

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11. Sulfuric acid is often called the "king of chemicals." Discuss its industrial importance, focusing on its production, structure, properties, and key applications in various industries.

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12. Explain the formation and structure of hypochlorous acid. Discuss its role in disinfection and water treatment processes. How does it act as an oxidizing agent?

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13. Describe the structure, preparation, and properties of chlorous acid. What are its chemical reactivity patterns, and how is it used in bleaching and other industrial processes?

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14. Discuss the preparation and properties of chloric acid. How does it behave as an oxidizing agent, and what are its safety concerns and applications in industrial chemistry?

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15. Perchloric acid is a strong acid with significant oxidizing properties. Discuss its structure, preparation, and uses. What safety measures are required when handling perchloric acid?

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16. Explain the synthesis, structure, and chemical behavior of phosphorus trichloride. Discuss its applications in the chemical industry, particularly in the synthesis of organophosphorus compounds.

7.23 References

1. Inorganic Chemistry by R.L. Dutta
2. Essentials of Physical Chemistry by B.S. Bahl
3. Concise Inorganic Chemistry (4th Edition) by J.D. Lee
4. General and Inorganic Chemistry by P.K. Dutta
5. General and Inorganic Chemistry by R. Sarka

Unit - 8 ❑ Elements of Bio-inorganic Chemistry

Structure

8.0 Objectives

- Understand the Fundamental Properties: To explore the physical and chemical properties of sodium, potassium, calcium, magnesium, iron, cobalt, and nickel, focusing on their reactivity, oxidation states, and acid-base characteristics.
- Analyze Redox Behavior: To investigate the oxidation-reduction reactions of these elements, emphasizing their roles in biological systems, energy storage, and electrochemical applications.
- Examine Industrial Applications: To understand the industrial relevance of these elements and their compounds in fields such as metallurgy, construction, agriculture, battery technology, and catalysis.
- Explore Acidic and Basic Behavior: To assess the acid-base nature of various compounds of these elements and their importance in industrial processes, pH regulation, and environmental chemistry.
- Study Environmental Impact: To explore the role of these elements in environmental chemistry, focusing on their effects on water systems, soil quality, and pollution mitigation through sustainable practices.

8.1 Introduction

In the grand tapestry of chemistry, certain elements stand out for their unique properties and critical roles in both biological systems and industrial processes. This chapter delves into the properties and applications of sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), cobalt (Co), and nickel (Ni). We will explore their oxidation states, acid-base characteristics, and their significance across various fields, including industrial, organic, and environmental chemistry.

8.2 Overview on the elements

Sodium (Na)

Sodium, an alkali metal, is characterized by its high reactivity, particularly with water. In its oxidation state of +1, sodium readily loses its outer electron. Sodium compounds, such as sodium chloride (NaCl), are essential in both biological systems and industrial applications.

Potassium (K)

Like sodium, potassium is an alkali metal and shares similar properties, though it is even more reactive. With an oxidation state of +1, potassium is vital for cellular functions in living organisms. Potassium compounds, such as potassium nitrate (KNO_3), have wide-ranging applications in fertilizers and explosives.

Calcium (Ca)

Calcium, an alkaline earth metal, commonly exhibits a +2 oxidation state. It plays a critical role in biological systems, particularly in bone formation. Calcium compounds, including calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$), are extensively used in construction, agriculture, and food industries.

Magnesium (Mg)

Magnesium, another alkaline earth metal, typically exists in the +2-oxidation state. It is crucial for many biological processes, including photosynthesis. Magnesium compounds, such as magnesium oxide (MgO) and magnesium sulfate ($MgSO_4$), are utilized in medicine, agriculture, and materials science.

Iron (Fe)

Iron, a transition metal, is central to industrial chemistry. It has multiple oxidation states, primarily +2 and +3, which contribute to its versatility. Iron compounds like iron oxide (Fe_2O_3) are pivotal in metallurgy and catalysis.

Cobalt (Co)

Cobalt, a transition metal, is characterized by its +2 and +3 oxidation states. It is essential in various industrial applications, including battery technology and catalysts. Cobalt compounds are also significant in organic synthesis, particularly in the production of vitamin B12.

Nickel (Ni)

Nickel, another transition metal, commonly exhibits oxidation states of +2 and +3. Its corrosion resistance makes it invaluable in alloy production. Nickel compounds are used in electroplating and as catalysts in organic reactions.

8.3 Oxidation and Reduction

Sodium and Potassium

Both sodium and potassium easily undergo oxidation, losing one electron to form Na^+ and K^+ ions, respectively. Their reduction typically involves the addition of electrons, which is crucial in electrochemical cells and battery technologies.

Calcium and Magnesium

Calcium and magnesium exhibit similar redox behavior. In their +2 oxidation states, they participate in oxidation-reduction reactions where they can be reduced to their elemental forms under certain conditions, especially in high-temperature environments.

Iron, Cobalt, and Nickel

Iron is well-known for its redox properties, where it can easily switch between its +2 and +3 states, making it a key player in biological systems and industrial processes. Cobalt and nickel also demonstrate significant redox capabilities, often acting as catalysts in oxidation-reduction reactions that are essential for organic synthesis and energy storage.

8.4 Acidic and Basic Nature of Compounds

Sodium and Potassium Compounds

Sodium and potassium hydroxides (NaOH and KOH) are strong bases, while their corresponding chlorides (NaCl and KCl) are neutral salts. These bases are used extensively in chemical synthesis and as pH regulators in various industrial processes.

Calcium and Magnesium Compounds

Calcium carbonate ($CaCO_3$) is a weak base that reacts with acids to produce carbon dioxide, while calcium hydroxide ($Ca(OH)_2$) is a strong base. Magnesium hydroxide ($Mg(OH)_2$) is a weak base and is commonly used as an antacid.

Iron, Cobalt, and Nickel Compounds

Iron(III) oxide (Fe_2O_3) and cobalt(II) hydroxide ($Co(OH)_2$) can exhibit acidic or basic characteristics depending on the surrounding conditions. Nickel compounds, particularly nickel(II) sulfate ($NiSO_4$), are neutral salts that can also participate in acid-base reactions depending on the medium.

8.5 Applications in Industrial Chemistry

Sodium and Potassium

Sodium and potassium compounds are extensively used in the production of glass, ceramics, and soaps. In agriculture, potassium fertilizers enhance crop yield, while sodium compounds play a role in food preservation and flavouring.

Calcium and Magnesium

Calcium compounds are fundamental in the construction industry, particularly calcium sulfate in drywall and calcium carbonate as a filler. Magnesium is essential in the manufacture of lightweight alloys used in aerospace and automotive applications.

Iron, Cobalt, and Nickel

Iron is the backbone of steel production, while cobalt and nickel are critical in manufacturing rechargeable batteries. Cobalt is particularly vital in the production of high-performance alloys, while nickel is essential in corrosion-resistant applications.

8.6 Environmental Chemistry

Sodium and Potassium

Sodium and potassium ions are crucial in maintaining the ionic balance in natural water systems. However, excessive use of potassium fertilizers can lead to nutrient runoff, impacting water quality.

Calcium and Magnesium

Calcium and magnesium compounds can mitigate acid rain's effects on soil and water quality, providing essential nutrients while neutralizing acidity.

Iron, Cobalt, and Nickel

Iron can be used in environmental remediation to treat contaminated groundwater, while cobalt and nickel are important in recycling processes. They contribute to sustainable practices, such as catalysing the breakdown of pollutants in organic waste.

8.6 Summary

This chapter explores the properties, oxidation states, acid-base characteristics, and applications of key elements—sodium, potassium, calcium, magnesium, iron, cobalt, and nickel. Sodium and potassium, as alkali metals, are highly reactive and play crucial roles in biological systems and industrial processes. Calcium and magnesium, both alkaline earth metals, are essential in areas ranging from bone health to construction materials. Iron, cobalt, and nickel, as transition metals, exhibit versatile redox properties and are integral in steel production, battery technologies, and catalysis.

The chapter also delves into the redox behavior of these elements, highlighting their significance in biological processes, energy storage, and electrochemical reactions. The acid-base nature of their compounds, such as sodium hydroxide, calcium carbonate, and iron oxide, is discussed in relation to industrial uses, including chemical synthesis, construction, and environmental applications.

Finally, the environmental impact of these elements is addressed, emphasizing their role in water quality, soil health, and pollution mitigation through sustainable practices like groundwater treatment and pollutant breakdown. This comprehensive analysis underscores the importance of these elements across various fields of chemistry and industry.

8.7 Sample Questions

A. Multiple Choice Type Questions

1. Which of the following elements is an alkali metal?
   a) Calcium
   b) Cobalt
   c) Sodium
   d) Iron
   Answer: c) Sodium

2. What is the common oxidation state of potassium in its compounds?
   a) +1
   b) +2
   c) +3
   d) +4
   Answer: a) +1
3. Which element is essential for bone formation in biological systems?
   a) Magnesium
   b) Sodium
   c) Iron
   d) Calcium
   Answer: d) Calcium
4. Magnesium is crucial for which biological process?
   a) Cellular respiration
   b) Photosynthesis
   c) Blood clotting
   d) Nerve conduction
   Answer: b) Photosynthesis
5. Iron primarily exhibits which two oxidation states?
   a) +1 and +2
   b) +2 and +3
   c) +3 and +4
   d) +1 and +3
   Answer: b) +2 and +3
6. Cobalt is widely used in which of the following applications?
   a) Fertilizers
   b) Battery technology
   c) Food preservation
   d) Construction materials
   Answer: b) Battery technology
7. Which element is known for its corrosion resistance and is used in alloy production?
   a) Nickel
   b) Potassium
   c) Sodium
   d) Iron
   Answer: a) Nickel
8. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are examples of what type of compounds?
   a) Acids
   b) Neutral salts
   c) Strong bases
   d) Weak bases
   Answer: c) Strong bases
9. Which compound is commonly used in agriculture as a fertilizer?
   a) Sodium chloride
   b) Potassium nitrate
   c) Magnesium sulfate
   d) Iron oxide
   Answer: b) Potassium nitrate

10. Excessive use of potassium fertilizers can lead to what environmental issue?
    a) Acid rain
    b) Soil erosion
    c) Nutrient runoff
    d) Air pollution
    Answer: c) Nutrient runoff

B. Short Type Questions

1. What is the common oxidation state of sodium, and why is it highly reactive?
2. Explain the role of potassium in cellular functions.
3. How is calcium important in both biological systems and the construction industry?
4. What is the significance of magnesium in photosynthesis?
5. Describe the redox behavior of iron in industrial and biological processes.
6. What are the primary industrial applications of cobalt?
7. Why is nickel widely used in the production of corrosion-resistant alloys?
8. Explain the acidic and basic nature of sodium and potassium hydroxides.
9. How do calcium and magnesium compounds help in mitigating acid rain's effects?
10. What environmental concerns arise from the excessive use of potassium fertilizers?

C. Assay Type Questions

1. Discuss the industrial and biological significance of sodium and potassium. Explore their properties, oxidation states, and how they are used in various fields such as agriculture, food preservation, and cellular functions in living organisms.
2. Analyze the roles of calcium and magnesium in both biological and industrial processes.

   Describe how these elements contribute to bone health, agriculture, construction, and other industries, while highlighting their acid-base characteristics and reactivity.
3. Explain the redox behavior of iron, cobalt, and nickel, and their importance in industrial chemistry.

   Discuss the oxidation states of these transition metals and their roles in metallurgical processes, battery technologies, and catalysis, with examples of compounds and applications.
4. Examine the environmental impact of sodium, potassium, calcium, magnesium, iron, cobalt, and nickel.Focus on how these elements contribute to environmental sustainability through pollution mitigation, nutrient cycling, and water quality management, while also addressing the negative effects of overuse.

5. Evaluate the acid-base properties of compounds of sodium, potassium, calcium, and magnesium, and their significance in industrial and environmental chemistry. Provide examples of compounds such as sodium hydroxide, calcium carbonate, and magnesium sulfate, and discuss their uses in various industries, including construction, medicine, and environmental management.

8.8 References

1. "Inorganic Chemistry" by Gary L. Miessler, Paul J. Fischer, and Donald A. Tarr. This textbook provides a comprehensive overview of the principles of inorganic chemistry, including the properties and behavior of various elements.
2. "Chemistry of the Elements" by N.N. Greenwood and A. Earnshaw. This reference book covers the chemistry of all elements, discussing their properties, reactions, and applications in various fields.
3. "Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life" by WolfgangKaim and Bernhard Schwederski. This book focuses on the role of inorganic elements in biological systems, including sodium, potassium, calcium, magnesium, iron, cobalt, and nickel.
4. "Environmental Chemistry" by Gary W. VanLoon and Stephen J. Duffy. This text addresses the environmental aspects of chemistry, including the behavior of various elements and their impact on ecosystems.
5. "Industrial Inorganic Chemistry" by R. C. Petrucci and H. E. W. G. Griess. This book covers the industrial applications of various inorganic compounds, providing insights into the uses of elements like sodium, potassium, calcium, and iron in industry.
6. "Principles of Chemistry: A Molecular Approach" by Nivaldo J. Tro. This introductory chemistry textbook discusses various chemical principles, including the properties and applications of different elements in both biological and industrial contexts.
7. "Metals in Biological Systems" by K. J. A. Smith. This book specifically addresses the roles of metals, including iron, cobalt, and nickel, in biological systems and their significance in human health.

Unit - 9 ❑ Hydrides of Boron

Structure

9.0 Objectives

1. Understand the Structure and Bonding in Boranes: Investigate the unique bonding patterns in boranes, such as multi-center bonding (3-center, 2-electron bonds), and how these contribute to their stability and reactivity.

2. Explore Synthesis Pathways: Develop efficient and safer methods for synthesizing boranes, improving upon classical approaches like the reaction of acids with metal borides.

3. Characterize Physical and Chemical Properties: Examine the air-sensitivity, thermal stability, and reactivity of boranes, especially their behavior in different chemical environments (e.g., in the presence of water or oxygen).

4. Investigate Applications in Energy Storage: Study boranes as potential materials for hydrogen storage, focusing on their capacity to release hydrogen and their reversibility in hydrogenation processes.

5. Develop Boranes for Organic Synthesis: Explore the use of boranes as reagents in organic chemistry, particularly in hydroboration reactions, and their potential for creating novel synthetic routes.

6. Examine Boranes in Medicinal Chemistry: Assess the role of boranes in medical applications, such as in boron neutron capture therapy (BNCT) for cancer treatment, focusing on their ability to selectively accumulate in tumor cells.

7. Study the Role of Boranes in Materials Science: Investigate the use of boranes in depositing boron-containing thin films or creating boron-based materials with unique properties, such as high hardness or chemical resistance.

8. Expand Theoretical Understanding of Borane Chemistry: Continue theoretical studies on the electronic structure and bonding of boranes to refine models and predict the behavior of new boron-hydrogen compounds.

9.1 Introduction

Boron hydrides, also known as **boranes**, are a class of chemical compounds consisting of boron (B) and hydrogen (H). These compounds are of great interest due to their unique bonding structures, reactivity, and potential applications in various fields, including materials science and energy storage.The systematic study of boranes began with Alfred Stock and his research group in 1912, continuing for nearly 25 years. Stock initially focused on reactions involving acids and magnesium boride, although more efficient methods have since been developed. Due to the extreme air-sensitivity of boranes (they ignite upon exposure to air), Stock pioneered the use of glass vacuum lines and specialized techniques to handle these compounds. This innovation was transformative, as it paved the way for handling oxygen- and moisture-sensitive substances in a broad range of inorganic chemistry.

Another prominent figure in borane chemistry is W.N. Lipscomb of Harvard University, whose theoretical work on borane bonding earned him the Nobel Prize in Chemistry in 1976. H.C. Brown of Purdue University also made significant contributions to the field, particularly in the application of boranes in organic synthesis, which led to him sharing the 1979 Nobel Prize in Chemistry. Their collective work greatly expanded the understanding and practical use of boranes, influencing modern chemistry in various ways.

9.2 Types and Structures

Boron hydrides can be classified based on their structure and the number of boron and hydrogen atoms present. Some important types include:

1. **Diborane (B_2H_6)** : One of the simplest and most studied boron hydrides, diborane consists of two boron atoms and six hydrogen atoms. The structure of diborane is unusual because it involves multi-center bonding, where two bridging hydrogen atoms are shared between two boron atoms, forming a "banana bond."
2. **Tetraborane (B_4H_{10})** : This compound has a more complex structure with four boron atoms. It also exhibits multi-center bonding.
3. **Decaborane ($B_{10}H_{14}$)** : Decaborane has a cage-like structure with ten boron atoms forming a polyhedral framework. It is more stable than smaller boranes and finds applications in rocket propellants and as a neutron absorber in nuclear reactors.

9.3 Diborane (B_2H_6)

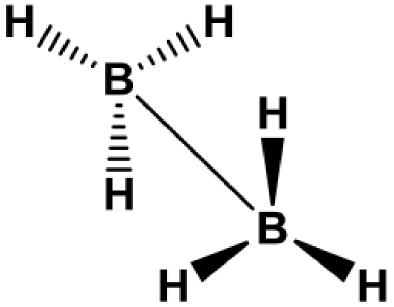
1912: Boranes first studied by Alfred Stock

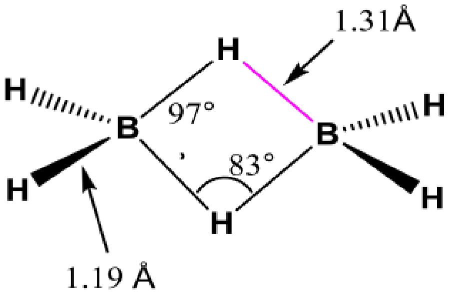
1925: diborane, ethane-like structure.

1934: diborane is diamagnetic

1937: Simon H. Bauer (electron diffraction), ethane-like structure.

Boron hydrides are a class ofelectron deficient compounds that have unusual bonding behavior andformcages andclusters. The electron deficient BH_3 is the simplest boron hydride which exists as a dimerB_2H_6 (diborane). The structure of B_2H_6 containsbridging B-H-B (or BHB) bonds; quite different to those of carbonhydrides.





The three main types of boron hydrides are (i) closo, (ii) nido and (iii) arachno with the general formulae, $BnHn^{2-}$, $BnHn^{+4}$ and $BnHn^{+6}$, respectively.

9.3.1 Structure of Diborane

Diborane (B_2H_6) is a fascinating compound because of its unusual bonding, which deviates from the conventional two-electron, two-center bond found in most covalent compounds. The bonding in diborane is characterized by **multi-center bonds**, specifically **three-center, two-electron (3c-2e) bonds**.

Diborane consists of two boron atoms and six hydrogen atoms. The molecule can be divided into two types of bonds:

1. **Terminal B-H Bonds**: Each boron atom forms two regular covalent bonds with hydrogen atoms, known as terminal hydrogen atoms. These are typical two-center, two-electron bonds (2c-2e), where two electrons are shared between the boron atom and the hydrogen atom.
2. **Bridging B-H-B Bonds**: The unique feature of diborane is the presence of two hydrogen atoms that are **bridging** between the two boron atoms. These bridging hydrogens form **three-center, two-electron bonds**. In each bridge, one hydrogen atom is shared between two boron atoms, creating a bond in which two electrons are spread over three atoms (the two borons and one hydrogen). This type of bond is sometimes referred to as a "banana bond" due to the curved shape it forms between the boron atoms.

Banana bonds are a type of bonding found in certain electron-deficient molecules, such as boranes (e.g., diborane, B_2H_6). These bonds occur when two atoms are bridged by a third atom, and only two electrons are shared across all three atoms, resulting in a **three-center, two-electron bond (3c-2e bond)**. The name "banana bond" comes from the curved appearance of the bond, which resembles the shape of a banana.

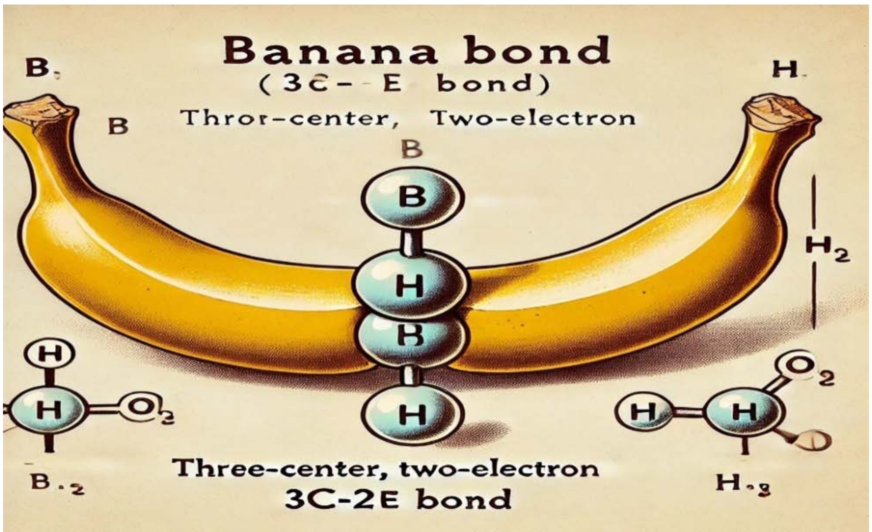
Characteristics of Banana Bonds

- **Electron Deficiency**: In a traditional covalent bond, two electrons are shared between two atoms (a two-center, two-electron bond). However, in banana bonds, two electrons are shared between three atoms, meaning there are fewer electrons available per bond than in a typical covalent bond. This makes the bond **electron-deficient**.
- **Three-Center Bonding**: In diborane, for example, each bridging hydrogen atom forms a bond with two boron atoms. The two electrons are delocalized over the three atoms (two boron and one hydrogen), creating a bond that is weaker and more flexible than a normal two-center bond.
- **Structural Implication**: Banana bonds result in a unique molecular structure where the bonds are slightly bent or curved, hence the "banana" description.

These bonds are significant in the chemistry of boron, aluminum, and other elements that form electron-deficient compounds.

Example: Diborane (B_2H_6)

In diborane, the two boron atoms are connected by two bridging hydrogen atoms through banana bonds. Each boron atom forms two standard covalent bonds with terminal hydrogen atoms, but the bridging hydrogen atoms form these special banana bonds between the two boron atoms.



9.3.2 Preparation of Diborane

The preparation of diborane (B_2H_6) involves the use of boron-containing compounds and reducing agents. There are several methods for its synthesis, each relying on chemical reactions that release diborane as a product. Below are some common methods:

1. Reaction of Boron Trifluoride with Hydride Reducing Agents

This is one of the most common laboratory methods for preparing diborane. In this method, boron trifluoride (BF_3) is reacted with a hydride donor, such as lithium aluminum hydride ($LiAlH_4$), which acts as a reducing agent.

Reaction: $4BF_3+3LiAlH_4 \longrightarrow 2B_2H_6+3LiF+3AlF_3$

In this reaction, boron trifluoride is reduced by lithium aluminum hydride, producing diborane along with lithium fluoride and aluminum fluoride as by-products.

2. Thermal Decomposition of Sodium Borohydride ($NaBH_4$)

Diborane can also be prepared by the thermal decomposition of sodium borohydride ($NaBH_4$), a readily available boron-hydrogen compound.

Reaction: $2NaBH4 \rightarrow B_2H_6+2NaH_2$

Upon heating, sodium borohydride decomposes to form diborane and sodium hydride.

3. Reaction of Boron Halides with Metal Hydrides

Another method involves the reaction between boron halides (like boron trichloride, BCl_3) and metal hydrides such as lithium hydride (LiH) or sodium hydride (NaH).

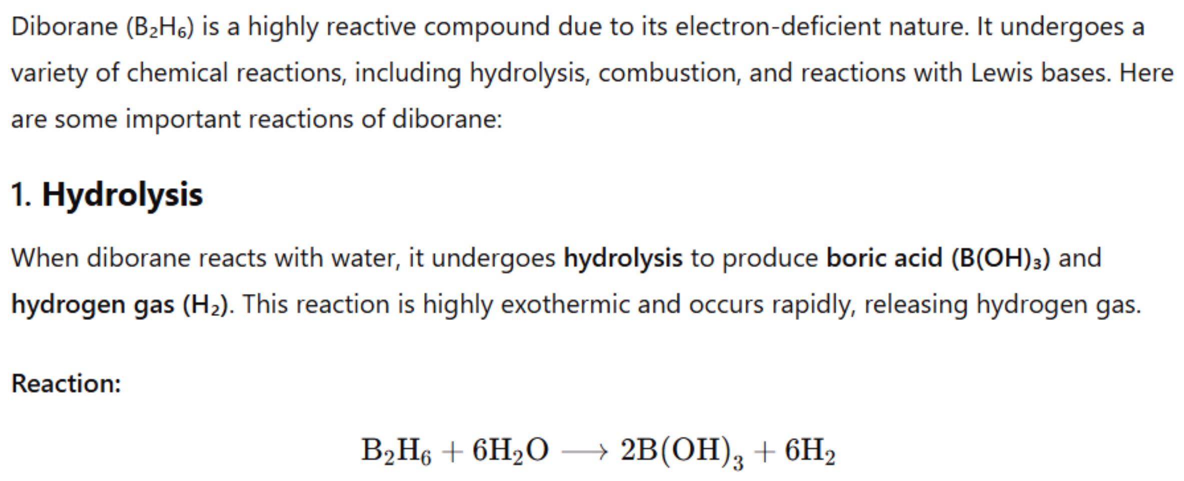
Reaction: $2BCl_3+6LiH \longrightarrow B_2H_6+6LiCl_2$

This method yields diborane along with lithium chloride as a by-product.

4. Electrochemical Method

In some cases, diborane can be prepared through an electrochemical method where boron electrodes are used in an electrolytic cell. In the presence of hydrogen, this method can lead to the formation of diborane.

9.3.3 Reaction of Diborane



Diborane (B_2H_6) is a highly reactive compound due to its electron-deficient nature. It undergoes a variety of chemical reactions, including hydrolysis, combustion, and reactions with Lewis bases. Here are some important reactions of diborane:

1. Hydrolysis

When diborane reacts with water, it undergoes **hydrolysis** to produce **boric acid ($B(OH)_3$)** and **hydrogen gas (H_2)**. This reaction is highly exothermic and occurs rapidly, releasing hydrogen gas.

Reaction:

$$B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$$

2. Combustion

Diborane is **pyrophoric**, meaning it ignites spontaneously in the presence of oxygen. When burned in air or oxygen, it reacts to form **boron trioxide (B_2O_3)** and water.

Reaction:

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

This reaction releases a large amount of heat and can be dangerous if not carefully controlled.

3. Reaction with Lewis Bases

Diborane is an electron-deficient molecule and acts as a **Lewis acid**. It readily forms adducts with **Lewis bases** such as ammonia (NH_3), forming compounds like **borane-ammonia complex ($B_2H_6 \cdot 2NH_3$)**.

Reaction:

$$B_2H_6 + 2NH_3 \longrightarrow 2BH_3NH_3$$

This is a classic example of a **donor-acceptor complex**, where ammonia donates electron pairs to diborane.

4. Reaction with Halogens

Diborane reacts with **halogens** such as chlorine or bromine, leading to the formation of **boron halides** and hydrogen halides.

Reaction with Chlorine:

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

Similarly, reactions with other halogens like bromine (Br_2) proceed in an analogous fashion.

5. Hydroboration Reaction

Diborane plays a key role in **hydroboration**, a reaction widely used in organic chemistry. In this reaction, diborane adds across the double bond of alkenes, resulting in the formation of **trialkylboranes**. The hydroboration reaction is important in the **synthesis of alcohols**.

Reaction:

$$B_2H_6 + 6RCH{=}CH_2 \longrightarrow 2B(RCH_2CH_2)_3$$

Here, diborane adds to the alkene, and the resulting borane derivative can be further oxidized to form an alcohol.

6. Reaction with Metal Hydrides

Diborane reacts with metal hydrides to form **borohydrides**. For example, it reacts with sodium hydride (NaH) to form **sodium borohydride ($NaBH_4$)**, an important reducing agent in organic chemistry.

Reaction:

$$B_2H_6 + 2NaH \longrightarrow 2NaBH_4$$

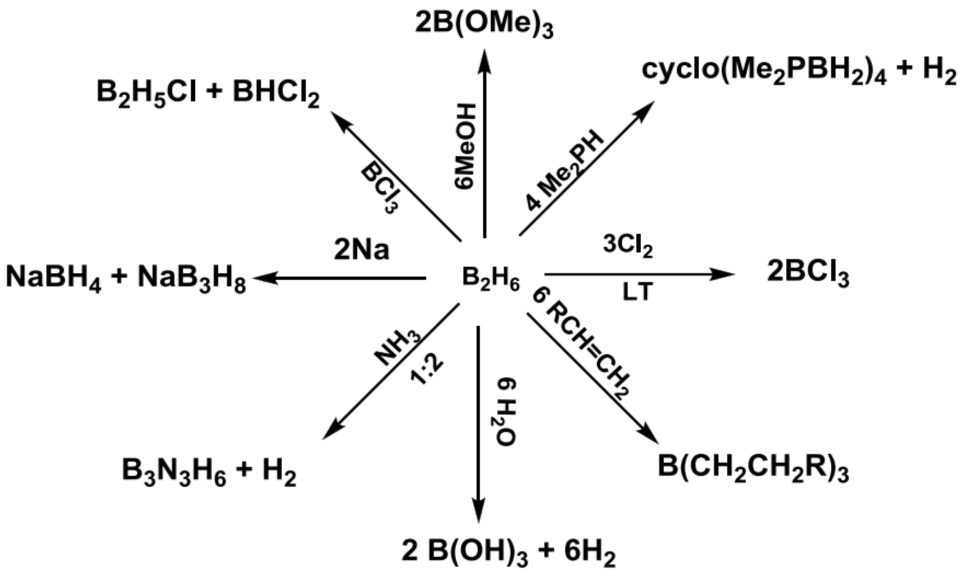
7. Reaction with Alkynes

Diborane reacts with alkynes in a manner similar to its reaction with alkenes. This is another example of hydroboration, where diborane adds across the triple bond of an alkyne to form a **dialkylborane**.

Reaction:

$$B_2H_6 + 2RC{\equiv}CH \longrightarrow 2RBH_2CH$$

Reactions of diborane



$$B_2H_6 + 2\,Et_3N \longrightarrow 2\,Et_3N.BH_3 \xrightarrow[-H_2]{B_4H_{10},\ 190\ °C} [Et3NH]_2\,[B_{12}H_{12}]$$

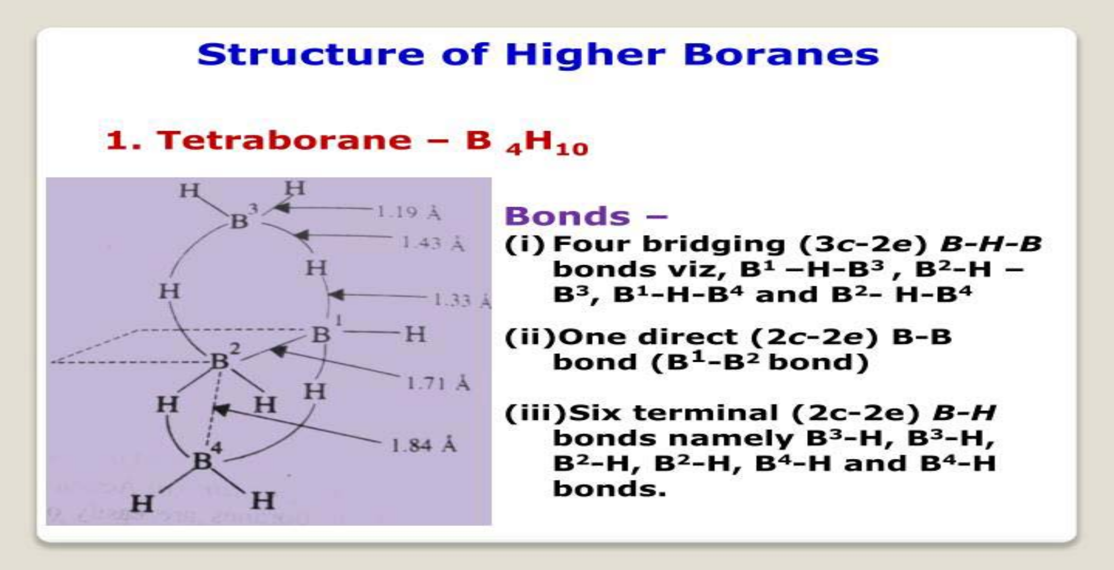
9.4 Tetraborane (B_4H_{10})

Tetraborane (B_4H_{10}) is a boron hydride that belongs to the class of **boranes**. Like other boranes, it consists of boron and hydrogen atoms and exhibits interesting bonding due to electron deficiency. Tetraborane is less commonly encountered than diborane (B_2H_6), but its structure and reactivity are important in the study of boron chemistry.

9.4.1 Structure of Tetraborane

The structure of **tetraborane (B_4H_{10})** is somewhat more complex than diborane. It consists of four boron atoms arranged in a non-planar, **butterfly-like shape**. The boron atoms are held together by both two-center, two-electron bonds (regular covalent bonds) and three-center, two-electron bonds (similar to those found in diborane).

- **Boron atoms**: The four boron atoms are located at the corners of a distorted tetrahedral geometry, forming a cluster.
- **Terminal hydrogens**: Each boron atom has at least one terminal hydrogen atom attached via standard two-center, two-electron bonds.
- **Bridging hydrogens**: Some of the hydrogens are shared between boron atoms, forming multi-center, two-electron bonds (like the "banana bonds" in diborane).



Structure of Higher Boranes

1. Tetraborane – B_4H_{10}

Bonds –

(i) Four bridging (3*c*-2*e*) *B-H-B* bonds viz, B^1–H-B^3, B^2-H – B^3, B^1-H-B^4 and B^2- H-B^4

(ii) One direct (2*c*-2*e*) B-B bond (B^1-B^2 bond)

(iii) Six terminal (2*c*-2*e*) *B-H* bonds namely B^3-H, B^3-H, B^2-H, B^2-H, B^4-H and B^4-H bonds.

9.4.2 Bonding in Tetraborane

In tetraborane, there are a combination of:

1. **Two-center, two-electron bonds (2c-2e)**: These are typical covalent bonds where each boron atom is directly bonded to a terminal hydrogen atom.
2. **Three-center, two-electron bonds (3c-2e)**: These are found between two boron atoms and a bridging hydrogen atom, similar to the bonding in diborane.

The structure of tetraborane reflects the electron-deficient nature of boron and its ability to form unusual bonding patterns to achieve stability.

9.4.3 Preparation of Tetraborane

Tetraborane can be prepared from **diborane (B_2H_6)** under controlled conditions, often by thermal decomposition or other chemical reactions involving the breakdown of larger borane clusters.

Reaction:

$$2B_2H_6 \rightarrow B_4H_{10} + H_2$$

In this reaction, diborane is heated to form tetraborane, releasing hydrogen gas as a by-product.

9.4.4 Properties of Tetraborane

- **Air Sensitivity**: Like other boranes, tetraborane is highly reactive and ignites spontaneously in air. It is typically handled in an inert atmosphere.
- **Toxicity**: Tetraborane is toxic and requires careful handling due to its reactivity and potential health hazards.
- **Reactivity**: Tetraborane can react with oxygen, water, and Lewis bases. It also serves as a precursor for the synthesis of higher boranes.

9.4.5 Reactions of Tetraborane

1. **Reaction with Oxygen**: Tetraborane combusts in the presence of oxygen to form boron trioxide (B_2O_3) and water.

$$B_4H_{10} + 5O_2 \longrightarrow 2B_2O_3 + 5H_2O$$

2. **Reaction with Water**: Tetraborane hydrolyzes in water to yield boric acid ($B(OH)_3$) and hydrogen gas.

$$B_4H_{10} + 10H_2O \longrightarrow 4B(OH)_3 + 10H_2$$

3. **Reaction with Lewis Bases**: Similar to other boranes, tetraborane forms adducts with Lewis bases like ammonia (NH_3).

9.4.6 Uses of Tetraborane

Though less commercially significant than diborane, tetraborane is used in research and as a precursor for synthesizing other boranes. Its high energy content and reactive nature have also led to some exploration of its use as a fuel in high-energy applications such as rocket propellants.

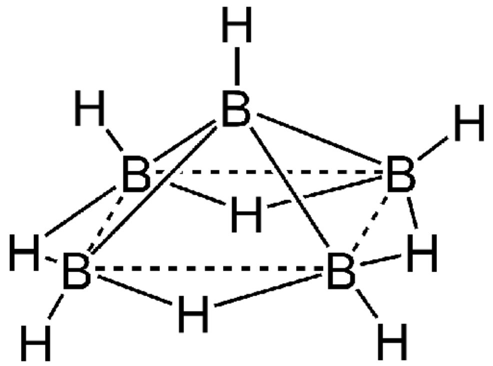
9.5 Pentaborane (9) (B_5H_9)

Pentaborane (B_5H_9) is a boron hydride that belongs to the family of boranes, composed of boron and hydrogen atoms. Its molecular formula indicates that it contains five boron atoms and nine hydrogen atoms. This compound is part of a broader group of boranes with various interesting bonding patterns due to their electron deficiency.

9.5.1 Structure of Pentaborane (B_5H_9)

The structure of pentaborane (BH_9) is unique and somewhat more complex than smaller boranes like diborane (B_2H_6) or tetraborane (B_4H_{10}). The molecule features:

- **Boron Cage**: The five boron atoms in pentaborane form a **pentagonal bipyramid**, a cage-like structure. Four of these boron atoms form a square base, while the fifth boron atom caps the square, resulting in a slightly distorted structure.
- **Terminal Hydrogens**: Four of the hydrogen atoms are attached directly to boron atoms as **terminal hydrogens** through standard two-center, two-electron bonds.
- **Bridging Hydrogens**: The remaining five hydrogen atoms are distributed as **bridging hydrogens** across the boron atoms, forming **three-center, two-electron bonds** (3c-2e bonds). This is similar to the bonding seen in diborane, where hydrogens bridge boron atoms.



Structure of Pentaborane(B_5H_9)

9.5.2 Bonding in Pentaborane

As in other boranes, pentaborane has both two-center, two-electron bonds and three-center, two-electron bonds. The electron deficiency in boranes leads to the formation of these multi-center bonds, allowing boron to achieve a more stable electronic structure despite having fewer valence electrons.

9.5.3 Preparation of Pentaborane (B_5H_9)

Pentaborane can be synthesized through the **pyrolysis of diborane (B_2H_6)** . This method involves heating diborane under specific conditions to induce a series of reactions that eventually lead to the formation of pentaborane.

Reaction:

$$3B_2H_6 \rightarrow B_5H_9 + B_2H_{10} + H_2$$

This process typically requires high temperatures and careful control to isolate pentaborane from other products formed during the reaction.

9.5.4Properties of Pentaborane (B_5H_9)

- **Air Sensitivity**: Pentaborane is **pyrophoric**, meaning it ignites spontaneously in the presence of air. It must be handled under inert conditions (e.g., nitrogen or argon atmosphere).
- **Toxicity**: Pentaborane is highly toxic and poses significant health risks if inhaled or ingested. It requires specialized equipment and safety protocols for handling.
- **Colour**: It is a colorless liquid at room temperature.
- **Reactivity**: Pentaborane is highly reactive, similar to other boranes, and can undergo hydrolysis, combustion, and reactions with Lewis bases.

9.5.5 Reactions of Pentaborane

1. **Combustion**: Pentaborane reacts violently with oxygen. When burned, it produces boron trioxide (B_2O_3) and water.

   $2B_5H_9 + 12O_2 \longrightarrow 5B_2O_3 + 9H_2O$

2. **Hydrolysis**: When pentaborane reacts with water, it hydrolyzes to form boric acid and hydrogen gas.

   $B_5H_9 + 18H_2O \longrightarrow 5B(OH)_3 + 9H_2$

3. **Reaction with Lewis Bases**: Pentaborane can react with Lewis bases, such as ammonia (NH_3), forming complexes like $B_5H_9 \cdot 2NH_3$

9.5.6 Uses of Pentaborane (B_5H_9)

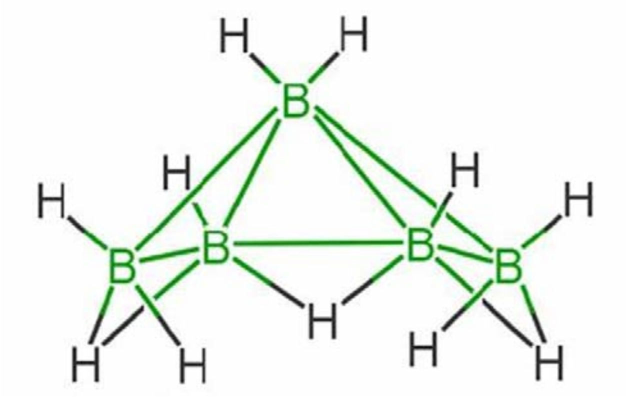
Pentaborane was once considered as a high-energy rocket fuel due to its high energy content. However, its toxicity and extreme reactivity made it unsuitable for widespread use. It is still used in research applications for the study of boron chemistry and boron-hydrogen compounds.

9.6 Pentaborane (11) (B_5H_{11})

Pentaborane, with the chemical formula B_5H_{11}, is a boron hydride compound. It is one of the many boranes, a family of compounds consisting of boron and hydrogen. Pentaborane (B_5H_{11}) has interesting structural, bonding, and chemical properties that make it notable among boron hydrides.

9.6.1 Structure of Pentaborane (B_5H_{11})

The structure of pentaborane (B_5H_{11}) consists of five boron atoms arranged in a distorted trigonal bipyramidal shape. The arrangement of the boron atoms can be described as a cluster, with hydrogen atoms bridging between some boron atoms (bridging hydrogens) and terminal hydrogens attached to individual borons. This structure is a hallmark of boranes, where three-center two-electron bonds are common. In pentaborane, four of the hydrogens are bridge hydrogens, while the remaining seven are terminal hydrogens.



Structure of Pentaborane (11) (B_5H_{11})

9.6.2 Bonding in Pentaborane(B_5H_{11})

The bonding in pentaborane (B_5H_{11}) is a mix of conventional two -center two-electron (2c-2e) bonds and delocalized three-center two-electron (3c-2e) bonds, which are characteristic of boranes. The three-center bonding occurs where a pair of electrons is shared between two boron atoms and a hydrogen atom, contributing to the stability of the boron cluster. This type of electron-deficient bonding is typical in boron compounds due to boron's tendency to form stable clusters with fewer electrons than typical covalent bonds.

9.6.3 Preparation of Pentaborane (B_5H_{11})

Pentaborane can be prepared through the thermal decomposition of diborane (B_2H_6) under controlled conditions. Some key preparation methods include:

- **Thermal decomposition**: Heating diborane at elevated temperatures leads to the production of higher boranes, including pentaborane.
- **Catalytic methods:** Reactions involving diborane with halogens or iodine can yield pentaborane.

These synthesis methods must be carefully managed because pentaborane is volatile and highly reactive.

9.6.4 Properties of Pentaborane(B_5H_{11})

- **Physical state**: Pentaborane is a colorless, highly volatile liquid at room temperature.
- **Odor**: It has a strong, unpleasant smell.
- **Flammability**: It is pyrophoric, meaning it can spontaneously ignite in air, and is highly combustible.
- **Toxicity**: Pentaborane is highly toxic, with serious health hazards upon inhalation or contact. It affects the central nervous system and can cause neurological damage.
- **Thermal instability**: Pentaborane decomposes at elevated temperatures, which poses challenges for its storage and handling.

9.6.5 Reactions of Pentaborane (B_5H_{11})

- **Oxidation**: Pentaborane reacts explosively with oxygen, forming boron oxides.

- **Hydrolysis**: It reacts with water or moisture, releasing hydrogen gas and forming boric acid.
- **Halogenation**: Pentaborane reacts with halogens (e.g., chlorine or bromine) to form halogenated boranes, which are more stable than the parent compound.

9.6.6 Uses of Pentaborane (B_5H_{11})

In the 1950s and 1960s, pentaborane was explored as a high-energy rocket fuel due to its high heat of combustion and hydrogen content, which could theoretically increase rocket performance. However, its use was abandoned due to its extreme reactivity, pyrophoric nature, toxicity, and the difficulty of handling it safely. Today, pentaborane is of academic interest, especially in studying boron-hydrogen bonding and the development of cluster compounds in inorganic chemistry.

9.7 Summary

9.3.1 Structure of Diborane

Diborane (B_2H_6) consists of two boron atoms and six hydrogen atoms. The structure is unique with two bridging hydrogen atoms between the boron atoms, forming a B-H-B three-center two-electron bond. The remaining four hydrogen atoms are terminal, bonded directly to each boron atom.

9.3.2 Preparation of Diborane

Diborane can be prepared through various methods, including the reduction of boron halides (like BF_3) with sodium hydride or through the action of lithium aluminum hydride on boron trichloride (BCl_3).

9.3.3 Reactions of Diborane

Diborane reacts with water to produce boric acid and hydrogen. It also reacts with Lewis bases to form adducts and undergoes hydrolysis in the presence of moisture. Diborane is a versatile reducing agent and reacts with alkenes and alkynes in organic synthesis.

9.4 Tetraborane (B_4H_{10})

9.4.1 Structure of Tetraborane

Tetraborane (B_4H_{10}) consists of four boron atoms connected by a combination of terminal and bridging hydrogen atoms. The structure features a compact, cage-like arrangement of boron and hydrogen atoms.

9.4.2 Bonding in Tetraborane

The bonding in tetraborane involves three-center two-electron bonds similar to diborane, where the hydrogen atoms form bridges between boron atoms. The bonding is electron-deficient, characteristic of boron hydrides.

9.4.3 Preparation of Tetraborane

Tetraborane can be synthesized by the pyrolysis of diborane or other boron hydrides under controlled conditions. It can also be formed in small quantities during certain reactions of diborane with organic compounds.

9.4.4 Properties of Tetraborane

Tetraborane is a colorless, volatile liquid. It is highly reactive and flammable, making it difficult to handle. The compound exhibits high reactivity with air and water, leading to its decomposition.

9.4.5 Reactions of Tetraborane

Tetraborane reacts with oxygen, halogens, and other electrophiles. It undergoes hydrolysis to produce boric acid and hydrogen. It can also form adducts with Lewis bases like amines and phosphines.

9.4.6 Uses of Tetraborane

Tetraborane has been studied as a potential rocket fuel due to its high energy content. It has also been explored in the development of boron-based chemical syntheses.

9.5 Pentaborane (B_5H_9)

9.5.1 Structure of Pentaborane (B_5H_9)

Pentaborane (B_5H_9) consists of five boron atoms arranged in a trigonal bipyramidal structure. It has nine hydrogen atoms, some of which bridge between boron atoms, similar to other boranes.

9.5.2 Bonding in Pentaborane

The bonding in pentaborane features both three-center two-electron bonds and two-center two-electron bonds. The hydrogen atoms act as bridges between the boron atoms, making the bonding electron-deficient.

9.5.3 Preparation of Pentaborane (B_5H_9)

Pentaborane can be prepared by the pyrolysis of diborane or through controlled reactions of diborane with other boron hydrides. It is usually synthesized in small quantities due to its hazardous nature.

9.5.4 Properties of Pentaborane

Pentaborane is a colorless, highly toxic, and volatile liquid. It is extremely reactive, especially with air, making it pyrophoric. It decomposes in the presence of moisture.

9.5.5 Reactions of Pentaborane

Pentaborane reacts with halogens, forming halogenated derivatives. It also reacts with bases to form adducts and with water, releasing hydrogen and forming boric acid.

9.5.6 Uses of Pentaborane

Pentaborane has been explored as a high-energy fuel, especially for military applications. However, its toxicity and handling risks limit its widespread use.

9.6 Pentaborane (B_5H_{11})

9.6.1 Structure of Pentaborane (B_5H_{11})

The structure of pentaborane (B_5H_{11}) is similar to B_5H_9 but with two additional hydrogen atoms. The boron atoms form a trigonal bipyramidal shape with hydrogen atoms bridging the boron atoms.

9.6.2 Bonding in Pentaborane (B_5H_{11})

The bonding in pentaborane involves three-center two-electron bonds between boron and hydrogen atoms, creating electron-deficient regions. This unique bonding contributes to its chemical reactivity.

9.6.3 Preparation of Pentaborane (B_5H_{11})

Pentaborane (B_5H_{11}) is typically prepared by hydrogenation of B_5H_9 under controlled conditions or by the pyrolysis of other boron hydrides.

9.6.4 Properties of Pentaborane (B_5H_{11})

Pentaborane (B_5H_{11}) is a volatile and highly reactive compound, exhibiting properties similar to B_5H_9. It is flammable, toxic, and reacts readily with water and air.

9.6.5 Reactions of Pentaborane (B_5H_{11})

Pentaborane reacts with halogens, water, and other electrophiles. It can form stable adducts with Lewis bases and undergoes hydrolysis to form boric acid and hydrogen.

9.6.6 Uses of Pentaborane (B_5H_{11})

Pentaborane (B_5H_{11}) has been studied as a potential fuel for high-energy applications. However, due to its hazardous nature, its practical use is limited.

9.8 Sample Questions

A. Multiple Types Questions

1. What type of bonding is present in diborane (B_2H_6)?

a) Two-center two-electron bonds
b) Three-center two-electron bonds
c) Ionic bonding
d) Metallic bonding

Answer: b) Three-center two-electron bonds

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2. Which of the following methods can be used to prepare diborane (B_2H_6)?

a) Reduction of boric acid with sodium hydride
b) Hydrolysis of boron oxide
c) Reduction of boron halides with sodium hydride
d) Oxidation of boron nitride

Answer: c) Reduction of boron halides with sodium hydride

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3. Which of the following compounds is highly pyrophoric and reacts with air?

a) Diborane (B_2H_6)
b) Tetraborane (B_4H_{10})
c) Pentaborane (B_5H_9)
d) Pentaborane (B_5H_{11})

Answer: c) Pentaborane (B_5H_9)

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4. The structure of tetraborane (B_4H_{10}) is best described as:

a) Linear
b) Cage-like
c) Planar
d) Cubic

Answer: b) Cage-like

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5. Which property of pentaborane (B_5H_{11}) makes it less favorable for widespread use?

a) Low reactivity
b) High toxicity
c) Low volatility
d) Stability in air

Answer: b) High toxicity

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6. Tetraborane (B_4H_{10}) can be prepared by:

a) Pyrolysis of diborane
b) Reduction of boron oxide
c) Electrolysis of boric acid
d) Direct reaction of boron and hydrogen

Answer: a) Pyrolysis of diborane

7. Which of the following is a use of tetraborane (B_4H_{10})?

a) As a rocket fuel
b) In the manufacture of fertilizers
c) As a catalyst in organic reactions
d) As a cleaning agent

Answer: a) As a rocket fuel

8. The bonding in pentaborane (B_5H_9) includes which of the following types?

a) Two-center two-electron bonds only
b) Three-center two-electron bonds only
c) Both two-center and three-center two-electron bonds
d) Ionic bonding

Answer: c) Both two-center and three-center two-electron bonds

9. Which reaction is common to both tetraborane (B_4H_{10}) and pentaborane (B_5H_{11})?

a) Reaction with water to form boric acid
b) Reaction with oxygen to form boron oxide
c) Reaction with sodium to form sodium borohydride
d) Reaction with alkenes to form organoboron compounds

Answer: a) Reaction with water to form boric acid

10. Which of the following is a product of the reaction of diborane (B_2H_6) with water?

a) Boron trioxide
b) Boric acid
c) Boron nitride
d) Sodium borohydride

Answer: b) Boric acid

B. Short Type Questions

1. What type of bonding is present in the structure of diborane (B_2H_6)?
2. How is diborane (B_2H_6) prepared?
3. What happens when diborane reacts with water?
4. Describe the structure of tetraborane (B_4H_{10}).
5. What is the nature of the bonding in tetraborane (B_4H_{10})?
6. How can tetraborane (B_4H_{10}) be synthesized?
7. List two properties of tetraborane (B_4H_{10}).
8. What are the common reactions of tetraborane (B_4H_{10})?
9. Mention one use of tetraborane (B_4H_{10}).
10. Describe the structure of pentaborane (B_5H_9).
11. What type of bonding is found in pentaborane (B_5H_9)?
12. How is pentaborane (B_5H_9) prepared?
13. State two properties of pentaborane (B_5H_9).
14. What are the common reactions of pentaborane (B_5H_9)?
15. Give one application of pentaborane (B_5H_9).
16. Explain the structure of pentaborane (B_5H_{11}).
17. How does the bonding in pentaborane (B_5H_{11}) differ from other boranes?
18. Describe a method for preparing pentaborane (B_5H_{11}).
19. List two properties of pentaborane (B_5H_{11}).
20. What is a typical reaction of pentaborane (B_5H_{11})?
21. Mention one use of pentaborane (B_5H_{11}).

C. Assay Type Questions

1. Discuss the structure and bonding of diborane (B_2H_6). How does its electron-deficient nature affect its stability and reactivity?

2. Describe the various methods of preparing diborane (B_2H_6). Highlight the key reactions that diborane undergoes and explain its role as a reducing agent in organic synthesis.

3. Explain the structure and bonding in tetraborane (B_4H_{10}). How does the three-center two-electron bond in tetraborane compare to that in diborane?

4. Describe the preparation methods of tetraborane (B_4H_{10}) and discuss its chemical properties. What challenges are associated with handling this compound?

5. Compare and contrast the structures of pentaborane (B_5H_9) and pentaborane (B_5H_{11}). How do these structures influence their respective chemical properties and reactivities?

6. Explain the synthesis of pentaborane (B_5H_9) and its reactions with different chemical species, such as halogens and water. Discuss the challenges of using pentaborane due to its high reactivity and toxicity.

7. Analyze the uses of tetraborane (B_4H_{10}) and pentaborane (B_5H_9) in high-energy fuel applications. Why were these compounds studied for rocket propulsion, and what are the safety concerns that limit their practical use?

8. Discuss the methods of preparing pentaborane (B_5H_{11}) and its key reactions. How does its bonding contribute to its unique chemical behavior?

9. Write a detailed essay on the properties and reactions of diborane (B_2H_6), tetraborane (B_4H_{10}), and pentaborane (B_5H_9). Compare their structural differences and explain how these differences affect their stability and reactivity.

10. Evaluate the electron-deficient bonding in boron hydrides, using diborane (B_2H_6), tetraborane (B_4H_{10}), and pentaborane (B_5H_{11}) as examples. Discuss the significance of three-center two-electron bonds in the chemistry of boron hydrides.

9.9 References

1. "Boron: Synthesis, Structure, and Properties" by N.N. Greenwood and A. Earnshaw
2. This book provides an extensive overview of boron chemistry, including boron hydrides, organoboron compounds, and the structure of boron compounds. It is a part of the famous "Chemistry of the Elements" series.
3. "Comprehensive Inorganic Chemistry II" (Volume 1, Boron Group) edited by J.C. Bailar
4. A detailed reference on group 13 elements, particularly boron, its compounds, and applications, including the hydrides and organoboron chemistry.
5. "Boron Hydride Chemistry" by E.L. Muetterties
6. This classic book focuses on the chemistry of boron hydrides, including their structures, bonding, and reactions.
7. "Boron Science: New Technologies and Applications" by Narayan Hosmane

8. A modern book that covers advances in boron chemistry, including boron-based materials, applications in nanotechnology, and medicinal chemistry.
9. "Boron Chemistry at the Beginning of the 21st Century" edited by Waldemar Siebert
10. This collection covers the state of boron chemistry, focusing on research developments and its applications in the 21st century.
11. "The Chemistry of Boron and Its Compounds" by Earl L. Muetterties and John D. Roberts
12. A comprehensive review of the chemistry of boron compounds, including boron hydrides and other boron-containing molecules.

Unit - 10 ❑ Compounds of P, S and Cl

Structure

10.0 Objectives

- Understand the different types of oxoacids of phosphorus, including orthophosphoric acid, hypophosphorous acid, and phosphorous acid.
- Analyze the roles of phosphorus oxoacids in biological, industrial, and environmental contexts.
- Study the acid strengths and reactivity trends of phosphorus oxoacids.
- Identify the key oxoacids of sulfur, such as sulfuric acid, sulfurous acid, and thiosulfuric acid.
- Investigate the industrial applications of sulfur oxoacids, including their use in chemical production and oxidation reactions.
- Learn about the different oxoacids of chlorine, including hypochlorous acid, chloric acid, and perchloric acid.
- Compare the oxidation states and reactivity patterns of chlorine oxoacids.
- Explore the structures and properties of halides and oxohalides of phosphorus, sulfur, and chlorine.
- Understand the reactivity of these compounds in different chemical processes and industrial applications.
- Analyze the use of halides and oxohalides as intermediates in organic synthesis and other chemical reactions.
- Understand the molecular structure and bonding of phosphorus trichloride.
- Explore its role as a reagent in the synthesis of organophosphorus compounds.
- Investigate the industrial applications of PCl_3 , including in flame retardants and insecticides.
- Study the reactivity and decomposition pathways of PCl_5 in various chemical reactions.

- Examine the structure and chemical behavior of thionyl chloride.
- Understand its use as a reagent in converting alcohols and carboxylic acids to chlorides.
- Investigate its industrial applications and safety precautions for handling $SOCl_2$.
- Study the molecular structure and bonding of sulfuryl chloride.
- Explore its use as a chlorinating agent in the production of sulfonyl chlorides.

10.1 Introduction

Phosphorus (P), sulfur (S), and chlorine (Cl) are essential elements in chemistry, each forming a wide range of compounds with significant industrial, environmental, and biological relevance. Among the most important of these compounds are their oxoacids and halides, which exhibit diverse chemical behavior due to varying oxidation states and bonding patterns.

Oxoacids are compounds containing an element, oxygen, and hydrogen, and play crucial roles in both organic and inorganic chemistry. Phosphorus forms a variety of oxoacids, including orthophosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), and hypophosphorous acid (H_3PO_2), which differ in their phosphorus oxidation states and structures. These oxoacids are essential in agriculture, industrial applications, and biological systems. Similarly, sulfur forms several oxoacids, such as sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3), which are fundamental in industrial processes, particularly in the production of chemicals and fertilizers. Chlorine also forms oxoacids like hypochlorous acid (HClO) and perchloric acid ($HClO_4$), which are strong oxidizing agents used in disinfection and organic synthesis.

In addition to oxoacids, the halides and oxohalides of phosphorus, sulfur, and chlorine are critical reagents in synthetic chemistry. Compounds such as phosphorus trichloride (PCl_3), phosphorus pentachloride (PCl_5), thionyl chloride ($SOCl_2$), and sulfuryl chloride (SO_2Cl_2) are widely used as chlorinating agents and intermediates in the production of various chemicals. These compounds exhibit diverse structures and reactivity patterns, making them versatile tools in both laboratory and industrial applications.

Understanding the structures, bonding, and reactivity of these oxoacids and halides is essential for grasping the broader chemistry of phosphorus, sulfur, and chlorine, as well as their impacts on industrial processes, environmental systems, and technological applications. This exploration provides insights into their roles in synthesis, catalysis, and environmental phenomena such as acid rain and pollution control.

10.2 Oxoacids of P

Phosphorus forms several oxoacids, which are compounds containing phosphorus, oxygen, and hydrogen, with varying oxidation states. The most common oxoacids of phosphorus include orthophosphoric acid (H_3PO_4), hypophosphorous acid (H_3PO_2), and phosphorous acid (H_3PO_3). These acids play significant roles in various chemical processes, such as in fertilizers, detergents, and industrial applications. The differences in their oxidation states and structural arrangements result in varying acid strengths and reactivity. Understanding these oxoacids is crucial to grasping phosphorus chemistry, particularly its role in biological and environmental systems.

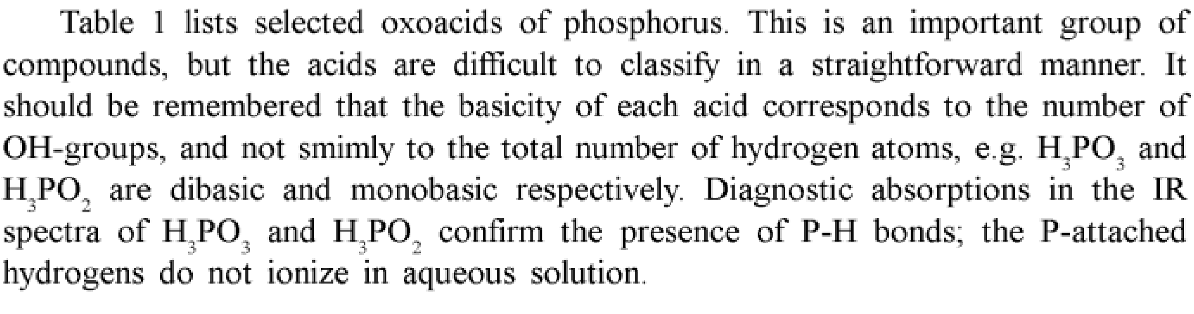


Table 1 lists selected oxoacids of phosphorus. This is an important group of compounds, but the acids are difficult to classify in a straightforward manner. It should be remembered that the basicity of each acid corresponds to the number of OH-groups, and not smimly to the total number of hydrogen atoms, e.g. H_3PO_3 and H_3PO_2 are dibasic and monobasic respectively. Diagnostic absorptions in the IR spectra of H_3PO_3 and H_3PO_2 confirm the presence of P-H bonds; the P-attached hydrogens do not ionize in aqueous solution.

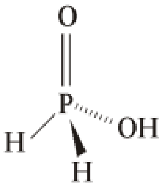
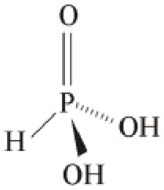
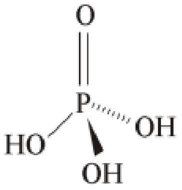
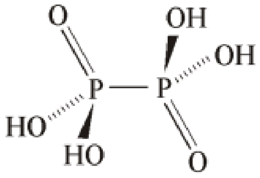
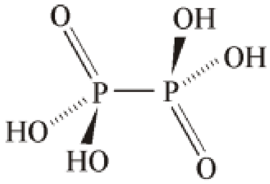
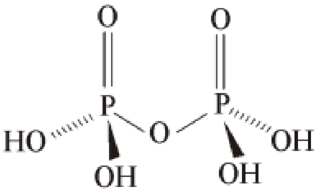
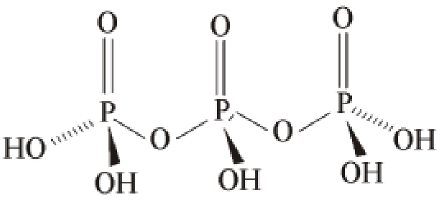
Formula	Name	Structure	pK_a values
H_3PO_2	Phosphinic acid (hypophosphorous acid)		$pK_a = 1.24$
H_3PO_3	Phosphonic acid (phosphorous acid)		$pK_a(1) = 2.00$; $pK_a(2) = 6.59$
H_3PO_4	Phosphinic acid (orthophosphoric acid)		$pK_a(1) = 2.21$; $pK_a(2) = 7.21$; $pK_a(3) = 12.67$
$H_4P_2O_6$	Hypophosphoric acid		$pK_a(1) = 2.2$; $pK_a(2) = 2.8$; $pK_a(3) = 7.3$; $pK_a(4) = 10.0$
$H_4P_2O_6$	Hypophosphoric acid		$pK_a(1) = 2.2$; $pK_a(2) = 2.8$; $pK_a(3) = 7.3$; $pK_a(4) = 10.0$
$H_4P_2O_7$	Diphosphoric acid (pyrophosphoric acid)		$pK_a(1) = 0.85$; $pK_a(2) = 1.49$; $pK_a(3) = 5.77$; $pK_a(4) = 8.22$
$H_5P_3O_{10}$	Triphosphoric acid		$pK_a(1) \leq 0$ $pK_a(2) = 0.89$; $pK_a(3) = 4.09$; $pK_a(4) = 6.98$; $pK_a(5) = 9.93$

Table : 1 Oxoacids of Phosphorus.

❑ Phosphinic acid (H_3PO_2) :

The reaction of white phosphorus with aqueous alkali produces the phosphinate (or hypophosphite) ion, $[H_2PO_2]^-$. By using $Ba(OH)_2$ as alkali, preciptating the Ba^{2+} ions as $BaSO_4$, and evaporating the aqueous solution, white deliquescent crystals of H_3PO_2 can be obtained. In aqueous solution, H_3PO_2 is a fairly strong monobasic acid

$$H_3PO_2 + H_2O = [H_3O]^+ + [H_2PO_2]^-$$

Phosphinic acid and its salts are reducing agents, and $NaH_2PO_2.H_2O$ is used industrially in a non-electrochemical reductive process which plates nickel onto, for example, steel. When heated, H_3PO_2 disproportionates according to the products being determined by reaction temperature.

$$3H_3PO_2 \rightarrow PH_3 + 2H_3PO_3 \text{ or } 2H_3PO_2 \rightarrow PH_3 + H_3PO_4$$

❑ Phosphonic acid (H_3PO_3) :

Phosphonic acid (commonly called phosphorous acid) may be crystallized from the solution obtained by adding ice-cold water to P_4O_6 or PCl_3. Pure H_3PO_3 forms colourless, deliquescent crystals (mp 343 K) and in the solid state, molecules of the acid (Table 1) are linked by hydrogen bonds to form a three dimensional network. In aqueous solution, it is dibasic.

$$H_3PO_3(aq) + H_2O = [H_3O]^+ + [H_2PO_3]^-$$
$$[H_2PO_3]^- + H_2O = [H_3O]^+ + [HPO_3]^{2-}$$

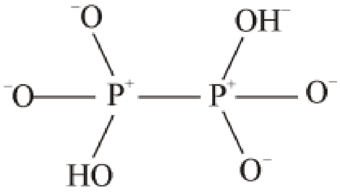
Salts containing the $[HPO_3]^{2-}$ ion are called phosphonates. Although the name ‘phosphite’ remains in common use, it is a possible source of confusion since esters of type $P(OR)_3$ are also called phosphites, e.g. $P(OEt)_3$ is triethlphosphite. Phosphonic acid is a reducing agent, but disproportionate when heated.

$$4H_3PO_3(470K) \rightarrow PH_3 + 3H_3PO_4$$

❑ Hypophosphoric acid ($H_4P_2O_6$) :

The reaction between red phosphorus and $NaCl$ or $NaClO_2$ yields $Na_2H_2P_2O_6$, which can be converted in aqueous solution into the dihydrate of the free acid which is best formulated as $[H_3O]_2[H_4P_2O_6]$. Dehydration using P_4O_{10} gives $H_4P_2O_6$. All four terminal P-O bonds are of equal length (157 pm), and the bonding description shown in Fig. 20.

$$H_4P_2O_6 + H_2O \rightarrow H_3PO_3 + H_3PO_4$$



❑ Phosphoric acid, H_3PO_4 and its derivatives :

Phosphoric acid is made from phosphate rock or by hydration of P_4O_{10}

$$Ca_3(PO_4)_2 + 3H_2SO_4(conc.) \rightarrow 2H_3PO_4 + 3CaSO_4$$

The qure acid forms deliquescent, colourless crystals (mp 315K). It has a molecular structure with P-OH and P-O bond distances of 157 and 152 pm; this difference is significantly less than in P_4O_{10} and is the result of extensive hydrogen bonding in the crystalline state which links H_3PO_4 molecules into a layered network. On standing, crystalline H_3PO_4 rapidly forms a viscous liquid. In this and in the commercially available 85% (by weight with water) acid, extensive hydrogen bonding is responsble for the syrupy nature of the acid. In dilute aqueous solutions, acid molecules are hydrogen-bonded to water molecules rather than to each other. When H_3PO_4 is heated at 510K, it is dehydrated to diphosphoric acid. Comparison of the structures of these acids (Table 1) shows that water is eliminated with concomitant P-O-P bridge formation. Further heating yields triphosphoric acid.

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

$$H_3PO_4 + H_4P_2O_7 \rightarrow H_5P_3O_{10} + H_2O$$

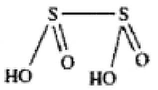
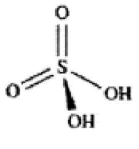
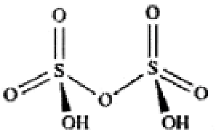
RESOURCES, ENVIRONMENTAL AND BLOLOGICAL

Phosphate fertilizers : essential to crops but are they damaging our lakes ?

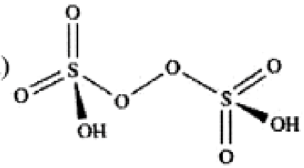
Worldwide demand for fertilizers is enormous and world consumption is increasing at a rate of between 2% and 3% per year. Phosphorus is an esential plant nutrient and up to 90% (depending on country) of phosphate rock that is mixed is consumed in the manufacture of phosphorus containing fertilizers. Insoluble phosphate rock is treated with concentrated H_2SO_4 to generate soluble super phosphate fertilizers containing $Ca(H_2PO_4)_2$ mixed with $CaSO_4$ an other sulfates; reaction between phosphate rock and H_3PO_4 gives triple superphosphate, mainly $Ca(H_2PO_4)_2$. Ammonium phosphate fertilizers are valuable sources of both N and P. Environmentalists are concerned about the effects of phosphates and polyphosphates from fertilizers and detergents have on the natural balance of populations. Phosphates in run-off water which flows into lakes contribute to the ecessive growth of algae (eutrophication), the presence of which depletes the lakes of O_2, thereby affecting fish and other water-life. However, the issue of phosphates in lakes is not clear-cut: recent field studies indicate adding phosphates to acid lakes (the result of acid rain pollution) stimulates plant growth, which in leads to production of $[OH]^-$, which neutralizes excess acid.

10.3 Oxoacids of S

Sulfur forms a wide variety of oxoacids, with sulfuric acid (H_2SO_4) being the most well-known and widely used in industrial applications. Other important oxoacids include sulfurous acid (H_2SO_3), thiosulfuric acid ($H_2S_2O_3$), and peroxosulfuric acids (e.g., H_2SO_5). These oxoacids vary in the oxidation state of sulfur and in their structural complexity. Sulfur oxoacids are essential in many chemical processes, including oxidation-reduction reactions and acid-base chemistry, and they play key roles in the environment, especially in the formation of acid rain.

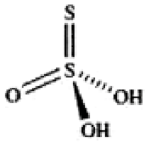
Formula	Name	Structure	pK$_a$ values (298K)
$H_2S_2O_4$	Dithionous acid (tetraoxodisulfuric acid)		$pK_a(1) = 0.35; pK_a(2) = 2.45$
H_2SO_3	Sulfurous acid (trioxodisulfuric acid)		$pK_a(1) = 1.82; pK_a(2) = 6.9$
H_2SO_4	Sulfuric acid (tetraoxosulfuric acid)		$pK_a(2) = 1.92$
$H_2S_2O_7$	Disulfuric acid (μ-oxo-hexaoxodisulfuric acid)		$pK_a(1) = 3.1$

$H_2S_2O_8$ Peroxodisulfuric acid
(μ-peroxo-hexaoxodisulfuric acid)



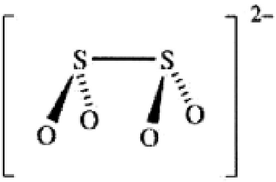
$pK_a(1) = 0.6; pK_a(2) = 1.74$

$H_2S_2O_3$ Thiosulfuric acid
(trioxothiosulfuric acid)



❑ Dithionous acid ($H_2S_2O_4$) :

Dithionite is prepared by reduction of sulfite in aqueous solution by *Zn* or *Na* amalgam and possesses eclipsed structure



$$2[SO_3]^{-2} + 2H_2O + 2e^- \rightleftharpoons 4[OH]^- + [S_2O_4]^{2-}$$

$$E^o = -1.12V$$

In aqueous solutions, $[S_2O_4]^{2-}$ is oxidized by air but in the absence of air, it undergoes according to the following reaction.

$$[S_2O_4]^{2-} + H_2O \rightarrow [S_2O_3]^{2-} + 2[HSO_3]^-$$

❑ Sulfurous and disulfurous acids (H_2SO_3 and $H_2S_2O_5$) :

Neither 'sulfurous acid' nor 'disulfurous acid' has been isolated as a free acid. Salts containing the sulfite ion, $[SO_3]^{2-}$ are well established (e.g. Na_2SO_3 and K_2SO_3 are comercially available) and are quite good reducing agents. Applications of sulfites include those as food preservatives, e.g. an additive in wines. The $[SO_3]^{2-}$ ion has a trigonal pyramidal structure with delocalized bonding ($S–O$ = 151 pm, $\angle OSO$ = 106°). Although the $[HSO_3]^-$ ion exists in solution, and slts such as $NaHSO_3$ (used as a bleaching agent) may be isolated. Evaporation of a solution of $NaHSO_3$ which has been saturated with SO_2 results in the formation of $Na_2S_2O_5$. The $[S_2O_5]^{2-}$ ion is the only known derived anion of disulfurous acid.

❑ Dithionic acid, $H_2S_2O_6$:

Dithionic acid is another sulfur oxoacid that is only known in aquous solution (in which it behaves as a strong acid) or in the form of salts containing the dithionate, $[S_2O_6]^{2-}$ ion. Such salts can be isolated as crystalline solids. The dithonate ion can be prepared by controlled oxidation of $[SO_3]^{2-}$

$$MnO_2 + 2[SO_3]^{2-} + 4H^+ \rightarrow Mn^{2+} + [S_2O_6]^{2-} + 2H_2O$$

❑ Sulfuric Acid (H_2SO_4)

Hydrogen sulfate is an oily, dense liquid that freezes at 10°C. Concentrated sulfuric acid is a water mixture with an acid concentration of 18 mol/L. Hydrogen sulfate mixes with water very exothermically. For this reason, it should be slowly added to water, not the reverse process, and the mixture should be stirred continuously. The molecule contains a tetrahedral arrangement of oxygen atoms around the central sulfur atom (Figure 16.18). The short bond lengths and the high bond energies suggest that there must be double bond character in the sulfur bonds to each terminal oxygen atom.

❑ Reactions of Sulfuric Acid :

We usually think of sulfuric acid as just an acid, but infact it can react in five different ways :

☐ Dilute sulfuric acid is used most often as an acid. It is a strong, diprotic acid, forming two ions, the hydrogen sulfate ion and the sulfate ion :

$$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

The first equilibrium lies far to the right, but the second one, less so. Thus, the predominant species in a solution of sulfuric acid are the hydronium ion and the hydrogen sulfate ion.

☐ Sulfuric acid can also act as a dehydrating agent. The concentrated acid will remove the elements of water from a number of compounds. For example sugar is converted to carbon and water. This exothermic reactions is spectacular :

$$C_{12}H_{22}O_{11}(s) + H_2SO_4(l) \rightarrow 12C(s) + 11H_2O(g) + H_2SO_4(aq)$$

The acid serves this function in a number of important organic reactions. For example, addition of concentrated sulfuric acid to ethanol produces ethene, C_2H_4, or ethoxyethane, $(C_2H_5)_2O$, depending on the reaction conditions :

$$C_2H_5OH(l) + H_2SO_4(l) \rightarrow C_2H_5OSO_3H(aq) + H_2O(l)$$

$$C_2H_5OSO_3H(aq) \rightarrow H_2SO_4(aq)[\text{excess acid}] + C_2H_4(g)$$

$$C_2H_5OSO_3H(aq) \rightarrow C_2H_5OH(l) \rightarrow (C_2H_5)_2O(l) + H_2SO_4(aq)[\text{excess ethanol}]$$

☐ Although sulfuric acid is not as strongly oxidizing as nitrie acid, if it is hot and concentrated, it will function as an oxidizing agent. For example, hot concentrated sulfuric acid reacts with copper metal to give the copper(II) ion, and the sulfuric acid itself is reduced to sulfur dioxide and water :

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e$$

$$2H_2SO_4(l) + 2e \rightarrow SO_2(g) + 2H_2O(l) + SO_4^{2-}(aq)$$

☐ Sulfuric acid can act as a sulfonating agent. The concentrated acid is used in organic chemistry to replace a hydrogen atom by the sulfonic acid group ($-SO_3H$) :

$$H_2SO_4(l) + CH_3C_6H_5(l) \rightarrow CH_3C_6H_4SO_3H(s) + H_2O(l)$$

☐ The Industrial Synthesis of Sulfuric Acid :

Sulfuric acid is synthesized in larger quantities than any other chemical. All synthetic routes use sulfur dioxide, and in some plants this reactant is obtained directly from the flue gases of smelting processes. However, in North America most of the sulfur dioxide is produced by burning molten sulfur in dry air :

$$S(l) + O_2(g) \rightarrow SO_2(g)$$

It is more difficult to oxidize sulfur dioxide further. There is a kinetic barrier to the formation of sulfur trioxide. Thus, an effective catalyst must be uded to obtain commercially useful rates of reaction. We also need to ensure that the position of equilibrium is to the right side of the equation. To accomplish this, we invoke the Le Chatelier principle, which predicts that an increase in pressure will favor the side of the equation with the fewer moles of gas—in this case, the product side. This reaction is also exothermic; thus, the choice of temperature must be high enough to produce a reasonable rate of reaction, even though these conditions will result in a decreased yield. In the *contact process*, pure, dry dulfur dioxide and dry air are passed through a catalyst of vanadium (*V*) oxide on an inert support. The gas mixture is heated to between 400° and 500°c, which is the optimum temperature for conversion to sulfur trioxide with a reasonable yield at an acceptable rate :

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5,\Delta} 2SO_3(g)$$

Sulfur trioxide reacts violently with water. However, it does react more controllably with concentrated sulfuric acid itself to give pyrosulfuric acid, $H_2S_2O_7$:

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

The pyrosulfuric acid is then diluted with water to produce an additional mole of sulfuric acid :

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

All steps in the process are exothermic. In fact, the entire process of converting elemental sulfur to sulfuric acid produces 535 kJ/mol of heat. An essential feature of any sulfuric acid plant is effective utilization of this waste heat, either as direct

10.4 Oxoacids of Cl

Chlorine also forms several oxoacids, including hypochlorous acid (HClO), chlorous acid ($HClO_2$), chloric acid ($HClO_3$), and perchloric acid ($HClO_4$). These oxoacids are strong oxidizing agents, and their strength increases with the number of oxygen atoms attached to chlorine. The oxoacids of chlorine are important in both industrial and environmental chemistry, often used as disinfectants, bleaching agents, and in the production of explosives. The stability and reactivity of chlorine oxoacids depend on their oxidation states and molecular structures.

10.5 Halides and Oxohalides of P, S, and Cl

Phosphorus, sulfur, and chlorine form various halides and oxohalides, which are compounds consisting of halogens and oxygen atoms bonded to these elements. These compounds are widely used in chemical industries, especially in the synthesis of other chemicals and as intermediates in organic reactions. Halides like phosphorus trichloride (PCl_3), phosphorus pentachloride (PCl_5), thionyl chloride ($SOCl_2$), and sulfuryl chloride (SO_2Cl_2) exhibit distinct structures and properties, making them versatile reagents in synthetic and industrial chemistry.

10.5 PCl_3

Phosphorus trichloride (PCl_3) is a colourless, fuming liquid that reacts readily with water and alcohols, producing phosphorous acid and hydrogen chloride. It is a key industrial chemical used in the production of organophosphorus compounds, insecticides, and flame retardants. The molecule has a trigonal pyramidal structure, and its reactivity is largely due to the lone pair of electrons on the phosphorus atom.

Chemical Structure and Formula

- Molecular Formula: PCl_3

- Molecular Weight: 137.33 g/mol
- Structure: Phosphorus trichloride has a trigonal pyramidal structure with phosphorus (P) at the center. The phosphorus atom is bonded to three chlorine (Cl) atoms, and the lone pair of electrons on the phosphorus gives it this pyramidal geometry.
- Bonding: The central phosphorus atom uses its valence electrons to form covalent bonds with chlorine atoms.

Physical Properties

- Appearance: Colourless to slightly yellow fuming liquid.
- Density: 1.574 g/cm^3 at 20°C.
- Melting Point: -93.6°C.
- Boiling Point: 76.1°C.
- Solubility: PCl_3 reacts with water to form phosphorous acid (H_3PO_3) and hydrogen chloride (HCl), so it is not stable in aqueous solutions but is soluble in organic solvents like benzene and carbon tetrachloride.

Reactivity and Chemical Properties

- Reactivity with Water: Phosphorus trichloride hydrolyzes rapidly upon contact with water, forming phosphorous acid (H_3PO_3) and hydrochloric acid (HCl): $PCl_3+3H_2O \rightarrow H_3PO_3+3HCl$
- Chlorinating Agent: PCl_3 is used to chlorinate alcohols and carboxylic acids to produce alkyl chlorides and acyl chlorides, respectively: $ROH+PCl_3 \rightarrow RCl+H_3PO_3$

- Redox Properties: Phosphorus in PCl_3 has an oxidation state of +3 and can act as a reducing agent in some reactions.
- Reaction with Oxygen: Upon exposure to air, PCl_3 can oxidize to form phosphorus oxychloride ($POCl_3$): $2PCl_3 + O_2 \rightarrow 2POCl_3$

Applications

- Production of Phosphorus Compounds: PCl_3 is a precursor for many other phosphorus compounds, such as phosphorus pentachloride (PCl_5), phosphites, and phosphonates.
- Pharmaceutical Industry: It is used in the synthesis of organophosphorus compounds, which are essential intermediates in the production of pharmaceuticals, agrochemicals, and flame retardants.
- Plastic and Polymer Industry: Phosphorus trichloride is used in the production of plasticizers, which enhance the flexibility and durability of plastics and polymers.
- Manufacture of Insecticides and Herbicides: PCl_3 is used to produce phosphorus-based pesticides and herbicides, such as glyphosate.
- Flame Retardants: Phosphorus compounds derived from PCl_3 are used in the formulation of flame retardants for plastics and textiles.

Handling and Safety

- Toxicity: Phosphorus trichloride is highly toxic and corrosive. Inhalation of its fumes can cause severe damage to the respiratory system, and contact with the skin or eyes can lead to burns. Its reaction with moisture releases hydrogen chloride gas (HCl), which is also hazardous.
- Storage: PCl_3 should be stored in tightly sealed containers, in a cool, dry place, away from moisture and incompatible substances like water and strong oxidizing agents.

- Hazards: Reacts violently with water, producing hydrochloric acid and phosphorous acid. It is highly reactive with air and must be handled under controlled conditions to prevent exposure to moisture and oxygen.
- PPE Requirements: Proper personal protective equipment (PPE), including gloves, goggles, face shields, and respirators, should be used when handling PCl_3. Operations should be carried out in fume hoods to avoid inhalation of vapors.

Reactions

- Hydrolysis: As mentioned earlier, PCl_3 reacts with water to form phosphorous acid (H_3PO_3) and hydrogen chloride (HCl).
- Reaction with Alcohols: PCl_3 reacts with alcohols to form alkyl chlorides and phosphorous acid: $3ROH+PCl_3 \rightarrow 3RCl+H_3PO_3$
- Reaction with Carboxylic Acids: Similarly, PCl_3 reacts with carboxylic acids to produce acyl chlorides and phosphorous acid: $3RCOOH+PCl_3 \rightarrow 3RCOCl+H_3PO_3$
- Oxidation: In the presence of oxygen, PCl_3 can be oxidized to phosphorus oxychloride ($POCl_3$), which is an important intermediate in chemical synthesis: $2PCl_3+O_2 \rightarrow 2POCl_3$

Industrial Production

- Synthesis: Phosphorus trichloride is produced by reacting elemental white phosphorus (P_4) with chlorine gas (Cl_2): $P_4+6Cl_2 \rightarrow 4PCl_3$
- The reaction occurs in a controlled environment, usually in the gas phase, to ensure high yield and purity.

Environmental Impact

- Toxicity to the Environment: Phosphorus trichloride is harmful to aquatic life and the environment. Its hydrolysis products, phosphorous acid and hydrochloric acid, can contribute to water and soil contamination.

- Air Pollution: The release of PCl_3 fumes or its by-products (HCl and H_3PO_3) into the air can contribute to air pollution, making it important to control emissions during manufacturing and use.

Comparison with Other Phosphorus Chlorides

PCl_3 vs. Phosphorus Pentachloride (PCl_5): PCl_5 is a stronger chlorinating agent than PCl_3. While PCl_3 is primarily used for the production of other phosphorus compounds and moderate chlorination reactions, PCl_5 is more reactive and used for more demanding chlorination tasks.

PCl_3 vs. Phosphorus Oxychloride ($POCl_3$): $POCl_3$ is used in different synthetic applications, particularly for phosphorylating agents and flame retardants, while PCl_3 is more commonly used as a general reagent for chlorination and in the production of organophosphorus compounds.

10.6 PCl_5

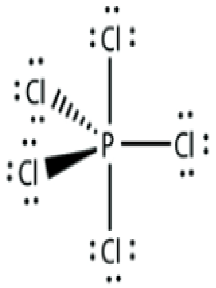
Phosphorus pentachloride (PCl_5) is a yellowish solid that exists in two forms: a solid ionic form and a gaseous molecular form. It is widely used as a chlorinating agent, especially in the conversion of hydroxyl groups (-OH) into chloride groups (-Cl) in organic synthesis. In its molecular form, PCl_5adopts a trigonal bipyramidal geometry, making it an interesting example of expanded octet bonding.

Chemical Structure and Formula

- Molecular Formula: PCl_5
- Molecular Weight: 208.24 g/mol
- Structure: In the solid state, PCl_5 has a trigonal bipyramidal structure, with phosphorus (P) at the center. Three chlorine atoms are equatorially positioned, and two are axially positioned. In the gas phase, PCl_5 can dissociate into PCl_3 and Cl_2, showing dynamic behavior.

- Bonding: The central phosphorus atom in PCl_5 forms five bonds with chlorine atoms, using expanded octet bonding with d-orbitals to accommodate more than eight electrons.

Structure of PCl_5: The hybridization of P in PCl_5 is sp^3d. The geometry of the molecule is trigonal bipyramid. The axial and equatorial bond distances are 2.14 Å and 2.04 Å respectively.



Physical Properties

- Appearance: Pale yellow or greenish-white crystalline solid.
- Density: 2.1 g/cm^3 at 25°C.
- Melting Point: 160°C (with decomposition).
- Boiling Point: Sublimes at 166°C under normal atmospheric pressure.
- Solubility: Reacts vigorously with water but is soluble in some organic solvents like benzene and carbon tetrachloride.

Reactivity and Chemical Properties

- Hydrolysis: Phosphorus pentachloride reacts violently with water, forming phosphoric acid (H_3PO_4) and hydrogen chloride (HCl): $PCl_5+4H_2O \rightarrow H_3PO_4+5HCl$

  This makes it highly reactive in moist environments.
- Chlorinating Agent: PCl_5 is widely used in organic chemistry as a powerful chlorinating agent, converting alcohols, carboxylic acids, and amines into their corresponding chlorides. For example: $RCOOH+PCl_5 \rightarrow RCOCl+POCl_3+HCl$

- Reaction with Bases: It reacts with bases such as ammonia (NH_3), yielding phosphorus-containing products like phosphoryl chloride ($POCl_3$) and amine salts.

Applications

- Organic Synthesis: PCl_5 is extensively used for converting hydroxyl groups (-OH) into chloride groups (-Cl), which is crucial in the synthesis of acyl chlorides from carboxylic acids and alkyl chlorides from alcohols. For example: $ROH+PCl_5 \rightarrow RCl+POCl_3+HCl$
- Pharmaceuticals and Agrochemicals: Used in the production of chlorinated intermediates that are precursors to various pharmaceutical drugs, pesticides, and herbicides.
- Production of Phosphoryl Chloride ($POCl_3$): PCl_5 is a key reagent for producing phosphoryl chloride, another important chlorinating agent used in organic synthesis, especially for reactions that introduce phosphoryl groups into molecules.
- Lithium Battery Industry: Phosphorus pentachloride is used in the preparation of lithium-ion battery electrolytes, helping in the synthesis of organophosphorus compounds.
- Dyes and Pigments: It's employed in the synthesis of certain dyes, pigments, and other colorants.

Handling and Safety

- Toxicity: PCl_5 is highly corrosive and toxic. It can cause severe skin burns, eye damage, and respiratory problems if inhaled or exposed to skin. The fumes are also irritating due to the release of hydrogen chloride (HCl) gas when it comes into contact with moisture.

- Decomposition: When heated or exposed to moisture, PCl_5 decomposes into $POCl_3$ and HCl. Both products are harmful, so it must be handled in a dry, well-ventilated environment or under a fume hood.
- Storage: PCl_5 should be stored in tightly sealed containers, away from moisture, in a cool, dry place to prevent decomposition. It is sensitive to light and humidity.
- PPE Requirements: Appropriate personal protective equipment (PPE) like gloves, goggles, and a lab coat should be used, along with fume hoods for ventilation.

Reactions

- Reaction with Water: As mentioned, PCl_5 reacts violently with water, producing phosphoric acid and hydrochloric acid. Care must be taken to avoid accidental exposure to moisture.
- Reaction with Alcohols and Carboxylic Acids: PCl_5 reacts with alcohols to form alkyl chlorides and with carboxylic acids to form acyl chlorides.
- Reaction with Ammonia: When PCl_5 reacts with ammonia, it forms phosphorus nitride and ammonium chloride: $PCl_5+4NH_3 \rightarrow P(NH_2)_3+5NH_4Cl$
- Reaction with Sulfur Dioxide: Phosphorus pentachloride reacts with sulfur dioxide to form sulfuryl chloride (SO_2Cl_2) and phosphoryl chloride ($POCl_3$): $PCl_5+SO_2 \rightarrow SO_2Cl_2+POCl_3$

Industrial Production

- Synthesis: Phosphorus pentachloride is typically produced by the direct chlorination of phosphorus trichloride (PCl_3) with chlorine gas (Cl_2) in a controlled environment:

$$PCl_3+Cl_2 \rightarrow PCl_5$$

- This process occurs in a reaction chamber under dry conditions to prevent the formation of undesired by-products due to moisture contamination.

Environmental Impact

- Hazards: PCl_5 releases HCl gas when it comes into contact with moisture in the environment, contributing to atmospheric pollution. Both HCl and $POCl_3$ are corrosive and toxic, making it essential to follow strict handling and disposal procedures.
- Disposal: Phosphorus pentachloride waste must be neutralized before disposal. It can be neutralized with a basic solution like sodium carbonate or calcium hydroxide before being discarded in compliance with local regulations.

Comparison with Other Chlorinating Agents

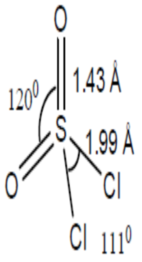
- PCl_5 vs. Thionyl Chloride ($SOCl_2$): While both PCl_5 and $SOCl_2$ are used for chlorination, PCl_5 is typically employed when a stronger chlorinating agent is required. Thionyl chloride has the advantage of producing gaseous by-products (SO_2 and HCl), making it easier to remove from the reaction.
- PCl_5 vs. Phosphorus Trichloride (PCl_3): PCl_5 is more reactive than PCl_3 due to the higher oxidation state of phosphorus. PCl_3 is also used in some chlorination processes, but PCl_5 is preferred when a more vigorous reaction is needed.

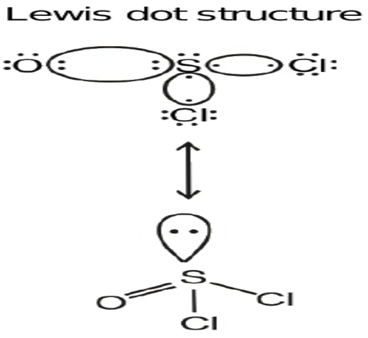
10.7 $SOCl_2$

Thionyl chloride ($SOCl_2$) is an inorganic compound widely used as a chlorinating agent in both industrial and laboratory settings. Here’s a detailed overview: Chemical Structure and Formula

- Molecular Formula: $SOCl_2$
- Molecular Weight: 118.97 g/mol

- Structure: Thionyl chloride consists of one sulfur atom (S) double-bonded to an oxygen atom (O) and single-bonded to two chlorine atoms (Cl). It has a trigonal pyramidal structure due to the lone pair on sulfur.





Physical Properties

- Appearance: A colourless to pale yellow liquid.
- Density: 1.638 g/cm³ at 25°C.
- Melting Point: -104.5°C.
- Boiling Point: 74.6°C.
- Solubility: Thionyl chloride reacts violently with water, releasing sulfur dioxide (SO_2) and hydrogen chloride (HCl). It is, however, soluble in organic solvents like benzene and chloroform.

Reactivity and Chemical Properties

- Reactivity: Thionyl chloride is highly reactive and is primarily used as a chlorinating agent. It decomposes in the presence of moisture, yielding sulfur dioxide and hydrogen chloride: $SOCl_2 + H_2O \rightarrow SO_2 + 2HCl$
- Chlorinating Agent: It is widely used to convert alcohols, carboxylic acids, and other compounds into chlorides.

For example: $ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$

This reaction is commonly used in organic synthesis to replace hydroxyl groups with chloride.

Applications

- Organic Synthesis: Thionyl chloride is commonly used in the production of acyl chlorides from carboxylic acids, and alkyl chlorides from alcohols. The chlorination is efficient, with by-products (SO_2 and HCl) easily removed from the reaction medium.
- Lithium Batteries: $SOCl_2$ is used in lithium-thionyl chloride ($Li\text{-}SOCl_2$) batteries, known for high energy density and long shelf life. These batteries are employed in applications like military, aerospace, and electronics.
- Pharmaceuticals and Agrochemicals: It's used to synthesize chlorinated intermediates that are key precursors in various pharmaceuticals and agrochemical products.
- Dye and Pigment Industries: Used in the production of dyes and pigments as a chlorinating agent.

Handling and Safety

- Toxicity: Thionyl chloride is corrosive and harmful if inhaled, ingested, or in contact with skin. Its reaction with water or moisture produces toxic and corrosive gases (SO_2 and HCl), which can be dangerous if inhaled in large amounts.
- Storage: $SOCl_2$ should be stored in a tightly sealed container away from moisture, in a cool, dry place. Since it's sensitive to water, it's crucial to avoid exposure to humidity.
- Hazards: Reacts violently with water, alcohols, and amines. It is a lachrymator, meaning it can irritate the eyes and respiratory tract.

Environmental Impact

- Decomposition: The reaction with water releases gases (SO_2 and HCl) that are harmful to the environment. These can contribute to air pollution and acid rain. Proper disposal and handling practices are necessary to minimize environmental harm.

Industrial Production

- Thionyl chloride is synthesized by reacting sulfur dioxide (SO_2) with sulfur dichloride (SCl_2) or by chlorinating sulfur dioxide in the presence of chlorine gas.

$$SO_2 + SCl_2 \rightarrow 2SOCl_2$$

10.8 SO_2Cl_2

Sulfuryl chloride (SO_2Cl_2) is a colourless liquid used as a chlorinating agent in organic synthesis. It consists of sulfur bonded to two chlorine atoms and two oxygen atoms, forming a tetrahedral structure. SO_2Cl_2can decompose to produce sulfur dioxide and chlorine gas, making it useful in various chemical reactions. It is often employed in the production of sulfonyl chlorides, which are intermediates in the synthesis of dyes and pharmaceuticals.

Chemical Structure and Formula

- Molecular Formula: SO_2Cl_2
- Molecular Weight: 134.96 g/mol
- Structure: The sulfur atom (S) is double-bonded to two oxygen atoms (O) and single-bonded to two chlorine atoms (Cl). The geometry around sulfur is tetrahedral.

Physical Properties

- Appearance: A colorless to pale yellow liquid.
- Density: 1.667 g/cm^3 at 25°C.
- Melting Point: -54.1°C.
- Boiling Point: 69.3°C.

- Solubility: Reacts with water, decomposing to produce sulfuric acid (H_2SO_4) and hydrogen chloride (HCl), and it is soluble in organic solvents like benzene and carbon tetrachloride.

Reactivity and Chemical Properties

- Reactivity: Sulfuryl chloride is primarily used as a chlorinating and oxidizing agent. It decomposes in the presence of moisture, releasing HCl and sulfuric acid: $SO_2Cl_2+H_2O\rightarrow H_2SO_4+2HCl$
- Chlorinating Agent: It is widely used for the chlorination of alkanes, aromatics, and other compounds. Its reactivity is comparable to that of chlorine gas but easier to handle: $R\text{-}H+SO_2Cl_2\rightarrow R\text{-}Cl+SO_2+HCl$
- Oxidizing Agent: In some reactions, SO_2Cl_2 acts as a source of both chlorine and oxygen atoms, facilitating oxidation and chlorination.

Applications

- Organic Synthesis: Sulfuryl chloride is widely used to chlorinate hydrocarbons and other organic molecules. The chlorination typically involves free-radical mechanisms, often initiated by heat or light.
- Sulfonation Agent: It is involved in the sulfonation of organic compounds, adding sulfonyl groups ($-SO_2$) to molecules, which is useful in the production of detergents, dyes, and pharmaceuticals.
- Preparation of Intermediates: In the pharmaceutical industry, sulfuryl chloride is used to produce chlorinated intermediates that serve as precursors to drugs and fine chemicals.
- Rubber and Plastic Industry: It is used in the modification of polymers and rubbers by introducing chlorine atoms into the polymer chains, affecting the physical properties of the materials.

Handling and Safety

- Toxicity: Sulfuryl chloride is highly corrosive and toxic. It can cause severe burns on contact with skin and eyes, and inhalation of its vapours can damage the respiratory system. The hydrolysis products (HCl and H_2SO_4) are also highly corrosive.
- Storage: SO_2Cl_2 should be stored in tightly sealed containers, away from moisture and direct sunlight, as it is sensitive to water and decomposes slowly in the presence of light.
- Hazards: Reacts violently with water and alcohols. It is a lachrymator, meaning it can irritate the eyes and respiratory tract. It must be handled with proper personal protective equipment (PPE) in well-ventilated areas or fume hoods.

Industrial Production

- Synthesis: Sulfuryl chloride is produced by the reaction of sulfur dioxide (SO_2) and chlorine gas (Cl_2) in the presence of a catalyst, such as activated carbon, under high temperatures. This reaction is exothermic: $SO_2+Cl_2 \rightarrow SO_2Cl_2$

  The production process needs controlled conditions to avoid the formation of unwanted by-products like sulfur dichloride (SCl_2).

Environmental Impact

- Decomposition Products: The decomposition of SO_2Cl_2 produces sulfur dioxide (SO_2) and hydrogen chloride (HCl), both of which can contribute to air pollution and acid rain. Therefore, proper disposal methods and containment are crucial to minimize environmental harm.
- Spill Response: In the event of a spill, it is necessary to contain and neutralize the product with an appropriate neutralizing agent, such as sodium bicarbonate ($NaHCO_3$), while avoiding water contact until controlled.

Comparison with Other Chlorinating Agents

- Sulfuryl chloride vs. Thionyl chloride ($SOCl_2$): Both are widely used chlorinating agents, but sulfuryl chloride is typically less reactive than thionyl chloride. Thionyl chloride reacts more readily with alcohols and carboxylic acids to produce alkyl and acyl chlorides, whereas sulfuryl chloride is often preferred for chlorinating saturated hydrocarbons and some aromatic compounds.

10.9 Summary

Oxoacids of Phosphorus (P): Phosphorus forms various oxoacids, such as phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), and hypophosphorous acid (H_3PO_2). These oxoacids differ in oxidation states, number of oxygen atoms, and bonding patterns. Phosphoric acid is the most stable and widely used.

Oxoacids of Sulfur (S): Sulfur forms several oxoacids, including sulfuric acid (H_2SO_4), sulfurous acid (H_2SO_3), and peroxysulfuric acid (H_2SO_5). These acids vary in oxidation states and reactivity. Sulfuric acid is particularly significant due to its industrial applications and strong acidic nature.

Oxoacids of Chlorine (Cl): Chlorine forms oxoacids such as hypochlorous acid (HClO), chlorous acid ($HClO_2$), chloric acid ($HClO_3$), and perchloric acid ($HClO_4$). These oxoacids display increasing oxidation states from +1 to +7, with perchloric acid being the most oxidizing and stable in aqueous solution.

Halides and Oxohalides of Phosphorus, Sulfur, and Chlorine: Phosphorus, sulfur, and chlorine form various halides and oxohalides. These compounds, such as PCl_3, PCl_5, $SOCl_2$, and SO_2Cl_2, have diverse applications in organic synthesis and industrial processes.

PCl_3 (Phosphorus Trichloride): PCl_3 is a reactive phosphorus halide, primarily used as a reagent in organic chemistry for producing organophosphorus compounds and in the synthesis of pesticides.

PCl_5 (Phosphorus Pentachloride): PCl_5 serves as an oxidizing and chlorinating agent in chemical reactions, often used to convert alcohols to alkyl chlorides and carboxylic acids to acyl chlorides.

$SOCl_2$ (Thionyl Chloride): $SOCl_2$ iscommonly used as a chlorinating agent, especially in the conversion of carboxylic acids into acyl chlorides. It decomposes upon heating, producing sulfur dioxide and chlorine gas.

SO_2Cl_2 (Sulfuryl Chloride): SO_2Cl_2 is a chlorinating and sulfonating agent used in organic synthesis and in preparing certain chemicals. It decomposes into SO_2 and Cl_2 upon heating, and is useful in introducing both sulfur and chlorine into compounds.

10.10 Sample Questions

A. Multiple Choice Type Questions

1. Which of the following is the most stable oxoacid of phosphorus?

A) Hypophosphorous acid (H_3PO_2)
B) Phosphoric acid (H_3PO_4)
C) Phosphorous acid (H_3PO_3)
D) Metaphosphoric acid (HPO_3)
Answer: B) Phosphoric acid (H_3PO_4)

2. What is the oxidation state of sulfur in sulfuric acid (H_2SO_4)?

A) +2
B) +4
C) +6
D) +8
Answer: C) +6

3. Which oxoacid of chlorine has the highest oxidation state?

A) Hypochlorous acid ($HClO$)
B) Chlorous acid ($HClO_2$)
C) Chloric acid ($HClO_3$)
D) Perchloric acid ($HClO_4$)
Answer: D) Perchloric acid ($HClO_4$)

4. What is the primary use of phosphorus trichloride (PCl_3) in chemical synthesis?

A) As an oxidizing agent
B) As a dehydrating agent
C) As a reagent to produce organophosphorus compounds
D) As a catalyst in hydrogenation reactions
Answer: C) As a reagent to produce organophosphorus compounds

5. Which of the following compounds is commonly used to convert carboxylic acids into acyl chlorides?

A) Phosphoric acid
B) Thionyl chloride ($SOCl_2$)
C) Sulfur dioxide
D) Phosphorous acid
Answer: B) Thionyl chloride ($SOCl_2$)

6. What are the decomposition products of sulfuryl chloride (SO_2Cl_2)?

A) SO_2 and Cl_2
B) SO_3 and Cl_2
C) SO_3 and HCl
D) SO_2 and HCl
Answer: A) SO_2 and Cl_2

7. Which of the following is an oxohalide of sulfur?

A) PCl_5
B) SO_3
C) $SOCl_2$
D) H_2SO_4
Answer: C) $SOCl_2$

8. What is the oxidation state of phosphorus in phosphorus pentachloride (PCl_5)?

A) +1
B) +3
C) +5
D) -3
Answer: C) +5

9. Which oxoacid of sulfur is known for its strong acidic properties and industrial significance?

A) Sulfurous acid (H_2SO_3)
B) Sulfuric acid (H_2SO_4)
C) Thiosulfuric acid ($H_2S_2O_3$)
D) Peroxysulfuric acid (H_2SO_5)
Answer: B) Sulfuric acid (H_2SO_4)

10. Which oxoacid of phosphorus has the lowest oxidation state of phosphorus?

A) Phosphoric acid (H_3PO_4)
B) Hypophosphorous acid (H_3PO_2)
C) Phosphorous acid (H_3PO_3)
D) Pyrophosphoric acid ($H_4P_2O_7$)
Answer: B) Hypophosphorous acid (H_3PO_2)

B. Short Type Questions

1. **What are oxoacids of phosphorus, and how do they differ from each other?**

   Answer: Oxoacids of phosphorus are acids that contain phosphorus, oxygen, and hydrogen atoms. They differ in their oxidation states and the number of oxygen atoms bonded to phosphorus. Examples include phosphoric acid (H_3PO_4, oxidation state +5), phosphorous acid (H_3PO_3, +3), and hypophosphorous acid (H_3PO_2, +1).

2. **Why is sulfuric acid (H_2SO_4) considering a strong acid?**

   Answer: Sulfuric acid is considered a strong acid because it completely dissociates in water, releasing H^+ ions, and has a high degree of ionization. Its large number of oxygen atoms stabilizes the sulfate ion (SO_4^{2-}), making it a stable and powerful proton donor.

3. **List the oxidation states of chlorine in its oxoacids and give one example for each.**

   Answer: Chlorine has oxidation states of +1 (hypochlorous acid, HClO), +3 (chlorous acid, $HClO_2$), +5 (chloric acid, $HClO_3$), and +7 (perchloric acid, $HClO_4$) in its oxoacids.

4. **What is the main industrial application of phosphorus trichloride (PCl$_3$)?**

   Answer: Phosphorus trichloride is primarily used in the chemical industry as a reagent to produce organophosphorus compounds, such as pesticides, flame retardants, and plasticizers.

5. **How does thionyl chloride (SOCl$_2$) function as a chlorinating agent?**

   Answer: Thionyl chloride acts as a chlorinating agent by converting carboxylic acids into acyl chlorides. It reacts with the acid to release sulfur dioxide (SO$_2$) and hydrogen chloride (HCl), facilitating the formation of the acyl chloride.

6. **What is the chemical formula of sulfuryl chloride, and what are its common uses?**

   Answer: The chemical formula of sulfuryl chloride is SO_2Cl_2. It is commonly used as a chlorinating and sulfonating agent in organic synthesis, particularly in introducing chlorine or sulfur into compounds.

7. **Explain why PCl$_5$ acts as a chlorinating agent.**

   Answer: PCl$_5$ acts as a chlorinating agent due to its high reactivity and ability to donate chloride ions, which can replace hydroxyl groups in organic compounds to form chlorinated derivatives, such as alkyl chlorides or acyl chlorides.

8. **What are the decomposition products of sulfuryl chloride (SO_2Cl_2)?**

   Answer: Sulfuryl chloride decomposes to release sulfur dioxide (SO$_2$) and chlorine gas (Cl$_2$) upon heating or in the presence of water, making it useful as a source of both sulfur and chlorine atoms.

9. **Describe the structure of phosphoric acid (H_3PO_4) and its importance.**

   Answer: Phosphoric acid has a tetrahedral structure with a central phosphorus atom bonded to three hydroxyl groups (-OH) and one double-bonded oxygen atom. It is an important acid in fertilizers, food additives, and detergents due to its acidic properties and phosphorus content.

10. **What is the primary function of oxohalides like $SOCl_2$ in organic chemistry?**

    Answer: Oxohalides like $SOCl_2$ primarily function as chlorinating agents, used to convert hydroxyl-containing compounds, such as alcohols and carboxylic acids, into chlorinated derivatives, thereby facilitating substitution reactions in organic synthesis.

C. Assay Type Questions

1. Explain the structural differences and oxidation states between phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), and hypophosphorous acid (H_3PO_2). How do these differences affect their chemical properties?
2. Describe the preparation and primary uses of sulfuric acid (H_2SO_4) in industry. Why is it considered a vital chemical in various applications?
3. What is the trend in acidity among the oxoacids of chlorine (HClO, $HClO_2$, $HClO_3$, $HClO_4$), and how does it relate to the oxidation state of chlorine in each oxoacid?
4. Discuss the role of phosphorus trichloride (PCl_3) in the synthesis of organophosphorus compounds. What makes PCl_3 a suitable reagent in organic and industrial chemistry?
5. Describe the chemical reaction of thionyl chloride ($SOCl_2$) with a carboxylic acid. How does this reaction make $SOCl_2$ useful in organic synthesis?
6. Explain the structure and chemical properties of sulfuryl chloride (SO_2Cl_2). How is it used as a chlorinating and sulfonating agent in organic chemistry?

7. How does phosphorus pentachloride (PCl_5) act as a chlorinating agent in chemical reactions? Give examples of reactions where PCl_5 is used to introduce chloride ions into compounds.
8. Describe the decomposition of sulfuryl chloride (SO_2Cl_2) and explain how this property is utilized in chemical reactions or industrial applications.
9. Discuss the uses and significance of oxoacids of sulfur, such as sulfurous acid (H_2SO_3) and sulfuric acid (H_2SO_4). How do these acids differ in structure and reactivity?
10. Compare the reactivity and applications of the oxohalides of sulfur, such as thionyl chloride ($SOCl_2$) and sulfuryl chloride (SO_2Cl_2), in chlorination reactions. Why are these compounds favored in certain organic synthesis reactions?

10.11 References

1. "Concise Inorganic Chemistry" by J.D. Lee
2. "Inorganic Chemistry" by Shriver and Atkins
3. "A Textbook of Inorganic Chemistry" by A.K. De
4. "Inorganic Chemistry" by Puri, Sharma, and Kalia
5. "Principles of Inorganic Chemistry" by B.R. Puri, L.R. Sharma, and K.C. Kalia
6. "Advanced Inorganic Chemistry" by Gurdeep Raj
7. "Modern Inorganic Chemistry" by R.D. Madan
8. "Textbook of Inorganic Chemistry" by Satya Prakash, G.D. Tuli, S.K. Basu, and R.D. Madan

Unit - 11 ❑ Transition Elements (3d series)

Structure

11.0 Objectives

- Describe the general electronic configuration of 3d transition metals and explain how it influences their chemical properties.
- Identify the specific electronic configurations of 3d series elements and recognize exceptions, such as in chromium and copper.
- Explain the periodic trends in atomic size, ionization energy, and ionic radii across the 3d series.
- Correlate the variations in oxidation states, magnetic properties, and ionization energies across the series to their electronic configurations.
- Describe the variable oxidation states of 3d transition elements and explain how these states contribute to their versatility in chemical reactions.
- Investigate common oxidation states for each element in the series and understand their stability in different compounds.
- Understand the causes of magnetic properties in 3d transition metals and distinguish between paramagnetism and diamagnetism.
- Describe why transition metal compounds are often colored, and explain how d-d transitions contribute to these optical properties.
- Explain the ability of transition metals to form complex ions and coordinate bonds.
- Identify common ligands and geometries found in coordination complexes of 3d metals, and understand their roles in biological and industrial processes.
- Recognize the significance of 3d transition metals in industrial applications, such as catalysts in chemical processes, electronic materials, and magnetic devices.
- Understand the importance of transition metals in biological systems, such as iron in hemoglobin and copper in enzymes.

11.1 Introduction

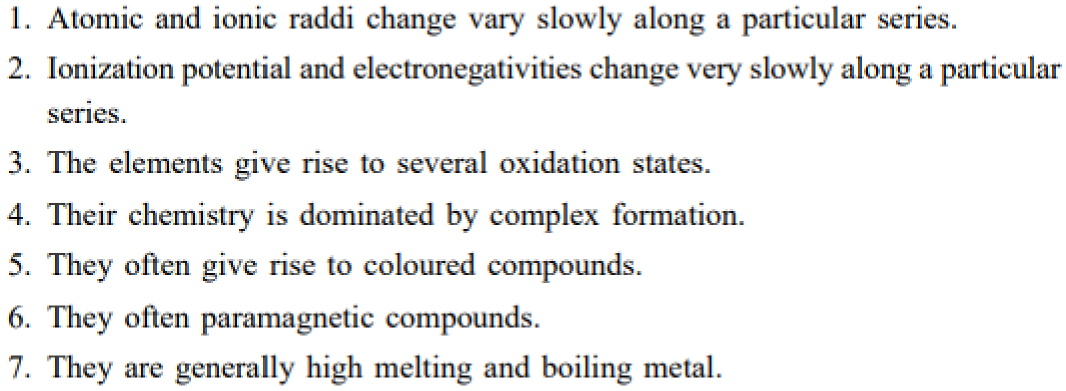
Transition elements, also known as transition metals, are a group of elements located in the d-block of the periodic table, encompassing elements from groups 3 to 12. These elements are typically characterized by the presence of partially filled d-orbitals, which give rise to unique chemical and physical properties not seen in s- or p-block elements. The transition metals include the 3d, 4d, and 5d series, with the 3d series spanning from scandium (Sc) to zinc (Zn).

The distinctive features of transition elements include their ability to exhibit variable oxidation states, formation of colored compounds, and paramagnetic behavior due to unpaired electrons. These properties are largely a result of the d-electrons, which have energies close to the outer s-electrons, allowing for flexibility in bonding and electron exchange. Additionally, transition metals often act as catalysts in chemical reactions due to their ability to change oxidation states and form complex ions with a variety of ligands.

In industrial and biological contexts, transition metals are essential due to their versatility. They are found in critical roles, such as in catalysis (e.g., iron in the Haber process for ammonia synthesis), electronics (e.g., copper in wiring), and biological systems (e.g., iron in hemoglobin and magnesium in chlorophyll). Their unique chemistry and widespread applications make transition elements an essential area of study within inorganic chemistry.

11.2 General Group Trends with Special Reference to Electronic Configuration

3d-elements have following general features:



1. Atomic and ionic raddi change vary slowly along a particular series.
2. Ionization potential and electronegativities change very slowly along a particular series.
3. The elements give rise to several oxidation states.
4. Their chemistry is dominated by complex formation.
5. They often give rise to coloured compounds.
6. They often paramagnetic compounds.
7. They are generally high melting and boiling metal.

The 3d elements, or first-row transition metals, span from Scandium (Sc, atomic number 21) to Zinc (Zn, atomic number 30) and exhibit several unique trends in properties across the series. These trends are closely tied to the filling of the 3d orbitals and have a significant impact on the elements' chemical behavior, physical properties, and reactivity.

- The general electronic configuration for 3d elements is $[Ar]3d^{1-10}4s^{0-2}$.
- The 4s orbital is filled first, as it is slightly lower in energy than the 3d orbital. However, after filling the 4s orbital, the 3d orbitals are populated.
- Exceptions to the expected configuration include chromium (Cr, $[Ar]3d^5 4s^1$) and copper (Cu, $[Ar]3d^{10}4s^1$), where half-filled and fully filled d-subshells confer additional stability.

The 3d elements, spanning from Scandium (Sc) to Zinc (Zn), can be classified based on their electronic configurations, which play a central role in their chemical properties, oxidation states, and overall behavior. Here is a classification based on their electron configurations:

1. Early 3d Elements (Scandium to Vanadium):

- These elements have a small number of d-electrons and incomplete filling of the 3d subshell.
- They commonly exhibit lower oxidation states and often have fewer paired electrons, resulting in higher magnetic moments.
- **Elements**:
    - **Scandium (Sc)**: $[Ar]\ 3d^1 4s^2$
    - **Titanium (Ti)**: $[Ar]\ 3d^2 4s^2$
    - **Vanadium (V)**: $[Ar]\ 3d^3 4s^2$

2. Middle 3d Elements (Chromium to Iron):

- These elements reach half-filled configurations in the 3d subshell, which provides extra stability, particularly in chromium and manganese.

- They exhibit a wide range of oxidation states due to the availability of both 3d and 4s electrons for bonding.
- Chromium and manganese are notable for their maximum oxidation states, such as +6 for Cr and +7 for Mn.
- **Elements**:
  - **Chromium (Cr)**: [Ar] $3d^5 4s^1$ (exception: half-filled d-subshell stability)
  - **Manganese (Mn)**: [Ar] $3d^5 4s^2$
  - **Iron (Fe)**: [Ar] $3d^6 4s^2$

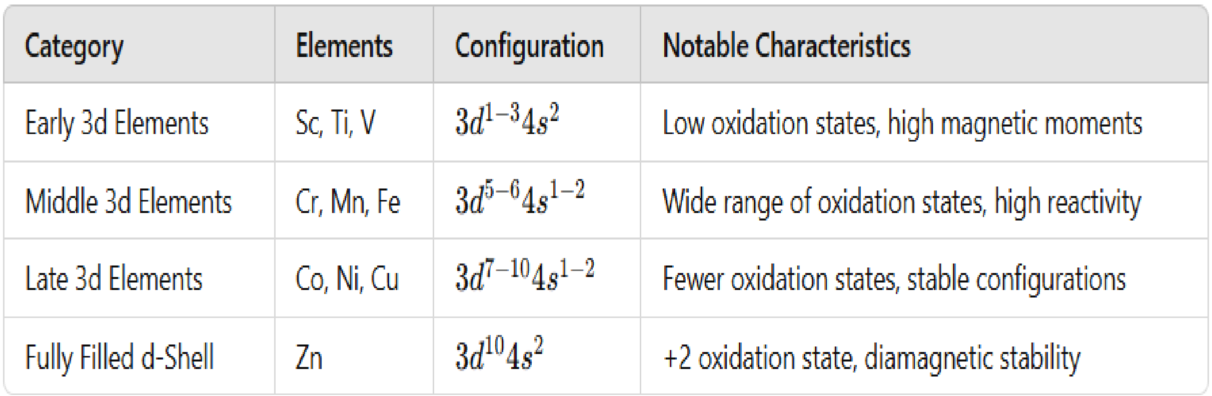
3. Late 3d Elements (Cobalt to Copper):

- In these elements, the 3d subshell becomes increasingly filled, reducing the number of available oxidation states.
- They generally exhibit oxidation states of +2 and +3, with fewer higher oxidation states.
- Copper has a nearly complete 3d subshell, achieving extra stability in the +1-oxidation state.
- **Elements**:
  - **Cobalt (Co)**: [Ar] $3d^7 4s^2$
  - **Nickel (Ni)**: [Ar] $3d^8 4s^2$
  - **Copper (Cu)**: [Ar] $3d^{10} 4s^1$ (exception: full d-subshell stability)

4. Fully Filled d-Shell Element (Zinc):

- Zinc has a fully filled 3d subshell, resulting in a stable configuration that limits its chemistry primarily to the +2-oxidation state.
- Zinc’s d-electrons are not easily involved in bonding, and it is largely diamagnetic.
- **Element**:
  - **Zinc (Zn)**: [Ar] $3d^{10} 4s^2$

Summary Table



Category	Elements	Configuration	Notable Characteristics
Early 3d Elements	Sc, Ti, V	$3d^{1-3}4s^{2}$	Low oxidation states, high magnetic moments
Middle 3d Elements	Cr, Mn, Fe	$3d^{5-6}4s^{1-2}$	Wide range of oxidation states, high reactivity
Late 3d Elements	Co, Ni, Cu	$3d^{7-10}4s^{1-2}$	Fewer oxidation states, stable configurations
Fully Filled d-Shell	Zn	$3d^{10}4s^{2}$	+2 oxidation state, diamagnetic stability

11.3 Variable Valency

Variable valency, or variable oxidation states, is a notable characteristic of 3d transition elements. This property arises due to the involvement of both the 3d and 4s electrons in bonding and the relative energies of these orbitals. Variable valency in 3d transition elements is a critical aspect of their chemistry, allowing them to engage in a wide variety of reactions and form numerous compounds. This characteristic underlies their applications in catalysis, complex formation, and biological systems, making them indispensable in many chemical and industrial processes. The ability to exhibit different oxidation states reflects their unique electronic structure and the influence of surrounding ligands.

General Concept of Variable Valency

Definition: Variable valency refers to the ability of an element to exist in multiple oxidation states or valencies in its compounds. For transition metals, this typically results from the relatively close energy levels of the d and s orbitals.

Importance: Variable valency is essential for the diverse chemistry of transition metals, enabling them to participate in various chemical reactions, form complex ions, and act as catalysts.

Trends in Variable Valency Among 3d Elements

Early 3d Elements:

- **Scandium (Sc)**: Typically exhibits a +3-oxidation state, as it loses all three valence electrons (2 from the 4s and 1 from the 3d).
- **Titanium (Ti)**: Commonly shows +4 and +3 oxidation states. It can lose all four valence electrons for the +4 state or three for the +3 state.
- **Vanadium (V)**: Exhibits a wide range of oxidation states from +2 to +5. The +5-oxidation state is particularly stable in oxides and vanadates.

Middle 3d Elements:

- **Chromium (Cr)**: Displays oxidation states of +2, +3, and +6. The +6 state is found in chromates and dichromates, while the +3 state is common in many compounds.
- **Manganese (Mn)**: Known for its +2, +4, +6, and +7 oxidation states. The +7 state is found in permanganates, while the +4 state is found in oxides.
- **Iron (Fe)**: Exhibits +2 and +3 oxidation states, with the +3 state being more stable in aqueous solutions. Iron compounds like $FeCl_3$ and FeO are common.

Late 3d Elements:

- **Cobalt (Co)**: Common oxidation states include +2 and +3. Cobalt(II) and Cobalt(III) compounds are prevalent, with Co(III) often found in complex compounds.
- **Nickel (Ni)**: Primarily exhibits +2 and +3 oxidation states. Nickel(II) compounds are widely used, while nickel(III) is less stable.

- **Copper (Cu)**: Exhibits +1 and +2 oxidation states, with copper(I) compounds being less common due to their instability in the presence of oxygen. Copper(II) is more prevalent.

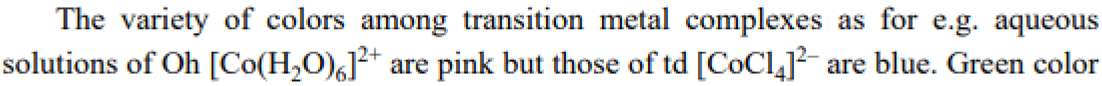
Zinc (Zn):

- Zinc is unique among the 3d elements as it predominantly exists in the +2-oxidation state due to its fully filled 3d subshell ($3d^{10}4s^2$). It does not exhibit variable valency like other transition metals.

Factors Influencing Variable Valency

- **Energy Levels**: The close energy levels of the 3d and 4s orbitals allow for the loss of different numbers of electrons, leading to multiple oxidation states.
- **Stability of Electron Configurations**: Half-filled (e.g., $3d^5$) and fully filled (e.g., $3d^{10}$) configurations provide extra stability, influencing the stability of certain oxidation states.
- **Ligand Effects**: The nature of ligands surrounding a metal ion can stabilize specific oxidation states. Strong field ligands can promote higher oxidation states by stabilizing the electron configurations.

11.4 Colour of Transition Elements



The variety of colors among transition metal complexes as for e.g. aqueous solutions of Oh $[Co(H_2O)_6]^{2+}$ are pink but those of td $[CoCl_4]^{2-}$ are blue. Green color of aqueous $[Ni(H_2O)_6]^{2+}$ turns blue when ammonia is added to the solution to give $[Ni(NH_3)_6]^{2+}$. The reduction of violet $[Cr(H_2O)_6]^{3+}$ gives bright blue $[Cr(H_2O)_6]^{2+}$. As with all colors, these arise from electronic transitions between levels whose spacing correspond to the wave lengths available in visible light. (Of course, when a photon of visible light is absorbed, it is its complementary color that we actually see.) The color of the complexes originates from two sources. (a) *d–d* transition (b) Charge transfer transition.

(a) ***d–d* transition :** Transitions are frequently referred to as *d-d* transitions because they involve the molecular orbital that are mainly metal *d-* in character (the e_g and t_{2g} or *e* and t_2 orbital in Oh and *td* complexes, respectively). Obviously, the colors produced are intimately related to the magnitude of the spacing between these levels. Since these spacing depends on factors such as the geometry of the complex, the nature of the ligands present, and the oxidation state of the central metal ion, electronic spectra of complexes can provide valuable information related to bonding and structure. In complex $[Ti(H_2O)_6]^{+3}$ the dl electron present is in the t_{2g} set, on irradiation with blue green light, the complex will absorb such energy to allow a transition of the t_{2g} electron to excited e_g set (*d-d* transition) and transmits purple violet color.

(b) **Charge transfer transition :** There are many compounds where metal atoms and ligands are highly different in both oxidizing and reducing properties, in such cases by absorbing energies there occurs transfer of charges (e^-) from reducing partner to oxidizing partner, and transmit energies in the near visible or in the U.V region of spectrum shows different colorization of the complexes. For these transitions the metal ions may or may not possess *d*-electrons e.g., Purple permanganate {Mn (VII), $3d^0$}, Yellow chromate {Cr(VI), $3d^0$}, dark red $[Fe(bpy)_3]^{2+}$, {Fe(II),$3d^6$}. The selection rules of electronic transitions are **(i)** Allowed transitions are those for which $\Delta S = 0$ *i.e.*, transitions are permitted between states of same spin multiplicity. **(ii)** and also $\Delta l = \pm 1$ thus allowed transition are $2s \rightarrow 2p$, $2s \rightarrow 3p$, $3p \rightarrow 3d$ but $3d \rightarrow 3d$, $1s \rightarrow 2s$, $3s \rightarrow 3d$ are not allowed *i.e.*, these are laport forbidden transitions.

All *d-d* transition in Oh complexes are formally laport forbidden yet the coordination complexes of transition metals are color. For this the colour arise due to *d-d* transition (i.e., Laport forbidden transition) are faint in nature.

If an electron moves from an orbital that is mainly ligand in character to one that is mainly metal in character is called ligand-to-metal charge transfer, LMCT. Condition for LMCT transition (i) The ideal ligand would have relatively low electron affinity i.e., it would have a filled orbital and would be readily oxidisable. Chalcogenides or heavier halides would be example of good choices. (ii) Metals are in high oxidation states etc. Example of LMCT is MnO_4^-, CrO_4^{2-}, HgI_2 (red), BiI_3 (orange-red) and PbI_2 (yellow).

If an electron moves from an orbital that is mainly metal in character to one that is mainly ligand character is metal-to-ligand charge transfer, MLCT. Condition for MLCT transition (i) Metal has low oxidation state (ii) ligands have empty π-antibonding orbitals i.e., Carbonmonoxide, pyridine, bipyridine, pyrazine and o-phenanthroline, shows these types of transitions, $[Fe(o\text{-}phen)_3]^{2+}$, $[Fe(bpy)_3]^{+2}$.

Example of Metal to Metal charge transfer (MMCT) transition, prussian blue or Turnbulls blue precipitate K Fe $Fe(CN)_6$. Iron present in Fe(II) and Fe (III) oxidation states, electron transfer is possible from Fe (II) to Fe (III). $K_2FeFe(CN)_6$ is colorless because both the irons are Fe (II) and there exists no scope for any charge transfer transition.

11.5 Magnetic of Transition Elements

Transition metal compounds are of enormous magnetochemical interest. In such no of *d*- electrons varies in different oxidation states. These *d*-electrons are perturbed to different extent due to complex formation. Strong donor ligands can force spin pairing. Stereochemistry, crystal field splitting, donor strength of the ligands, etc ultimately decide the magnetic properties of the complexes. The following equation applies to the first transition series elements

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}\ \text{BM}$$

Where μ_{S+L} represent total magnetic moment due to orbital and spin effect, L is resultant orbital angular momentum. S is resultant spin angular momentum.

In general for the complexes of the first transition series element, orbital motion of electron is restricted (L = 0) so that

$$\mu = \mu_{s(theo)} = \sqrt{4S(S+1)}\ \text{B.M Again S} = \frac{n}{2},\ n \text{ is no of unpaired electrons.}$$

$$\mu_{s(theo)} = \sqrt{4\frac{n}{2}\left(\frac{n}{2}+1\right)}\ \text{B.M} = \sqrt{n(n+2)}\ \text{B.M} \qquad \text{... (II)}$$

Equation (II) is the important relation between magnetic moment due to spin and no of unpaired electron. When there is absence of unpaired electrons in the central metal ion of any compound, it is diamagnetic in nature.

11.6 Catalytic Properties of Transition Elements

Transition metals are well known for their catalytic activities. Synthesis of ammonia makes use of iromolybdenum catalyst, that of sulphuric acid needs V_2O_5 or spongy platinum and so on. The catalytic activity of regular transition elements is undoubtedly due to availability of the *d*- orbitals. The *d*- orbitals being exposed to the surface, can participate in the formation of some activated complex which serves as intermediates in an overall chemical process. These intermediates produce reaction paths of lower activation energy for otherwise slow reactions and thus enhance the reaction rates.

11.7 Complex Formation

A dominant feature of the transition metal chemistry is complex formation. Higher the value of ionic potential (ϕ) $\left(= \frac{\text{cationic charge}}{\text{radious of cation}}\right)$ of transition metal ion exerts a greater attractive force on the donor atoms of ligands. This leads to complex formation.

11.8 Stability of Various Oxidation States for Mn, Fe And Cu.

The stability of various oxidation states for manganese (Mn), iron (Fe), and copper (Cu) is influenced by factors such as electronic configuration, the nature of ligands, and the overall environment in which these elements exist. Here’s a detailed overview of the oxidation states and their stability for these three transition metals:

Manganese (Mn)

1. **Common Oxidation States**:
    - **+2**: Mn^{2+} (stable)
    - **+3**: Mn^{3+} (relatively stable, but less common)
    - **+4**: Mn^{4+} (stable in oxides)
    - **+6**: Mn^{6+} (found in permanganates)
    - **+7**: Mn^{7+} (found in permanganate ion, $Mn0_4^-$, highly stable)
2. **Stability Trends**:
    - **Mn^{2+}** is the most stable oxidation state in aqueous solutions and is commonly encountered in various compounds (e.g., manganese sulfate, $MnSO_4$).

- **Mn^{7+}** in permanganate (MnO_4^-) is highly stable due to the strong oxidizing properties of this ion, which stabilizes the high oxidation state.
- **Mn^{4+}** and **Mn^{3+}** are relatively stable but can disproportionate under certain conditions:
  - **Mn^{3+}** can disproportionate to form **Mn^{2+}** and **Mn^{4+}** in alkaline solutions.
- The stability of Mn^{6+} is moderate, often seen in oxoanions like manganates (MnO_4^{2-}).

Iron (Fe)

1. **Common Oxidation States**:
   - **+2**: Fe^{2+} (stable)
   - **+3**: Fe^{3+} (stable)
   - **+4**: Fe^{4+} (less common, seen in some oxides)
   - **+6**: Fe^{6+} (very rare, found in some complex compounds)
2. **Stability Trends**:
   - **Fe^{2+}** is stable in reducing environments and is commonly found in compounds like ferrous sulfate ($FeSO_4$).
   - **Fe^{3+}** is more stable in oxidizing conditions, as seen in ferric oxide (Fe_2O_3) and ferric chloride ($FeCl_3$). The increased positive charge results in a smaller ionic radius and greater lattice energy in solid compounds, enhancing stability.
   - The oxidation state **+4** is less common but can occur in oxides like FeO_2 and some complexes.
   - **Fe^{6+}** is rare and generally unstable, usually only appearing in highly oxidizing environments or specific coordination compounds.

Copper (Cu)

1. **Common Oxidation States**:
   - **+1**: Cu^{+} (less stable, but encountered)
   - **+2**: Cu^{2+} (stable)
2. **Stability Trends**:
   - **Cu^{2+}** is the more stable and commonly encountered oxidation state, found in compounds such as copper(II) sulfate ($CuSO_4$) and copper(II) chloride ($CuCl_2$).
   - **Cu^{+}** is less stable due to its tendency to oxidize to Cu^{2+}, especially in the presence of oxygen or strong oxidizing agents. Copper(I) compounds are typically stable in non-oxidizing environments and in complexed forms (e.g., with ligands like chloride).
   - The stability of Cu^{2+} is enhanced due to its favorable electron configuration ([Ar] $3d^{10}4s^{1}$, where the presence of unpaired electrons in the 3d subshell contributes to its reactivity and stability.

11.9 Summary

Transition elements, particularly those in the 3d series, display unique characteristics largely determined by their electronic configurations. Their general group trends reveal variable valency, the formation of coloured compounds, magnetic properties, catalytic abilities, complex formation, and the stability of various oxidation states for specific elements such as Mn, Fe, and Cu.

1. **General Group Trends with Special Reference to Electronic Configuration**: The partially filled 3d orbitals in transition metals lead to a wide range of oxidation states, magnetic properties, and complex formation capabilities. Their typical electron configuration of $(n-1)d^{1-10}ns^{0-2}$ enables diverse bonding and stability across the series.
2. **Variable Valency**: Transition metals exhibit multiple oxidation states due to the close energies of their d and s orbitals. For example, manganese shows states from +2 to +7, while iron and copper commonly exist in +2 and +3 states, influenced by their electronic structures and specific chemical environments.
3. **Colour of Transition Elements**: The presence of unpaired d-electrons leads to d-d transitions when light is absorbed, resulting in the vibrant colours characteristic of many transition metal compounds. These colours vary based on the metal's oxidation state and the ligands surrounding it.
4. **Magnetic Properties of Transition Elements**: Unpaired d-electrons give rise to paramagnetism in many transition metals, where the magnetic moment is proportional to the number of unpaired electrons. Elements like Mn, with several unpaired electrons, exhibit strong magnetic properties, while fully paired d-electrons (e.g., in Zn) result in diamagnetic behavior.

5. **Catalytic Properties of Transition Elements**: Transition metals are effective catalysts due to their ability to adopt multiple oxidation states and form intermediate compounds, facilitating chemical reactions. Examples include iron in the Haber process and vanadium in the contact process.
6. **Complex Formation**: Transition metals readily form coordination complexes with various ligands due to their small, highly charged ions and the availability of vacant d-orbitals. These complexes are central in both industrial applications and biological systems (e.g., haemoglobin with iron).
7. **Stability of Various Oxidation States for Mn, Fe, and Cu**: Each of these metals exhibits distinct oxidation stability patterns, shaped by their electron configurations. Mn is most stable in the +2 and +7 states, Fe in +2 and +3, and Cu typically in +2. Environmental factors and ligands also play critical roles in stabilizing these states.

11.10 Sample Questions

A. Multiple Choice Type Questions

1. Which of the following is the first element in the 3d transition series?

   a) Scandium (Sc)

   b) Titanium (Ti)

   c) Manganese (Mn)

   d) Iron (Fe)

   Answer: a) Scandium (Sc)

2. What is the general electronic configuration of 3d transition elements?

   a) ns^2np^6

   b) $ns^2(n-1)d^{1-10}$

   c) $ns^2np^5(n-1)d^{1-10}$

d) $ns^1(n-1)d^{1-10}$

Answer: b) $ns^2(n-1)d^{1-10}$

3. Which of the following transition elements has the highest melting point?

   a) Iron (Fe)

   b) Chromium (Cr)

   c) Copper (Cu)

   d) Tungsten (W)

   Answer: b) Chromium (Cr)

4. Which element in the 3d series does NOT show variable oxidation states?

   a) Iron (Fe)

   b) Zinc (Zn)

   c) Copper (Cu)

   d) Manganese (Mn)

   Answer: b) Zinc (Zn)

5. Which of the following 3d transition elements is ferromagnetic?

   a) Chromium (Cr)

   b) Cobalt (Co)

   c) Copper (Cu)

   d) Zinc (Zn)

   Answer: b) Cobalt (Co)

6. Which transition element shows the highest number of oxidation states?

   a) Iron (Fe)

   b) Chromium (Cr)

   c) Manganese (Mn)

   d) Nickel (Ni)

Answer: c) Manganese (Mn)

7. Which is the most stable oxidation state for iron (Fe) in compounds?

a) +1

b) +2

c) +3

d) +4

Answer: c) +3

8. Which transition metal ion is colourless in aqueous solution?

a) Fe^{2+}

b) Cu^{2+}

c) Zn^{2+}

d) Mn^{2+}

Answer: c) Zn^{2+}

9. Which of the following is not a typical property of 3d transition metals?

a) High melting points

b) Forming colored compounds

c) Forming compounds with variable oxidation states

d) Low density

Answer: d) Low density

10. In which of the following compounds does copper have an oxidation state of +1?

a) CuCl

b) $CuSO_4$

c) $CuCl_2$

d) $Cu(NO_3)_2$

Answer: a) CuCl

11. Which of the following is the oxidation state of chromium in $K_2Cr_2O_7$?

    a) +2

    b) +3

    c) +6

    d) +7

    Answer: c) +6

12. Which 3d transition element is commonly used as a catalyst in the Haber process?

    a) Iron (Fe)

    b) Nickel (Ni)

    c) Copper (Cu)

    d) Manganese (Mn)

    Answer: a) Iron (Fe)

13. What is the coordination number of iron in $Fe(CO)_5$?

    a) 2

    b) 4

    c) 5

    d) 6

    Answer: c) 5

14. Which of the following elements has the configuration [Ar] $3d^{10}4S^1$?

    a) Copper (Cu)

    b) Zinc (Zn)

    c) Iron (Fe)

    d) Manganese (Mn)

    Answer: a) Copper (Cu)

15. The color of transition metal complexes is due to:

a) Absorption of light in the UV region

b) d-d transitions

c) Absorption of microwave radiation

d) Nuclear transitions

Answer: b) d-d transitions

B. Short Type Questions

1. **Q:** What is the common feature in the electronic configuration of transition elements?

   A: Transition elements have partially filled d-orbitals in their ground state or in any of their commonly occurring oxidation states.

2. **Q:** How does the atomic size change across the period in transition elements?

   A: Atomic size decreases slightly across the period due to increasing nuclear charge, but the effect is less pronounced than in s- and p-block elements.

3. **Q:** Why do transition elements exhibit variable valency?

   A: Transition elements exhibit variable valency due to the similar energy levels of their ns and (n-1)d electrons, which allows for the involvement of different numbers of d-electrons in bonding.

4. **Q:** Which element in the transition series shows the highest number of oxidation states, and why?

   A: Manganese shows the highest number of oxidation states, ranging from +2 to +7, due to the presence of multiple electrons in the 3d and 4s orbitals that can participate in bonding.

5. **Q:** Why are most transition elements coloured?

   A: Transition elements are coloured due to d-d electronic transitions within the partially filled d-orbitals, which absorb specific wavelengths of visible light.

6. **Q:** How does the oxidation state of a transition element affect its colour?

   A: Different oxidation states have different d-electron configurations, leading to different absorption of light wavelengths and hence different colours.

7. **Q:** What causes the magnetic properties of transition elements?

   A: The magnetic properties are caused by the presence of unpaired electrons in the d-orbitals, which create a magnetic moment.

8. **Q:** Why are some transition elements paramagnetic and others ferromagnetic?

   A: Elements with unpaired d-electrons are paramagnetic, while those with aligned unpaired spins in bulk (like Fe, Co, and Ni) exhibit ferromagnetism.

9. **Q:** Why do transition elements often act as catalysts?

   A: Transition elements can act as catalysts due to their ability to change oxidation states and to provide a surface for the reactants to adsorb and react, lowering activation energy.

10. **Q:** How does the presence of vacant d-orbitals in transition elements aid in catalysis?

    A: Vacant d-orbitals allow the transition metals to form intermediate complexes with reactants, facilitating various reactions.

11. **Q:** What allows transition elements to form complexes?

    A: The presence of vacant d-orbitals and their ability to accommodate lone pairs from ligands enable transition elements to form complexes.

12. **Q:** Why do transition elements form more stable complexes than s- and p-block elements?

    A: Transition elements form more stable complexes due to the strong metal-ligand bonding and the additional stabilization provided by their d-orbitals.

13. **Q:** What is the most stable oxidation state of manganese (Mn)?

    A: The most stable oxidation state of manganese is +2, but it can exhibit states from +2 to +7.

14. **Q:** Why is Fe^{3+} more stable than Fe^{2+} in aqueous solutions?

    A: Fe^{3+} is more stable than Fe^{2+} in aqueous solutions because it has a half-filled d^5 configuration, which provides extra stability.

15. **Q:** What is the most stable oxidation state for copper (Cu), and why?

    A: The most stable oxidation state for copper is +2, as it achieves a stable d^9 configuration, although Cu also exhibits a +1-oxidation state frequently.

C. Assay Type Questions

1. Describe how the electronic configuration of transition elements differs from s- and p-block elements.
2. Explain how this unique configuration impacts properties such as atomic size, ionization energy, and electronegativity across the group.
3. Examine the concept of variable valency in transition elements and the factors influencing it.
4. Outline the reasons why transition elements exhibit multiple oxidation states.
5. Provide examples of elements with multiple valencies and discuss the factors (like d-electron involvement) that influence these valencies.
6. Analyze the cause and significance of color in transition elements and their compounds.
7. Describe how the presence of d-electrons leads to the color in transition metals.
8. Discuss specific examples of transition metal ions and their colors, and explain how different factors, like oxidation states and ligand types, influence the observed color.

9. Explain the magnetic properties of transition elements and how they vary across the series.
10. Discuss the role of unpaired d-electrons in generating magnetic properties.
11. Compare the magnetic behaviors of paramagnetic, diamagnetic, and ferromagnetic transition metals, providing examples and reasons for these differences.
12. Evaluate the catalytic properties of transition metals and their role in industrial processes.
13. Describe why transition metals are efficient catalysts, highlighting the role of d-orbitals and variable oxidation states.
14. Discuss examples of industrial processes (like the Haber process, catalytic converters) where transition metals act as catalysts and the impact on reaction efficiency.
15. Discuss the ability of transition elements to form complex compounds and the factors affecting complex formation.
16. Explain the role of d-orbitals, charge density, and ligand types in complex formation.
17. Describe the importance of transition metal complexes in biological systems and industrial applications, with examples such as hemoglobin or coordination compounds in medicines.
18. Analyze the color variations in transition metal complexes and the factors influencing them.
19. Explain how ligand field theory helps to understand the color of transition metal complexes.
20. Discuss the effects of factors like oxidation state, ligand type, and geometry on the color of complexes, providing specific examples.
21. Compare the stability of various oxidation states for manganese (Mn), iron (Fe), and copper (Cu) and discuss the factors contributing to their stability.

22. Discuss the preferred oxidation states for Mn, Fe, and Cu and why certain oxidation states are more stable.
23. Explain the role of factors like electronic configuration, lattice energy, and hydration energy in stabilizing specific oxidation states.
24. Evaluate the trends in reactivity of transition metals across periods and down the groups in the periodic table.
25. Describe the trends in reactivity of transition metals with increasing atomic number.
26. Discuss factors like ionization energy, atomic radius, and bond dissociation energy that impact the reactivity of these elements, providing examples.
27. Discuss the significance of transition elements in biological systems, with examples.
28. Explain the roles of transition metals in biological processes, highlighting their functions in enzyme activity, oxygen transport, and electron transfer.
29. Provide examples of essential transition elements in biological systems, such as Fe in hemoglobin, Zn in enzymes, and Cu in electron transport, discussing their specific biological roles.

11.11 References

1. "Concise Inorganic Chemistry" by J.D. Lee
2. "Inorganic Chemistry" by Shriver and Atkins
3. "A Textbook of Inorganic Chemistry" by A.K. De
4. "Inorganic Chemistry" by Puri, Sharma, and Kalia
5. "Principles of Inorganic Chemistry" by B.R. Puri, L.R. Sharma, and K.C. Kalia
6. "Advanced Inorganic Chemistry" by Gurdeep Raj
7. "Modern Inorganic Chemistry" by R.D. Madan
8. "Textbook of Inorganic Chemistry" by Satya Prakash, G.D. Tuli, S.K. Basu, and R.D. Madan

Unit - 12 ❑ Basics of Coordination Chemistry

Structure

12.0 Objectives

- Understand the concept of primary and secondary valencies in coordination compounds.
- Explain the coordination number as proposed by Werner's Theory.
- Identify the difference between ionizable primary valency and non-ionizable secondary valency.
- Define the EAN rule and its importance in predicting the stability of coordination compounds.
- Calculate the effective atomic number for a given coordination complex.
- Describe the binding modes of ligands, including terminal and bridging modes.
- Understand the rules for naming coordination compounds based on IUPAC conventions.
- Differentiate between naming neutral, cationic, and anionic coordination compounds.
- Interpret the significance of high and low stability constants in the context of complex stability.
- Define a chelate and understand its formation via multidentate ligands.
- Explain the chelate effect and its role in enhancing complex stability.
- Identify the applications of chelates in industrial and biological contexts.
- Define intermetallic complexes and understand their structure with metal-metal bonds.
- Recognize the importance of intermetallic complexes in catalysis and material science.
- Discuss the unique properties and stability of intermetallic complexes due to metal-metal interactions.

12.1 Introduction

Coordination chemistry focuses on the complex interactions between central metal atoms or ions and surrounding molecules or ions called ligands. These compounds play essential roles in biological systems, industrial processes, and advanced materials. Understanding key theories and concepts, such as Werner's Theory and the Effective Atomic Number (EAN) Rule, allows chemists to predict and explain the formation, stability, and properties of coordination compounds. Additionally, the classification of ligands, naming conventions according to IUPAC, and stability constants help in describing the intricate bonding and structural characteristics of these compounds.

This study guide covers essential objectives in coordination chemistry, highlighting foundational theories, ligand classifications, bonding modes, and the stability of coordination compounds:

Werner's Theory: Key concepts of primary and secondary valencies and the coordination number of metal ions.

Effective Atomic Number (EAN) Rule: Guidelines for predicting stability in coordination compounds by comparing to noble gas configurations.

Classification of Ligands and Their Binding Modes: Types of ligands (monodentate, bidentate, etc.) and their specific binding characteristics.

IUPAC Nomenclature of Coordination Compounds: Standardized naming for compounds, including cases with up to two metal centers.

Overall and Stepwise Stability Constants: Measures of stability for entire complexes and individual metal-ligand bonds.

Chelates: Complexes formed with multidentate ligands, demonstrating enhanced stability due to the chelate effect.

Intermetallic Complexes: Compounds with metal-metal bonds, significant in catalysis and material science.

12.3 Werner's Theory

Alfred Werner in 1823, formulated his theory to describe the. Structure and formation of complex compounds or coordination compounds. In a series of compounds of cobalt(lll) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution. 1 mol $CoCl_3 \cdot 6NH_3$ (Yellow) → 3 mol AgCl

1 mol $CoCl_3 \cdot 5NH_3$ (Purple) → 2 mol AgCl

1 mol $CoCl_3 \cdot 4NH_3$ (Green) → I mol AgCl

I mol $CoCl_3 \cdot 4NH3$ (Violet) → 1 mol AgCl

On the basis of the observations Werner postulated the following points.

Postulates of Werner's Theory:

1. The central metal ions or the metal atoms in coordination compounds show two types of valency. They are the primary and secondary valency.

2. The primary valency relates to the oxidation state and the secondary valency relates to the coordination number. Primary valency is also called principal, ionisable or ionic valency, and secondary valency is non-ionic or non-ionisable.

3. The number of secondary valences is fixed for every metal atom or ion. It means that the coordination number is fixed.

4. The metal atom or ion works towards satisfying both its primary and secondary valencies A negative ion satisfies the primary valency. On the other hand, negative ions or neutral molecules satisfy secondary valencies. The ions or molecules which satisfy secondary valency or coordination number are directly attached to metal atom or ion. An anion can show a dual behaviour i.e. it may satisfy both primary and secondary valencies.

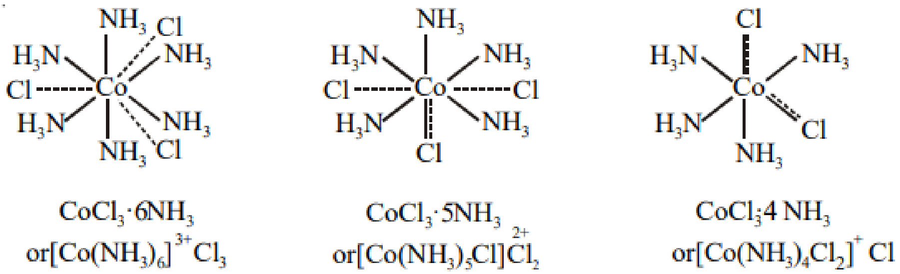
5. The secondary valencies point towards a fixed position in space. This is the reason behind the definite geometry of the coordinate compounds. For example, let us consider the case of a metal ion having six secondary valencies. They arrange octahedrally around the central metal ion or atom. If the metal ion has four secondary valencies, they arrange in either tetrahedral or square planar arrangement around the central metal ion or atom. Therefore, we see that the secondary valency determines the stereochemistry of the complex ion. On the other hand. the primary valency is non-directional.

Examples Based on Postulates of Werner's Theory Werner's theory is responsible for the formation of' structures of various cobalt amines. We will look at its explanation now. Cobalt has a primary valency (oxidation state) of three and exhibits secondary valency (coordination number) of 6. Werner represented the secondary valencies by thick lines (solid lines) and the primary valency by dashed lines (broken lines).

1) **$CoCl_3{\cdot}6NH_3$ Complex**: In this compound, the coordination number of cobalt(III) is 6 and NH_3 molecules satisfy all the 6 secondary valencies by binding to the metal centre by coordinate covalent bonds to form the inner coordination sphere Chloride ions satisfy the 3 primary valencies. These are non-directional in character. These chloride ions instantaneously precipitate on the addition of silver nitrate. The total number of ions, in this case, is 4, three chloride ions and one complex ion. The coordination sphere is shown within square bracket [ ] and moieties bound by primary valence outside the bracket in formulation of the compound, which is called outer coordination sphere.

2) **$CoCl_3{\cdot}5NH_3$ complex:** In this compound- cobalt has coordination number of 6. However, we" see that the number of NH_3 molecules decreases to 5. The chloride ion occupies the remaining one position of coordination. This chloride ion exhibits the dual behaviour as it satisfies the primary as well as the secondary valency. Werner showed its attachment with the central metal ion by a combined dashed—solid line.

3) $CoCl_3{\cdot}4NH_3$ complex: In this compound, two chloride ions exhibit the dual behaviour of satisfying both primary and secondary valencies. This compound gives a precipitate with silver nitrate corresponding to only one chloride ion and the total number of ions in this case, is 2. Hence, we can formulate it as $[CoCl_2(NH_3)_4]Cl$. (See Figure 1) Note: The coordination number of Co (III) (i.e. secondary valency) is always 6.



$CoCl_3{\cdot}6NH_3$ or$[Co(NH_3)_6]^{3+}Cl_3$

$CoCl_3{\cdot}5NH_3$ or$[Co(NH_3)_5Cl]^{2+}Cl_2$

$CoCl_3 4\,NH_3$ or$[Co(NH_3)_4Cl_2]^{+}$ Cl

Fig. 1 Designations and formulations of Co (III) ammires on the basis of Werner's theory.

12.4 EAN Rule

With the advent of electronic theory of valency, it was considered necessary to make some modifications of Werner's theory. Sidgwick adopted the Lewis concept of twoelectron covalent bond between two atoms in a molecule and introduced the new concept of coordinate bond (also called dative bond). The effective atomic number (EAN) of an atom is the number of protons that an electron in the element effectively 'sees' due to screening by inner-shell electrons. It is a measure of the electrostatic interaction between the negatively charged electrons and positively charged protons in the atom. One can view the electrons in an atom as being 'stacked' by energy outside the nucleus with the lowest energy electrons (such as the I s and 2s electrons) occupying the space closest to the nucleus. and electrons of higher energy are located further from the nucleus. The binding energy of an electron, or the energy needed to remove the electron from the atom, is a function of the electrostatic interaction between the negatively charged electrons and the positively charged nucleus. In iron, atomic number 26, for instance, the nucleus contains 26 protons. The electrons that are closest to the nucleus will 'see' nearly all of them. However, electrons further away are screened from the nucleus by other electrons in between and, feel less electrostatic interaction as a result. The 1s electron of iron (the closest one to the nucleus). sees an effective atomic number (number of protons) of 25. The reason why it is not 26 is because some of the electrons in the atom end up repelling the others, giving a net lower electrostatic interaction with the nucleus. One way of envisioning this effect is to imagine the Is electron sitting on one side of the 26 protons in the nucleus, with another electron sitting on the other side; each electron will feci less than the attractive force of 26 protons because the other electron contributes a repelling force. The 4s electrons in iron, which are furthest from the nucleus, feel an effective atomic number of only 5.43 because of the 25 electrons in between it and the nucleus screening the charge. According to Sidguick's concept, the ligands attached with the central metal ion or atom have atoms which have at least one unshared electron pair and donate this pair to the central metal for attachment. The bond thus established between the ligand and the metal is a coordinate or dative bond. This bond is not different from a covalent bond except that the ligand (donor) has donated the electron pair to the metal ion or atom (acceptor) and represented as M← L. Thus the structure of $[Co(NH_3)_6]^{3+}$ can be shown as Figure 2.

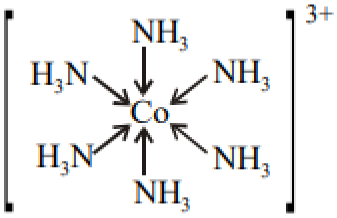


Fig. 2 (NH_3 molecules are the ligands and Co^{+3} the metal ion)

[Presently the bonds within the coordination sphere are not designated by an arrow to denote coordinate linkage, but by simple solid lines as given for covalent bonds.] Effective atomic number (EAN) is number that represents the total number of electrons surrounding the nucleus of a metal atom or ion in a metal complex. It is composed of the metal atom's (or ion's) electrons and the bonding electrons from the surrounding electrondonating atoms and molecules. Thus the effective atomic number of the cobalt ion in the complex $[Co(NH_3)_6]^{3+}$ is 36, the sum ol the number of electrons in the trivalent cobalt ion (24) and the number of bonding electrons from six surrounding ammonia molecules, each of which contributes an electron pair (2×6=12). EAN 36 of Co (III) is equal to the atomic number of Kr. Generally, EAN of central metal will be equal to the number of electrons in the nearest noble gas. If the EAN of the central metal is equal to the number of electrons in the nearest noble gas then the complex possesses greater stability. EAN = [(atomic number of central metal atom) - (the oxidation state of the metal) + (the number of electrons gained by the metal from the ligands through co-ordination)] or,

EAN = [Z metal - (oxidation state of the metal) + 2(coordination number of the metal)].

Example:

1. $[Co(NH_3)_6]^{3+}$ → EAN = [27 – 3 + 2(6)] = 36
2. $[MnCl_4]^{2-}$ → EAN = [25 – 3 + 8] = 31
3. $[Fe(CN)_6]^{4-}$ → EAN = [26 – 2 + 12] = 36
4. $[CoF_6]^{3-}$ → EAN = [27 – 3 + 12] = 36
5. $[Cr(H_2O)_6]^{3+}$ → EAN = [24 – 3 + 12] = 33
6. $Ni(CO)_4$ → EAN = [28 – 0 + 8] = 36
7. $[Cu(NH_3)_4]^{2+}$ → EAN = [29 – 2 + 8] = 35
8. $[Pt(NH_3)_4]^{2+}$ → EAN = [78 – 2 + 8] = 84
9. $[PtCl_4]^{2-}$ → EAN = [78 – 2 + 8] = 84
10. $[PtCl_6]^{2-}$ → EAN = [78 – 4 + 12] = 86

Exceptions:

As seen from the examples not all complexes follow EAN rule. Complexes of Ni(II), Co(II), Ag(I) etc., which have more than one possible coordination number, depending on the nature of the ligand, generally do not follow the rule.

12.5 Classification of Ligands and Their Binding Modes

Coordination compounds generally consist of a central metal atom or ion bonded to a fixed number of ions or molecules called ligands. The term 'dentate' means 'toothed', i.e. the number of position taken up by the ligand around the central metal atom or ion is its denticity.

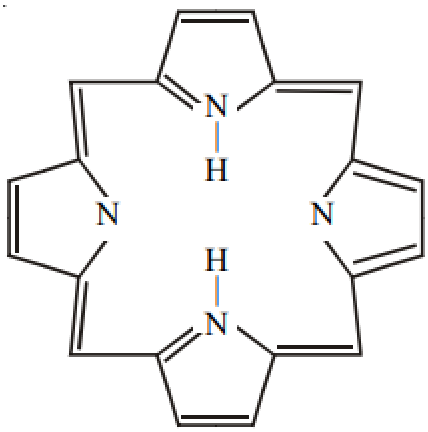
Ligands : These are the ions or molecules bound to the central atom/ion in the coordination entity (sphere). They may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)$; or even macromolecules, such as proteins.

Unidentate or mono dertate ligands : When a ligand is bound to a metal ion or atom through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be unidentate. They coordinate to the central metal atom or ion at one site only.

Bidentate ligands : When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane- 1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligands are said to be bidentate ligands. They take up two sites around the central metal.

Polydentate or multidentate ligands : When several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

Chelating ligands : When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion or atom simultaneously and thus produce one or more rings around the central atom or ion, are called chelate (pronounced Kelate)or chelating ligands (from Greek 'crab's claw'). The number of such ligating groups (donor atoms) is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Porphyrins are complexes containing a form of the porphin molecule shown in Figure 3. Important biomolecules like heme and chlorophyll are porphyrins. Chelating ligands form more stable complexes than ordinary ligands. This is also called the chelate effect. The stability of chelate depends upon the number of atoms in the ring.



Generally, chelating ligands which do not contain double bonds form stable complexes with five membered rings. On the other hand, the chelating ligands which contain double bonds form stable complexes with six membered rings. Chelating ligands with smaller groups form stable complexes, than with larger and bulky groups. This is because of steric reasons.

Ambidentate ligands : Ligands which can ligate through two or more different atoms, but in forming complexes only one donor atom is utilised for attachment at a given time are called ambidentate ligands. Examples of such ligands are the NO^{2-} and SCN^- ions. NO^{2-} ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly. SCN^- ion can coordinate through the sulphur or nitrogen atom. Other examples are CN^-, $S_2O_3^{2-}$, R_2SO, $SeCN^-$ etc.

Coordination number : The coordination number of a metal ion or atom in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded by σ bonds. For example, in the complex ions, $[PtCI_6]^{2-}$ and $[Ni(H_2O)_4]^{2+}$, the coordination number of Pt (IV) and Ni (II) are 6 and 4 respectively.

12.6 IUPAC Nomenclature of Coordination Compounds (Up to Two Metal Centers)

Rules for IUPAC nomenclature of coordination compounds:

In a coordination entity

1. The cation is named first in both positively and negatively charged coordination entities.
2. The ligands are named in an alphabetical order before the name of the central atom/ion. The prefixes di, tri, etc. are not to be considered while determining this alphabetical order.
3. Names of the anionic ligands end in –o, those of neutral ligands are the same except H_2O which is named aqua, NH_3 which is named ainmine, CO which is named carbonyl and NO which is named nitrosyl. These are placed within brackets ( ). Positively charged ligands have suffix –ium, e.g. $NH_2NH_3^+$ is hydrazinium and NO^+ is nitrosilium.
4. Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity.
5. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parenthesis.
6. Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis ( ).
7. If the complex ion is a cation, the metal is named same as the element.

8. If the complex ion is an anion, the name of the metal ends with the suffix. —ate.

9. For some metals, the Latin names are used in the complex anions, e.g.. ferrate for Fe.

10. The neutral complex molecule is named similar to that of the complex cation.

11. Complexes with two or more metal atoms/ions in the coordination sphere are called polynuclear complexes. In these complexes, the bridging group is indicated by separating it from the rest of the complex by hyphens and adding prefix μ before its name. μ should be repeated before the name of each bridging group. Two or more bridging groups of the same kind are indicated by di–μ–, tri-μ-, etc.

12. A gap should be left between naming of moieties outside and inside the coordination sphere e.g. $K_2[CoCl_4]$ is potassium tetrachlorocobaltate (II) or $[Co(NH_3)_6]$ d_3 is hexaamminecobalt (III) chloride. No gap is given in naming the moieties within the coordination sphere.

Names of Some Common Ligands

Anionic Ligands	Names
Br^-	bromo
F^-	fluoro
O^{2-}	oxo
OH^-	hydroxo
CN^-	cyano
$C_2O_4^{2-}$	oxalato
CO_3^{2-}	carbonato
CH_3COO^-	acetato

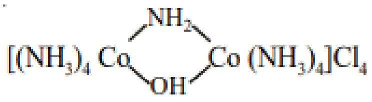
Neutral Ligands	Names
NH_3	ammine
H_2O	aqua
NO	Nitrosvl
CO	Carbonyl
O_2	dioxygen
N_2	dinitrogen
C_5H_5N	pyridine
$H_2NCH_2CH_2NH_2$	ethylenediamine.

Name of Metals in Anionic Complexes

Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate

Name of Metal	Name in an Anionic Complex
Silver	Argenate
Gold	Aurate
Tin	Stannate

Examples:

Sl. No.	Coordination Entity	IUPAC Name
I.	$[Cr(NH_3)_3(H_2O)_3]Cl_3$	triamminetriaquachromium(III) chloride
2.	$[Pt(NH_3)_5Cl]Br_3$	pentaamminechloroplatinum(V) bromide
3.	$[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$	dichlorobis(ethylenediamine)platinum(IV) chloride
4.	$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulfate
5.	$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II)
6.	$Na_2[NiCl_4]$	sodium tetrachloronickelate(II)
7.	$Pt(NH_3)_2Cl_4$	diamminetetrachloroplatinum(IV)
8.	$Fe(CO)_5$	pentacarbonyliron(O)
9.	$(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$	ammonium diaquabis (oxalato) nickelate(II)
10.	$[Ag(NH_3)_2][Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I)
11.	$[Fe(NH_3)_6](NO_3)_3$	hexaammineiron(III) nitrate
12.	$(NH_4)_2[CuCl_4]$	ammonium tetrachlorocuprate(II)
13.	$Na_3[FeCl(CN)_5]$	sodium monochloropentacyanoferrate(III)
14.	$K_3[CoF_6]$	potassium hexafluorocobaltate(III)
15.	$[CoBr(NH_3)_5]SO_4$	pentaamminebromocobalt (III) sulfate
16.	$[Fe(NH_3)_6][Cr(CN)_6]$	hexaammineiron(III) hexacyanochromate (III)
17.	$[Co(SO_4)(NH_3)_5]_4$	pentaamminesulfatocobalt(III) ion
18.	$[Fe(OH)(H_2O)_5]^{2+}$	pentaaquahydroxoironf III) ion
19.	 $[(NH_3)_5\,Cr\overset{OH}{}Cr(NH_3)_5]Cl_5$	μ-hydroxo-bis {pentaamminechromium (III) chloride or, pentamminechromium (III)-μ-hydroxo-chromium (III) chloride.
20.	 $[(NH_3)_4\,Co\overset{NH_2}{\underset{OH}{}}Co\,(NH_3)_4]Cl_4$	μ-amido-μ-hydroxo-octaammire dicobalt (iii) chloride.

12.7 Overall and Stepwise Stability Constants

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$M + 4L \rightleftharpoons ML_4 \text{ (M = mental ion/atom, L = monodentate ligand,}$$
$$\text{4 = coordination number)}$$

then, the larger the stability constant, the higher the proportion of ML_4that exists in solution. Free metal ions rarely exist in the solution so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and charge of the complexes and write four stability constants as follows:

$$M + L \rightleftharpoons ML; K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2; K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3; K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_3 + L \rightleftharpoons ML_4; K_4 = \frac{[ML_4]}{[ML_3][L]}$$

where K_1, K_2, etc., are referred to as stepwise stability constants. [ ] represents concentration of the species.

Alternatively, we can express the stability constants as :

$$M + L \rightleftharpoons ML \quad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \rightleftharpoons ML_2 \quad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L \rightleftharpoons ML_3 \quad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$M + 4L \rightleftharpoons ML_4 \quad \beta_4 = \frac{[ML_4]}{[M][L]^4}$$

where β_1, β_2 etc. are called overall stability constants.

The stepwise and overall stability constant are therefore related as follows:

$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ or more generally, $\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots K_n$

If we take as an example the steps involved in the formation of the cuprammonium ion. we have the following:

$$Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+} \; ; \; K_1 = \frac{[Cu(NH_3)]^{2+}}{[Cu^{2+}][NH_3]}$$

$$Cu(NH_3)^{2+} + NH_3 \; f \; [Cu(NH_3)_2{}^{2+}] \; ; \; K_2 = \frac{[Cu(NH_3)_2]^{2+}}{[Cu(NH_3)]^{2+}[NH_3]}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \; f \; [Cu(NH_3)_3]^{2+} \; ; \; K_3 = \frac{[Cu(NH_3)_3]^{2+}}{[Cu(NH_3)_2]^{2+}[NH_3]}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \; f \; [Cu(NH_3)_4]^{2+} \; ; \; K_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu(NH_3)_3]^{2+}[NH_3]}$$

where K_1, K_2 ...are the stepwise stability constants the overall stability constant is given by

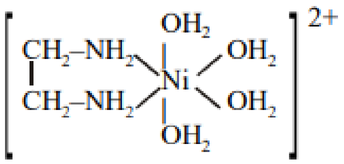
$$Cu^{2+} + 4NH_3 \; f \; [Cu(NH_3)_4)^{2+} \; ; \; \beta_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

12.8 Chelates

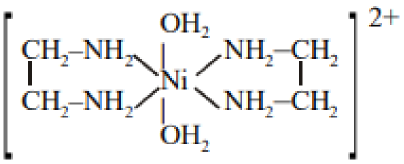
When bidentate or polydentate (multidentate) ligands form complexes through chelation, the stability constant increases. This is why, even for similar binding sites, chelating ligands form more stable complexes than non-chelating ligands (i.e. monodentate ligands).

Many essential biological chemicals are chelates. Chelates play important roles in oxsgen transport and in photosynthesis. Furthermore, many biological catalysts (enzymes) are chelates. In addition to their significance in living organisms, chelates are also economically important, both as products in themselves and as agents in the production of other chemicals. A chelate is a chemical compound composed of a metal ion or atom and a chelating agent. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. In other words, a chelating agent is a multidentate ligand. An example of a simple chelating agent is ethylenediamine ($NH_2\,CH_2\,CH_2\,NH_2$). Chelate rings are most stable when they have 5 or 6 members including the metal ion. The enhanced stability of chelate compounds is known as the chelate effect and mainly arises due to favourable entropy effect.

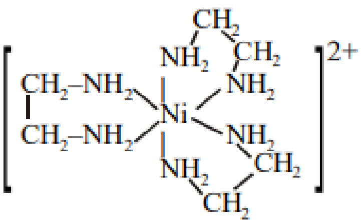
A single molecule of ethylenediamine can form two bonds to a transitionmetal ion such as nickel (II), NI^{2+}. The bonds form between the metal ion and the nitrogen atoms of -ethylenediamine. The nickel(II) ion can form six such bonds (coordination number 6), so a maximum of three ethylenediamine molecules can be attached to one Ni^{2+} ion.



chelate with one ethylenediamine ligand

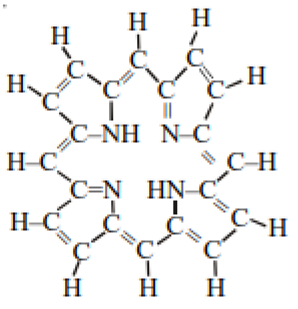


chelate with two ethylenediamine ligands

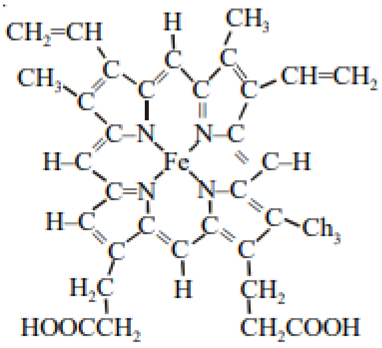


chelate with three ethylenediamine ligands

In the two structures on the left, the bonding capacity of the Ni^{2+} ion (6) is completed by water molecules. Each water molecule forms only one bond to Ni^{2+}, so water is not a chelating agent. Because the chelating agent is attached to the metal ion by several bonds, chelates tend to be more stable than complexes formed with monodentate ligands such as water.



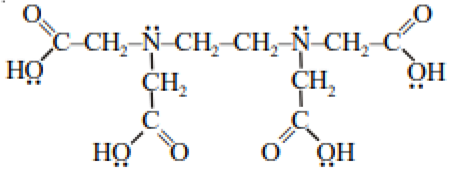
porphine



heme

Porphine is a chelating agent similar to ethylenediamine in that it forms bonds to a metal ion through nitrogen atoms. Each of the four nitrogen atoms in the center of the molecule can form a bond to a metal ion. Porphine is the simplest of a group of chelating agents called porphyrins. Porphyrins have a structure derived from porphine by replacing some of the outside hydrogen atoms with other groups of atoms. One important porphyrin chelate is heme, the central component of hemoglobin, which carries oxygen through the blood from the lungs to the tissues. Heme contains a porphyrin chelating agent bonded to an iron(ll) ion. Iron, like nickel, can form six bonds. Four of these bonds tie it to the porphyrin. One of iron's two remaining bonds holds an oxygen molecule as it is transported through the blood. Chlorophyll is another porphyrin chelate. In chlorophyll, the metal at the center of the chelate is a magnesium ion.

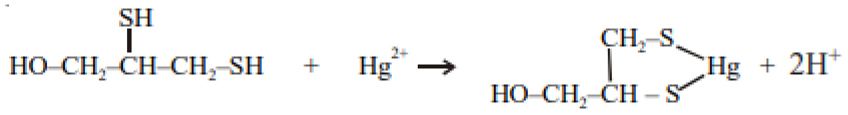
Chlorophyll, which is responsible for the green color of plant leaves, absorbs the light energy that is converted to chemical energy in the process of photosynthesis. Another biologically significant chelate is vitamin B-12. It is the only vitamin that contains a metal, a cobalt(ll) ion bonded to a porphyrin-like chelating agent. As far as is known, it is required in the diet of all higher animals. It is not synthesized by either higher plants or animals, but only by certain bacteria and molds. These are the sources of the B-12 found in animal products. Because vitamin B-12 is not found in higher plants, vegetarians must take care to include in their diets foods or supplements that contain the vitamin. A chelating agent of particular economic significance is ethylenediaminetetraacetic acid (EDTA).



ethylenediaminetetraacetic acid (EDTA)

EDTA is a versatile chelating agent. It can form four or six bonds with a metal ion, and it forms chelates with both transition-metal ions and main-group ions. EDTA is frequently used in soaps and detergents, because it forms complexes with calcium and magnesium ions. These ions are in hard water and interfere with the cleaning action of soaps and detergents. EDTA binds to them, sequestering them and preventing their interference. In the calcium complex. $[Ca(EDTA)]^{2-}$, EDTA is a tetradentate ligand, and chelation involves the two nitrogen atoms and two oxygen atoms in separate carboxyl ($–COC^-$) groups. EDTA is also used extensively as a stabilizing agent in the food industry. Food spoilage is often promoted by naturally-occurring enzymes that contain transition-metal ions. These enzymes catalyze the chemical reactions that occur during spoilage. EDTA deactivates these enzymes by removing the metal ions from them and forming stable chelates with them. It promotes color retention in dried bananas, beans, chick peas, canned clams, pecan pie filling, frozen potatoes, and canned shrimp. It improves flavor retention in canned carbonated beverages, salad dressings, mayonnaise, margarine, and sauces. It inhibits rancidity in salad dressings, mayonnaise, sauces, and sandwich spreads. EDTA salts are used in foods at levels ranging from 33 to 800 ppm. In other applications, EDTA dissolves the $CaCO_3$ scale deposited from hard water without the use of corrosive acid. EDTA is used in the separation of the rare earth elements from each other. The rare earth elements have very similar chemical properties, but the stability of their EDTA complexes varies slightly. This slight variation allows EDTA to effectively separate rare-earth ions. EDTA is used as an anticoagulant for stored blood in blood banks; it prevents coagulation by sequestering the calcium ions required for clotting. As an antidote for lead poisoning, calcium disodium EDTA exchanges its chelated calcium for lead, and the resulting lead chelate is rapidly excreted in the urine.

The calcium salt of EDTA, administered intravenously, is also used in the treatment of acute cadmium and iron poisoning. Dimercaprol (2.3-dimercapto-l-propanol) is an effective chelating agent for heavy metals such as arsenic, mercury, antimony, and gold. These heavy metals form particularly strong bonds to the sulfur atoms in dimercaprol.



dimercaprol

Dimercaprol was originally employed to treat the toxic effects of an arsenic-containing mustard gas called Lewisite [dichloro(2-chlorovinyl)arsine], which was used in World War I. The chelated metal cannot enter living cells and is rapidly excreted from the body. Since dimercaprol is water insoluble, it is dissolved in an oil base (often peanut oil) and injected intramuscularly).

12.9 Intermetallic Complexes

Intermetallic complexes are compounds formed from two or more metallic elements, often in precise stoichiometric ratios, where the metals are chemically bonded in an ordered structure. Unlike alloys, which are typically mixtures of metals without specific ordering, intermetallic complexes exhibit distinct structural arrangements that give them unique physical and chemical properties. These complexes are typically crystalline, and their bonding can range from metallic to covalent or ionic, depending on the nature of the constituent metals and their relative proportions.

Key Features of Intermetallic Complexes

1. **Ordered Crystal Structures**: Intermetallic complexes have well-defined crystal structures, often following stoichiometric ratios that yield distinct geometric arrangements. Common examples include BCC (body-centered cubic) and FCC (face-centered cubic) structures, each conferring specific properties to the material.
2. **Thermal Stability and High Melting Points**: Due to their ordered structures, intermetallic complexes tend to have high melting points and exhibit excellent thermal stability, making them suitable for applications requiring heat resistance, such as turbine engines and aerospace components.
3. **Magnetic and Electronic Properties**: Many intermetallic compounds possess unique magnetic and electronic behaviours. For instance, some intermetallics, like rare-earth compounds, display ferromagnetic or superconducting properties due to their electronic configurations and the nature of their bonding.
4. **Corrosion Resistance and Mechanical Strength**: Intermetallics like nickel-aluminide (NiAl) and titanium-aluminide (TiAl) are highly resistant to corrosion and maintain strength at elevated temperatures, making them ideal for high-performance applications in environments where other materials might degrade.

Synthesis and Applications

The synthesis of intermetallic complexes can be complex, as it requires precise control of temperature, pressure, and composition to ensure that the desired ordered structure forms.

Common methods include direct melting, solid-state diffusion, and chemical vapour deposition.

Applications of Intermetallics span across various fields:

- **Aerospace and Automotive**: Lightweight intermetallics with high strength-to-weight ratios, like titanium aluminides, are used in aircraft engines and high-performance automotive parts.
- **Catalysis**: Intermetallics of palladium, platinum, and other transition metals exhibit catalytic properties that make them effective in reactions like hydrogenation and dehydrogenation.
- **Magnetic and Electronic Devices**: Some intermetallics, especially those containing rare earth elements, are employed in electronic devices, magnetic storage media, and superconductors.

Some Examples of Intermetallic Complexes:

Intermetallic complexes exhibit unique properties due to the specific bonding and ordered arrangement of the metals involved. Here are some notable examples:

1. Nickel-Aluminide (NiAl)

- Structure: NiAl forms in a B2 structure (body-centered cubic) with a 1:1 stoichiometry.
- Properties: High melting point, excellent oxidation resistance, and good thermal conductivity.
- Applications: Used in turbine blades, heating elements, and high-temperature structural components in the aerospace industry.

2. Titanium-Aluminide (TiAl)

- Structure: TiAl typically forms in a γ-phase (face-centered tetragonal structure) with a 1:1 or 3:1 ratio.
- Properties: High strength-to-weight ratio, heat resistance, and good corrosion resistance.
- Applications: Applied in automotive and aerospace components, such as engine parts and turbochargers, where lightweight and heat resistance are crucial.

3. Iron-Aluminide (FeAl or Fe3Al)

- Structure: Iron-aluminides commonly form in B2 (FeAl) or D03 (Fe3Al) structures.

- Properties: Outstanding resistance to oxidation and sulfidation, particularly at high temperatures.
- Applications: Commonly used in high-temperature environments such as industrial heating equipment, boilers, and furnace parts.

4. Magnesium-Silicide (Mg2Si)

- Structure: Forms in an antifluorite crystal structure with a 2:1 Mg to Si ratio.
- Properties: Lightweight, high thermal stability, and semiconductor properties.
- Applications: Found in thermoelectric devices and lightweight structural materials.

5. Palladium-Silver (PdAg)

- Structure: Forms a continuous solid solution, often in face-centered cubic (FCC) structure.
- Properties: Excellent hydrogen permeability and good corrosion resistance.
- Applications: Commonly used in hydrogen purification and storage, as well as in certain catalytic reactions.

6. Copper-Zinc (CuZn) – Brass

- Structure: Typically forms in the β-phase with a B2 structure.
- Properties: Strong, corrosion-resistant, and has good electrical conductivity.
- Applications: Extensively used in electrical connectors, heat exchangers, and decorative items.

7. Rare-Earth Intermetallics (e.g., Nd2Fe14B)

- Structure: These compounds vary in structure; Nd2Fe14B forms a tetragonal crystal structure.
- Properties: Strong magnetic properties, often resulting in hard and high-energy permanent magnets.
- Applications: Widely used in high-strength magnets, such as those found in electric motors, wind turbines, and hard drives.

12.10 Summary

Alfred Werner’s theory is foundational for coordination chemistry, explaining the structure and bonding in coordination compounds. Werner proposed that metal ions have primary (oxidation state) and secondary valencies, with the latter corresponding to coordination numbers. His theory accounted for the arrangement of ligands around a central metal ion, leading to modern understanding of coordination compounds' geometric structures.

The EAN rule suggests that in stable complexes, the central metal atom tends to acquire an effective atomic number similar to the nearest noble gas by bonding with ligands. The EAN is calculated by summing the metal's electrons and the bonding electrons donated by ligands, helping to predict stability in coordination compounds.

Ligands are classified based on the number of donor atoms and their binding modes. Common types include monodentate (single donor site), bidentate, and polydentate ligands, with binding modes ranging from single-point attachment to forming rings (chelates) with metal centers. Ligand classification is essential for predicting the structure and properties of complexes.

IUPAC guidelines standardize the naming of coordination compounds, following rules based on the central metal, ligand type, and coordination number. For complexes with up to two metal centers, nomenclature also considers the arrangement and linking of metal ions, ensuring consistent naming across coordination chemistry.

The stability of a complex can be quantified through stability constants, with overall stability constants describing the total formation of a complex and stepwise constants reflecting each sequential ligand binding step. These constants provide insights into the complex’s stability and the ligand affinity for the central metal ion.

Chelates are coordination compounds where a ligand forms multiple bonds with a metal ion, creating a ring structure. Chelate formation, also known as the chelate effect, typically enhances complex stability due to the increased binding strength and entropic favorability.

Intermetallic complexes are compounds with specific ratios of two or more metals, exhibiting ordered crystalline structures and distinct bonding characteristics. Unlike coordination compounds, intermetallics have unique properties such as high thermal stability, magnetism, and corrosion resistance, and are widely used in structural and electronic applications.

12.11 Sample Questions

A. Multiple Type Questions

1. According to Werner's Theory, the secondary valency of a metal is associated with:

A) Oxidation state

B) Coordination number

C) Crystal structure

D) Magnetic properties

Answer: B) Coordination number

2. The Effective Atomic Number (EAN) Rule suggests that the metal in a stable complex tends to:

A) Have an EAN equal to its atomic number

B) Match the atomic number of the nearest alkali metal

C) Match the atomic number of the nearest noble gas

D) Match the coordination number of the complex

Answer: C) Match the atomic number of the nearest noble gas

3. A ligand that can form two bonds to a metal center is known as:

A) Monodentate

B) Bidentate

C) Polydentate

D) Tridentate

Answer: B) Bidentate

4. Which of the following is true about IUPAC nomenclature for coordination compounds?

A) Anionic ligands are named with the suffix "ium"

B) Ligands are listed in alphabetical order regardless of charge

C) The oxidation state of the metal is not included

D) Ligands with multiple donor atoms are always named with "poly"

Answer: B) Ligands are listed in alphabetical order regardless of charge

5. The overall stability constant (β) of a complex is:

A) The sum of all stepwise stability constants

B) The product of all stepwise stability constants

C) The ratio of the metal ion concentration to ligand concentration

D) The inverse of the dissociation constant

Answer: B) The product of all stepwise stability constants

6. Chelates are typically more stable than complexes with monodentate ligands due to:

A) Increased entropy and the chelate effect

B) Decreased entropy and weaker metal-ligand bonds

C) Higher oxidation state of the metal

D) Formation of ionic bonds

Answer: A) Increased entropy and the chelate effect

7. Which of the following correctly describes an intermetallic complex?

A) It consists of metals and non-metals in a random arrangement

B) It has a specific ordered arrangement of two or more metals

C) It is primarily used for catalysis in organic reactions

D) It has no defined stoichiometric composition

Answer: B) It has a specific ordered arrangement of two or more metals

8. In the complex $[Co(NH_3)_6]Cl_3$, the oxidation state of cobalt (Co) is:

A) 0

B) +1

C) +2

D) +3

Answer: D) +3

9. A ligand like EDTA, which can bind to a metal through multiple atoms, is classified as:

A) Monodentate

B) Bidentate

C) Tridentate

D) Hexadentate

Answer: D) Hexadentate

10. Which of the following compounds is most likely to exhibit a chelate effect?

A) $[Fe(CN)_6]^{4-}$

B) $[Ni(NH_3)_6]^{2+}$

C) $[Cu(EDTA)]^{2-}$

D) $[Ag(NH_3)_2]^+$

Answer: C) $[Cu(EDTA)]^{2-}$

B. Short Type Questions

1. What is Werner’s Theory in coordination chemistry?

   Answer: Werner's Theory, proposed by Alfred Werner, explains coordination compounds' structure and bonding. It states that metal ions have primary valency (oxidation state) and secondary valency (coordination number). The secondary valency corresponds to the number of ligands directly bonded to the metal ion, leading to specific geometric structures.

2. What does the Effective Atomic Number (EAN) rule state?

   Answer: The EAN rule suggests that the metal in a stable complex tends to attain an effective atomic number equal to the nearest noble gas by accepting electron pairs from ligands. This rule helps in predicting the stability of coordination complexes.

3. How are ligands classified based on their denticity?

   Answer: Ligands are classified based on the number of donor atoms they possess. Monodentate ligands have one donor atom, bidentate ligands have two, and polydentate ligands have multiple donor atoms that can bind to a metal center simultaneously. Polydentate ligands form more stable complexes by creating ring structures around the metal.

4. Explain the chelate effect in coordination chemistry.

   Answer: The chelate effect refers to the increased stability of a complex when a ligand forms multiple bonds with a metal ion, creating a ring structure. This effect arises due to increased entropy and stronger binding resulting from the multiple bonding points, which makes chelates more stable than complexes with monodentate ligands.

5. What is the difference between stepwise stability constants and overall stability constants?

Answer: Stepwise stability constants (K_1, K_2, etc.) refer to the individual binding constants for each successive ligand attaching to the metal ion. The overall stability constant (β) is the product of these stepwise constants, reflecting the total stability of the complex.

6. Describe the IUPAC naming convention for coordination compounds.

Answer: IUPAC naming rules for coordination compounds prioritize listing ligands alphabetically before the metal. Anionic ligands typically end in "-o," and the oxidation state of the metal is specified in Roman numerals. If there are multiple metal centers, bridging ligands are indicated with the prefix "μ."

7. What are intermetallic complexes, and how do they differ from coordination complexes?

Answer: Intermetallic complexes are compounds formed by two or more metals in a specific, ordered crystal structure. Unlike coordination complexes, which involve a central metal ion and ligands, intermetallics consist of metallic bonding and are used for properties like thermal stability and magnetism, rather than catalytic or biological roles.

8. Why do bidentate and polydentate ligands form more stable complexes than monodentate ligands?

Answer: Bidentate and polydentate ligands form more stable complexes due to the chelate effect, where multiple bonds between the ligand and the metal create ring structures. These rings increase stability through greater binding strength and an entropy-driven process, making the complex less likely to dissociate.

9. What is the significance of the coordination number in coordination chemistry?

Answer: The coordination number represents the number of ligand atoms directly bonded to the central metal ion in a complex. It determines the geometry of the complex (e.g., octahedral for a coordination number of 6) and influences the compound's stability, reactivity, and physical properties.

10. How does the EAN rule help in predicting complex stability?

Answer: The EAN rule helps in predicting complex stability by suggesting that metal complexes with an EAN equivalent to the nearest noble gas configuration tend to be more stable. This configuration implies a full, stable electron shell around the metal ion, reducing reactivity and making the complex more robust.

Unit - 13 ❑ Coordination Compounds and Isomerism

Structure

13.0 Objectives

After going through this unit one should able to know the following terms:

- VBT, hybridisation and corresponding structure for complexes
- Definition and types of structural isomerism, geometrical isomerism and optical isomerism
- Distinction between *cis* and *trans* isomers
- Resolution of optical isomers
- IUPAC system nomenclature of complexes

13.1 Introduction

Valence Bond theory provides the hybridization for octahedral complexes. To understand the hybridization of coordination compounds VBT is important. In know that the transition metals form a large number of complexes in which the metal atoms are bound to a number of anions or neutral molecules by sharing of electrons. These compounds are now called coordination compounds. The chemistry of these compounds is a significant and demanding area of current inorganic chemistry. New thoughts of chemical bonding and molecular structure have provided imminent into the functioning of these compounds as essential components of biological organism. Coordination compounds have many applications in electroplating, textile dyeing and medicinal chemistry. Therefore, the study about coordination chemistry is very vital.

13.2 Valence bond theory for complex

a) Metal ion will make available a no of orbitals equal to coordination for theformation of covalent bond with the ligands.

b) Metal ion uses hybrid orbital involving *s*, *p* and *d* orbitals for accepting electronpair from ligands.

c) The hybridized orbitals are so directed as to facilitate their occupation by electronpairs coming from donor ligands. [when σ-bond is formed between metal andligand]

d) The non-bonding electrons of metal ion are then re-organised to occupy theremaining metal orbitals, obeying Hund’s rule.

e) In addition to σ-bond between metal and ligand a σ-bond may be formed byoverlap of filled orbital of metal with vacant orbitals of ligand and thereby bondmultiplicity occurs. Such bond multiplicity will arise particularly for complexesof metal ion of low oxidation state.

f) Stereo chemistry of complex is decided by the nature of hybridization on metalion and also from this hybridization we can predict magneto chemistry of thecomplexes.

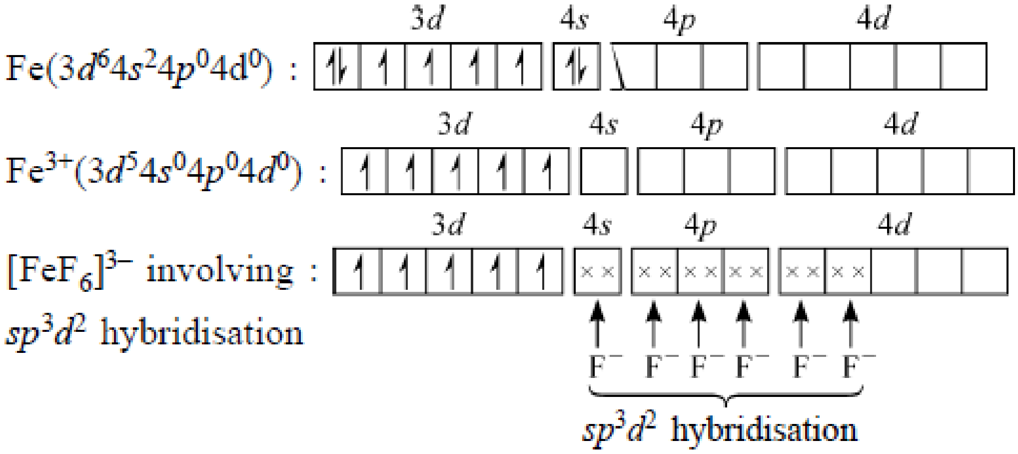
g) Important types of hybridization occurring in first row transition metal compounds are shown below.

AO's involved	Hybridisation	Structure
$4s$, $4px$, $4py$ and $4pz$	Sp^3	td
$3d_{x^2-y^2}$, $4s$, $4px$, $4py$	dsp^2	Square planner
$4s$, $4px$, $4py$, $4pz$, $4d_{x^2-y^2}$ and $4dz^2$	sp^3d^2 (outer orbital)	Oh
$3d_{x^2-y^2}$, $3d_{z^3}$, $4s$, $4px$, $4py$, $4pz$	d^2sp^3(inner orbital)	Oh

13.2.1 sp^3d^2-hybridisation in outer orbital octahedral complexes

This type of hybridisation takes place in those octahedral complex ions which contain weak ligands having more electronegative donor centre (e.g. Oxygen, fluorine etc.). Weak ligands are those which cannot force the electrons of d_{z2} and d_{x2-y2} orbitals of inner shell to occupy d_{xy}, d_{yz}, d_{zx} orbitals of the same shell. Thus in this hybridisation $(n - 1]d_{z^2}$and $(n - 1)\ d_{x^2-y^2}$orbitals are not available for hybridisation.

In place of these orbitals, we use nd_{z2} and $nd_{x^2-y^2}$orbitals (these d-orbitals belong to the outer shell) and hence sp^3d^2hybridisation can be represented as ns, np_x, np_y, np_z, nd_{z^2}, $nd_{x^2-y^2}$. This hybridisation show that all the six orbitals involved in hybridisation belong to the higher energy level (outer shell). This discussion shows that in case of Oh ion of $3d$ transition series, d-orbitals used in hybridisation are $4d_{z^2}$and $4d_{x^2-y^2}$orbitals. Since two d-orbitals are from outer shell (i.e., n-th shell) and the sp^3d^2hybridisation are called outer *orbital Oh complexes.* This type of hybridisation has comparatively greater no of unpaired electrons than the inner orbital octahedral complexes, these are also called *spin free or high spin octahedral complexes,* e.g. $[FeF_6]^{3-}$ion, in which iron present as Fe^{3+} state of electronic configuration $3d5^4s^04p^0$.

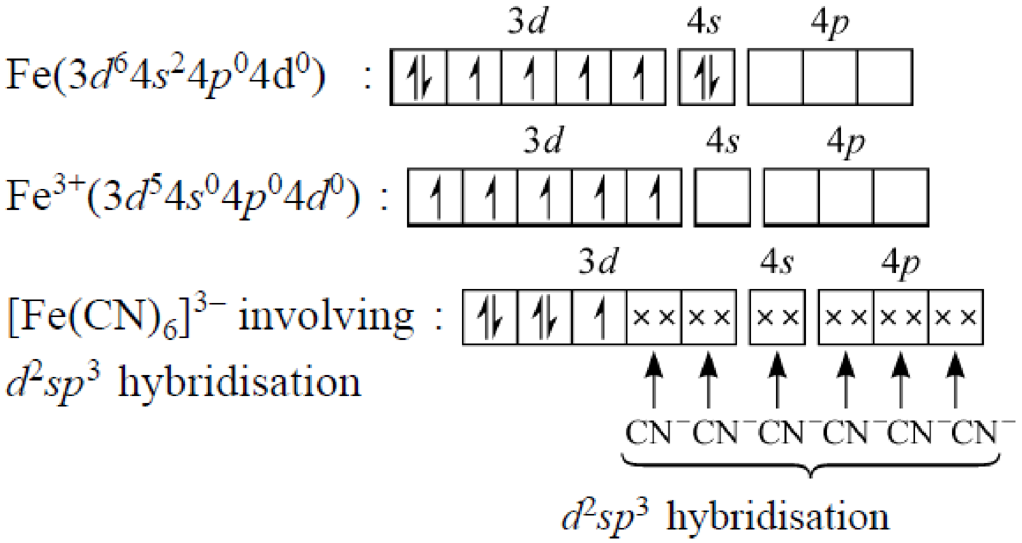


Again Cr^{2+} ion having outermost electronic configuration ($3d^4$) shows outer orbital octahedral complexes (sp^3d^2 hybridisation) in the complex $[Cr(H_2O)_6]SO_4$, having paramagnetism behavior equivalent to four unpaired electrons. Ni^{+2} ion also having outermost electronic configuration ($3d^8$) shows outer orbital octahedral complexes (sp^3d^2 hybridisation) in the complex $[Ni(NH_3)_6]Cl_2$ shows paramagnetism behavior equivalent to two unpaired electrons. [CoF6]3+ ion of central metal $Co^{3+}(3d^6)$ has paramagnetic character corresponding to the presence of four unpaired electrons in 3*d*-orbitals, shows outer orbital octahedral complexes having sp^3d^2 hybridisation. Cu^{2+} ion in $[Cu(NH_3)_4]Cl_2$ complex having coordination no 4, shows tetrahedral geometry (sp^3 hybridisation).

13.2.2 d^2sp^3-hybridisation in inner orbital octahedral complexes

Octahedral complexes in which the central atom is d^2sp^3 hybridised are called inner-orbital octahedral complexes. This type hybridisation takes place in those Oh complexes which contain strong field ligand having low electronegative donor centre (e.g. phosphorous and Arsenic etc.). In the formation of six d^2sp^3 hybrid orbitals, two (n–1) *d*-orbitals, one *ns,* three *np* orbitals combine together and form six d^2sp^3 hybrid orbitals. Since in this hybridisation used two *d* orbitals coming from inner shell [i.e., (n–1) shell] this type of hybridisation is called inner orbital octahedral complexes.

These are also called **spin paired or low spin complexes.** E.g. $[Fe(CN)_6]^{3-}$, here iron present in as Fe^{3+} ion whose valance shell electronic configuration $3d^5$.



Due to presence of one unpaired electron in [Fe(CN)$_6$]$^{3-}$ it behaves as paramagnetic equivalent to one unpaired electron in nature.

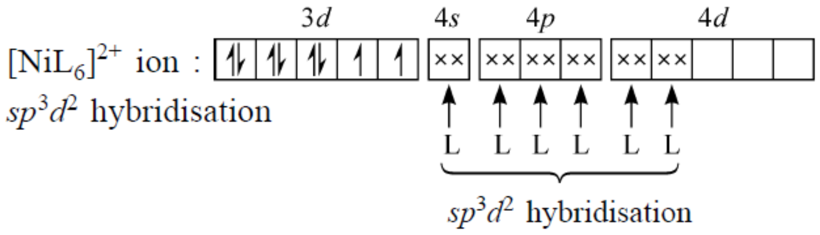
Again Cr^{3+} ion having outermost electronic configuration (3d^3) shows inner orbital octahedral complexes (d^2sp^3 hybridisation) in the complex [Cr(NH$_3$)$_6$]Br$_3$, having paramagnetism behavior equivalent to three unpaired electrons. [Co(NH$_3$)$_6$]Cl$_3$ complex having central metal ion Co$^{3+(}$3d^6) shows inner orbital octahedral complexes (d^2sp^3 hybridisation) has diamagnetic in nature due to absence of unpaired electrons in 3*d*-orbitals.

Again due to absence of two vacant *d*-orbitals in the outermost 3*d* orbitals of the cupper ions it does not form any inner orbital octahedral complexes. [Ni(CN)$_4$]$^{2-}$ is the example of four coordinate square planer geometry (dsp^2 hybridisation) and diamagnetic in nature. In Ni(CO)$_4$ having Ni(0) shows tetrahedral geometry (sp^3 hybridisation) diamagnetic in nature. In Na$_2$[CoCl$_4$], Central metal Co$_{2+}$(3d^7) and as Cl$^-$ is weak field ligand shows tetrahedral geometry (sp^3 hybridisation) having magnetic moment 3.87 B.M.

In [NiCl$_4$]$^{2-}$ and [Ni(CN)$_4$]$^{2-}$ having Ni(II) is central ion (3d^8), shows four coordinate outer orbital tetrahedral (sp^3 hybridization) and inner orbital square planer (dsp^2 hybridization) complexes respectively as CN$^-$ ligand is higher in strength than Cl$^-$ ligand strength.

Question: Explain why it shows all octahedral complexes of Ni2+ ion mustbe outer-orbital complexes?

Ans: The electronic configuration of Ni^{2+} ion (3d^8) indicates that two inner *d*-orbitals(3*d*-orbitals) cannot be made available to allow d^2sp^3 hybridisation. However,by using two 4*d*-orbitals sp^3d^2 hybridisation may be possible.



N.B. : Same case arises for complexes having the central ion $Cu^{2+}(3d^9)$ and Cu^{1+} (d^{10}) ion shows outer orbital octahedral complexes of example $[Cu(NH_3)_6]^{2+}$ and $[Cu(NH_3)_6]^{+}$ respectively.

13.2.3 Limitation of VBT

a.) VBT cannot predict distortion of Oh complex of Cu (II) i.e., *d*9 system andTi(III) i.e., *d*1 system.

b.) VBT neglects the excited state complexes and hence no thermodynamicsproperties can be predicted.

c.) VBT cannot explain spectra (colours) of the complexes.

d.) VBT cannot explain in details about the magnetic properties of the complexes.

13.3 Outer orbital complexes

In accordance with valence bond theory, octahedral metal-complexes can be divided into two types. Outer orbital complexes: Complexes with sp^3d^2 hybridization are generally) labile in nature. Valence bond theory proposed that the bonds in this hybridization are generally weaker than d^2sp^3 and therefore they show labile character.

Outer orbital complexes are coordination complexes in which the central metal atom or ion uses its outer (higher-energy) orbitals for bonding with ligands. In these complexes, the metal typically uses its d, s, and p orbitals from the outermost (or penultimate) shell rather than its inner or lower-energy orbitals.

Here are some key features of outer orbital complexes:

1. Orbital Hybridization: Outer orbital complexes often involve the use of sp^3d^2 or sp^3d hybridization, where d-orbitals from the outer (valence) shell of the metal atom are hybridized. This results in complexes with octahedral or trigonal bipyramidal geometries, respectively.
2. Electron Configuration: Outer orbital complexes are common in transition metals where the d-orbitals of the outermost shell are involved. For example, a transition metal with a $3d^3$ configuration may use its $4d^4$ or $5d^5$ orbitals to form an outer orbital complex.

3. Ligand Field Theory: In outer orbital complexes, the crystal field stabilization energy (CFSE) is generally lower than in inner orbital complexes because the metal-ligand interactions are weaker. Ligands tend to experience weaker crystal fields, leading to high-spin complexes (especially with weak-field ligands).
4. Magnetic Properties: Due to the high-spin nature, outer orbital complexes often have unpaired electrons, making them paramagnetic.

Example:

Consider $[FeF_6]^{3-}$:

- Here, the Fe^{3+} ion (which has a $3d^5$configuration) uses its 4s, 4p, and $4d^4$ orbitals, resulting in sp^3d^2 hybridization and an octahedral structure.
- Fluoride (F^-) is a weak-field ligand, so pairing of electrons in the $3d^3$ orbitals doesn't occur, and the complex is high-spin with unpaired electrons.

13.4 Inner orbital complexes

Inner orbital complexes are coordination complexes in which the central metal ion uses its inner (or lower-energy) d-orbitals for bonding with ligands. In these complexes, the metal often undergoes hybridization involving its lower-energy orbitals, leading to stronger metal-ligand interactions and distinct electronic properties compared to outer orbital complexes.

Key Features of Inner Orbital Complexes:

- Orbital Hybridization: In inner orbital complexes, the central metal ion uses the inner d-orbitals (such as $3d^3$ for a 3rd-period element like transition metals) for hybridization. This often leads to d^2sp^3 hybridization in octahedral geometries, allowing the use of lower-energy d-orbitals.
- Ligand Field Theory: Inner orbital complexes are typically formed with strong-field ligands (e.g., CN^-, NO^{2-}), which can cause electron pairing in the metal's d-orbitals. This results in high crystal field stabilization energy (CFSE), promoting low-spin configurations, where electrons pair up rather than remain unpaired.
- Magnetic Properties: Due to electron pairing in lower-energy orbitals, inner orbital complexes are often low-spin and may exhibit diamagnetic properties (having no unpaired electrons). However, this depends on the specific ligand field strength and the metal ion.

- Stability and Bond Strength: Inner orbital complexes generally have stronger metal-ligand bonds due to more stable and effective overlap between the ligands and the lower-energy d-orbitals of the metal.

Example:

Consider $[Fe(CN)_6]^{4-}$:

- The Fe^{2+} ion has a $3d^6$ electron configuration. When forming $[Fe(CN)_6]^{4-}$, which contains the strong-field ligand CN^-, electron pairing occurs within the $3d^3$orbitals. This results in d^2sp^3 hybridization involving the lower-energy $3d^3$-orbitals.
- The complex adopts a low-spin configuration with no unpaired electrons, making it diamagnetic.
- The use of inner orbitals in hybridization makes this an inner orbital complex, with stronger and more stable bonding than if the outer d-orbitals were involved.

13.5Complexes of Cr, Fe, Co, Ni and Cu (coordination numbers 4 and 6).

Chromium (Cr) Complexes:

I. Coordination Number 4

- Example: $[CrCl_4]^-$
- Geometry: Tetrahedral (common with halide ligands)
- Hybridization: sp^3
- Spin State: High-spin configuration, as tetrahedral complexes generally have weak field ligands.

II. Coordination Number 6

- Example: $[Cr(H_2O)_6]^{3+}$
- Geometry: Octahedral
- Hybridization: d^2sp^3
- Spin State: High-spin with weak-field ligands (e.g., H_2O); can be low-spin with strong-field ligands (e.g., CN^-).

Iron (Fe) Complexes

III. Coordination Number 4

- Example: $[FeCl_4]^-$

- Geometry: Tetrahedral (typical with halide ligands)
- Hybridization: sp^3
- Spin State: High-spin, since tetrahedral complexes with weak-field ligands like chloride tend to not have enough field strength to pair electrons.
- Example: $[Fe(CO)_4]$ (neutral complex)
- Geometry: Tetrahedral
- Hybridization: sp^3
- Spin State: Low-spin, as CO is a strong-field ligand that causes electron pairing.

IV. Coordination Number 6

- Example: $[Fe(CN)_6]^{4-}$
- Geometry: Octahedral
- Hybridization: d^2sp^3
- Spin State: Low-spin, as CN^- is a strong-field ligand.
- Example: $[Fe(H_2O)_6]^{3+}$
- Geometry: Octahedral
- Hybridization: d^2sp^3
- Spin State: High-spin with weak-field ligands (e.g., H_2O).

Cobalt (Co) Complexes

- Coordination Number 4
- Example: $[CoCl_4]^{2-}$
- Geometry: Tetrahedral
- Hybridization: sp^3
- Spin State: High-spin with weak-field ligands like chloride.
- Example: $[Co(CO)_4]$ (neutral complex)
- Geometry: Tetrahedral
- Hybridization: sp^3
- Spin State: Low-spin, due to the strong-field ligand CO

V. Coordination Number 6

- Example: $[Co(NH_3)_6]^{3+}$
- Geometry: Octahedral

- Hybridization: d^2sp^3
- Spin State: Low-spin with strong-field ligands like NH_3.
- Example: $[CoF_6]^{3-}$
- Geometry: Octahedral
- Hybridization: sp^3d^2
- Spin State: High-spin with weak-field ligands like fluoride.

Nickel (Ni) Complexes

- Coordination Number 4
- Example: $[Ni(CN)_4]^{2-}$
- Geometry: Square planar (common for d8d^8d8 metal ions like Ni^{2+})
- Hybridization: dsp^2
- Spin State: Low-spin with strong-field ligands such as CN^-.
- Example: $[NiCl_4]^{2-}$
- Geometry: Tetrahedral
- Hybridization: sp^3
- Spin State: High-spin with weak-field ligands like chloride.

VI. Coordination Number 6

- Example: $[Ni(H_2O)_6]^{2+}$
- Geometry: Octahedral
- Hybridization: d^2sp^3
- Spin State: High-spin with weak-field ligands.

Copper (Cu) Complexes

VII. Coordination Number 4

- Example: $[Cu(NH_3)_4]^{2+}$
- Geometry: Square planar (common for d^9 systems like Cu^{2+})
- Hybridization: dsp^2
- Spin State: Typically, low-spin due to d^9 electron configuration and ligand field stabilization.
- Example: $[CuCl_4]^{2-}$
- Geometry: Tetrahedral

- Hybridization: sp^3
- Spin State: High-spin due to weak-field ligand chloride.

VIII. Coordination Number 6

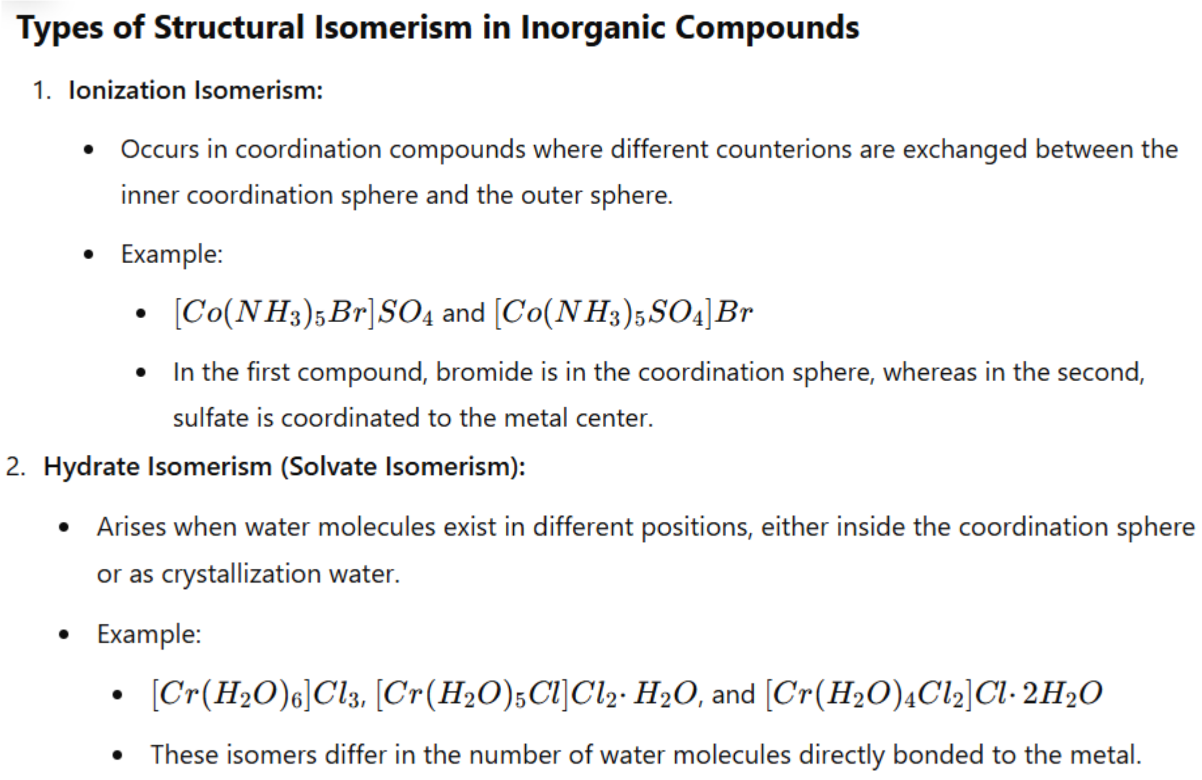
- Example: $[Cu(H_2O)_6]^{2+}$
- Geometry: Octahedral, though usually distorted due to the Jahn-Teller effect (common for d^9 complexes).
- Hybridization: d^2sp^3
- Spin State: Generally high-spin

13.6Isomerism

Two or more complexes with same empirical compositions but it different properties are called isomers and the phenomenon is known as isomerism. Isomerism of complexes are mainly divides into two types such as Structural isomerism and Stereoisomerism.

13.7Structural Isomerism

Structural isomerism in inorganic chemistry refers to compounds that have the same molecular formula but differ in the connectivity of atoms or the arrangement of ligands around the central atom. This leads to variations in chemical and physical properties.



Types of Structural Isomerism in Inorganic Compounds

1. **Ionization Isomerism:**
   - Occurs in coordination compounds where different counterions are exchanged between the inner coordination sphere and the outer sphere.
   - Example:
     - $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$
     - In the first compound, bromide is in the coordination sphere, whereas in the second, sulfate is coordinated to the metal center.
2. **Hydrate Isomerism (Solvate Isomerism):**
   - Arises when water molecules exist in different positions, either inside the coordination sphere or as crystallization water.
   - Example:
     - $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
     - These isomers differ in the number of water molecules directly bonded to the metal.

3. **Linkage Isomerism:**
   - Occurs when a ligand can coordinate to the metal through two different donor atoms.
   - Example:
     - $[Co(NH_3)_5(NO_2)]^{2+}$ (Nitro complex, $-NO_2$)
     - $[Co(NH_3)_5(ONO)]^{2+}$ (Nitrito complex, $-ONO$)
     - The ligand (NO_2^-) binds through nitrogen in the nitro form and through oxygen in the nitrito form.
4. **Coordination Isomerism:**
   - Found in compounds where both cationic and anionic complexes are present, and the distribution of ligands between them changes.
   - Example:
     - $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
     - Here, the ligands around cobalt and chromium are swapped.
5. **Polymerization Isomerism:**
   - Occurs when isomers have the same empirical formula but different molecular compositions, leading to polymeric structures.
   - Example:
     - $[Pt(NH_3)_2Cl_2]$ (simple unit) and $[Pt(NH_3)_2]Cl_2$ (polymeric form with bridged Pt centers).

13.8Stereoisomerism in complexes with coordination numbers 4 and 6

Stereoisomerism occurs when coordination compounds have the same connectivity of atoms but differ in spatial arrangement. This type of isomerism is commonly observed in **coordination complexes** with coordination numbers **4 (tetrahedral and square planar) and 6 (octahedral).**

Stereoisomerism in Coordination Number 4:

(A) Geometrical Isomerism (Square Planar Complexes)

- **Occurs in square planar complexes** of the type $[MA_2B_2]$ or $[MABCD]$, where ligands can be arranged differently around the metal center.
- **Cis and Trans Isomerism:**
    - **Cis-isomer:** Two identical ligands are adjacent to each other.
    - **Trans-isomer:** Two identical ligands are opposite to each other.

Example:

- $[Pt(NH_3)_2Cl_2]$ **(Platin Complex)**
    - **Cis-isomer**: Used as an anticancer drug (**Cisplatin**).
    - **Trans-isomer**: Biologically inactive (**Transplatin**).

(B) Optical Isomerism (Tetrahedral Complexes)

- **Occurs in tetrahedral complexes** of the type $[M(AB)_2]$ where the metal is coordinated by bidentate ligands.
- **Non-superimposable mirror images (enantiomers)** exist, leading to optical activity.

Example:

- $[Be(en)_2]^{2+}$ (where **en** = ethylenediamine)
    - Exists as two **enantiomers**, which rotate plane-polarized light in opposite directions.

Stereoisomerism in Coordination Number 6 (Octahedral Complexes):

(A) Geometrical Isomerism

- **Occurs in octahedral complexes** of the type $[MA_4B_2]$ or $[MA_3B_3]$.
- **Cis and Trans Isomerism:**
    - **Cis-isomer:** Similar ligands are adjacent.
    - **Trans-isomer:** Similar ligands are opposite.

Example:

- ($[Co(NH_3)_4Cl_2]^+$
    - **Cis-isomer**: More reactive due to closer Cl atoms.
    - **Trans-isomer**: Less reactive.
- $[Co(NH_3)_3(NO_2)_3]$
    - **Facial (fac) isomer**: Three NO_2 groups are at adjacent positions (same face).
    - **Meridional (mer) isomer**: Three NO_2 groups are positioned along a meridian.

(B) Optical Isomerism

- **Occurs in octahedral complexes** where ligands create a non-superimposable mirror image.
- Common in **tris-chelate complexes** with bidentate ligands like ethylenediamine (**en**) or oxalate ($C_2O_4^{2-}$).

Example:

- $[Cr(ox)_3]^{3-}$ (ox = oxalate)
    - Exists as **two enantiomers**, which rotate plane-polarized light in opposite directions.

(C) Cisplatin vs. Transplatin Case Study

- **Cisplatin** (**cis-**$[Pt(NH_3)_2Cl_2]$) is used in cancer treatment.
- **Transplatin** (**trans-**$[Pt(NH_3)_2Cl_2]$) is **biologically inactive**.

13.9Summary

sp^3d^2-Hybridisation in Outer Orbital Octahedral Complexes:

In outer orbital octahedral complexes, the central metal ion uses its outer d, s, and p orbitals to form hybrid orbitals. This results in sp^3d^2 hybridisation, where six ligands coordinate around the metal. These complexes are usually high-spin, as electrons do not pair up due to weak ligand fields

d^2sp^3-Hybridisation in Inner Orbital Octahedral Complexes:

Inner orbital octahedral complexes involve the use of the inner (lower-energy) d-orbitals for hybridisation, resulting in d^2sp^3 hybridisation. These complexes often exhibit low-spin configurations due to strong ligand fields, causing electron pairing in lower-energy orbitals.

Limitation of VBT:

Valence Bond Theory (VBT) has limitations, including:

- It does not explain the colour of complexes.
- It does not differentiate between high-spin and low-spin states effectively.
- It lacks a quantitative approach to magnetic properties.
- It cannot predict the relative stabilities of complexes accurately.

Outer Orbital Complexes:

These complexes use orbitals from the outermost shells (sp^3d^2 hybridisation), leading to high-spin states due to weak field ligands. They often exhibit paramagnetic behavior.

Inner Orbital Complexes:

These involve hybridisation using inner d-orbitals (d^2sp^3 hybridisation), usually leading to low-spin states with strong field ligands. Such complexes are often diamagnetic.

Complexes of Cr, Fe, Co, Ni, and Cu (Coordination Numbers 4 and 6):

- Chromium (Cr): Forms both tetrahedral and octahedral complexes, often exhibiting variable oxidation states.
- Iron (Fe): Forms both high-spin and low-spin complexes, common oxidation states being +2 and +3.
- Cobalt (Co): Exhibits coordination numbers 4 and 6, forming tetrahedral (high-spin) and octahedral (low-spin) complexes.
- Nickel (Ni): Forms square planar, tetrahedral, and octahedral complexes, with oxidation states of +2 and +3.
- Copper (Cu): Forms mainly square planar and distorted octahedral complexes due to the Jahn-Teller effect.

Isomerism:

Isomerism in coordination compounds arises due to different spatial and connectivity arrangements of ligand.

Structural Isomerism:

This includes:

- Linkage isomerism (ligands bind through different atoms).
- Coordination isomerism (exchange of ligands between metal centers).
- Ionization isomerism (exchange of counterions with coordinated ligands).
- Hydrate isomerism (differing number of water molecules in coordination).

Stereoisomerism in Complexes with Coordination Numbers 4 and 6:

- Tetrahedral (Coordination Number 4): Can show optical isomerism if ligands are arranged asymmetrically.
- Square Planar (Coordination Number 4): Shows cis-trans isomerism, especially in Pt(II) and Pd(II) complexes.
- Octahedral (Coordination Number 6): Can exhibit both cis-trans and optical isomerism, common in chelating ligands like ethylenediamine (en).

13.10 Sample Questions

A.Multiple Type Questions

1. What type of hybridisation is observed in inner orbital octahedral complexes?

A) sp^3d^2
B) d^2sp^3
C) sp^3d^3
D) dsp^2

2. Which of the following is NOT a limitation of Valence Bond Theory?

A) Cannot explain the color of complexes
B) Fails to predict magnetic behavior
C) Does not distinguish between high-spin and low-spin states
D) Accurately determines crystal field stabilization energy (CFSE)

3. Outer orbital complexes are usually formed when the ligands are:

A) Weak field ligands
B) Strong field ligands
C) Neutral ligands
D) Chelating ligands

4. Which transition metal complex is most likely to form an inner orbital octahedral complex?

A) $[FeF6]^{3-}$
B) $[Co(NH_3)_6]^{3+}$
C) $[NiCl_4]^{2-}$
D) $(NH_3)_4]^{2+}$

5. Which oxidation state of chromium (Cr) is most commonly involved in octahedral coordination?

A) +1
B) +2
C) +3
D) +6

6. In square planar complexes (coordination number 4), which type of isomerism is commonly observed?

A) Optical isomerism
B) Cis-trans isomerism
C) Linkage isomerism
D) Hydrate isomerism

7. Which metal complex is likely to exhibit Jahn-Teller distortion?

A) $[Ni(CN)_4]^{2-}$
B) $[Fe(CN)_6]^{4-}$
C) $[Cu(H_2O)_6]^{2+}$
D) $[Co(NH_3)_6]^{3+}$

8. What is the coordination number of a metal ion in an octahedral complex?

A) 2
B) 4
C) 6
D) 8

9. Which type of isomerism occurs when a ligand can bind to the metal through two different atoms?

A) Ionization isomerism
B) Linkage isomerism
C) Coordination isomerism
D) Geometrical isomerism

10. Which of the following statements about optical isomerism in octahedral complexes is true?

A) It is observed only in tetrahedral complexes
B) It occurs when a complex has a plane of symmetry
C) It is common in octahedral complexes with chelating ligands like ethylenediamine
D) It is not possible in metal complexes

B.Short Type Questions

1. What type of orbitals are involved in sp^3d^2 hybridisation?
2. Are outer orbital octahedral complexes usually high-spin or low-spin?

3. Give an example of a complex that exhibits sp^3d^2 hybridisation.
4. Which orbitals participate in d^2sp^3 hybridisation?
5. How does ligand strength affect d^2sp^3 hybridisation?
6. Provide an example of an inner orbital octahedral complex.
7. Why does VBT fail to explain the color of coordination complexes?
8. How does VBT struggle with predicting magnetic properties?
9. What is one major drawback of VBT in explaining high-spin and low-spin complexes?
10. What type of d-orbitals are used in outer orbital complexes?
11. Why are outer orbital complexes usually paramagnetic?
12. Give an example of a metal complex that forms an outer orbital complex.
13. Which orbitals are used for hybridisation in inner orbital complexes?
14. Why are inner orbital complexes often diamagnetic?
15. Provide an example of an inner orbital complex with a strong field ligand.
16. What is the common coordination number for Cr(III) complexes?
17. Which oxidation states of Fe commonly form octahedral complexes?
18. What type of geometry does $[NiCl_4]^{2-}$ adopt?
19. Why do Cu(II) complexes often exhibit Jahn-Teller distortion?
20. Give an example of a square planar Ni(II) complex.
21. What is the difference between structural isomerism and stereoisomerism?
22. Name two types of isomerism observed in coordination complexes.
23. What kind of isomerism occurs due to the different spatial arrangements of ligands?
24. Define linkage isomerism with an example.
25. What is coordination isomerism? Provide an example.
26. How does ionization isomerism occur in coordination compounds?

27. What is cis-trans isomerism, and in which type of complexes is it commonly found?
28. How does optical isomerism arise in octahedral complexes?
29. Provide an example of a tetrahedral complex that exhibits optical isomerism.

C.Assay Type Questions

1. Explain sp^3d^2 hybridisation in outer orbital octahedral complexes with an example. Discuss the electronic configuration and magnetic properties of such complexes.
2. Describe d^2sp^3 hybridisation in inner orbital octahedral complexes with an example. How does ligand strength influence the formation of inner orbital complexes?
3. Discuss the limitations of Valence Bond Theory (VBT). Why is VBT unable to explain color, magnetism, and stability of complexes accurately?
4. Differentiate between outer orbital and inner orbital complexes. How does ligand field strength affect the spin state and hybridisation of these complexes?
5. Describe the coordination behavior of Cr, Fe, Co, Ni, and Cu in complexes with coordination numbers 4 and 6. Provide examples and discuss the effect of ligand field strength on their geometry and magnetic properties.
6. What is isomerism in coordination complexes? Explain the different types of isomerism observed in such complexes with suitable examples.
7. Explain structural isomerism in coordination complexes. Discuss linkage, ionization, coordination, and hydrate isomerism with examples.
8. Describe stereoisomerism in coordination complexes. How do geometrical (cis-trans) and optical isomerism arise in complexes with coordination numbers 4 and 6?
9. Compare and contrast high-spin and low-spin complexes. How does crystal field splitting energy influence their formation? Provide examples.

10. Discuss the role of ligand field strength in determining the geometry and hybridisation of coordination complexes. How does the spectrochemical series help in predicting the nature of complexes?

13.11 References

1. **Text Book of Coordination Chemistry**
   R. K. Sharma, this textbook offers a comprehensive overview of coordination chemistry, including discussions on valence bond theory, hybridization, and isomerism in coordination compounds. ISBN-13: 978-8183562232.
2. Introduction to Coordination Chemistry
   Geoffrey A. Lawrance, this book introduces the fundamental concepts of coordination chemistry, including bonding theories, structure, and isomerism of coordination compounds. ISBN-13: 978-0470018668.
3. **Valence Bond Theory (Theoretical and Computational Chemistry Series)**
   David Cooper, this volume presents a comprehensive overview of valence bond theory, discussing its theoretical foundations and applications in understanding the bonding in coordination compounds. ISBN-13: 978-0444508898.

Unit - 14 ❑ Radioactivity

Structure

14.0 Objectives

- Understand the factors affecting the stability of an atomic nucleus.
- Explain why some nuclei are stable while others undergo radioactive decay.
- Define the neutron-to-proton (n/p) ratio and its significance in nuclear stability.
- Identify stable and unstable nuclei based on their n/p ratios.
- Explain the different types of radioactive decay: alpha, beta, gamma, and others.
- Describe the changes occurring in the nucleus during each type of decay.
- Define nuclear fission and describe its mechanism.
- Explain the chain reaction process and its applications in nuclear power plants.
- Discuss the advantages and risks of fission energy.

14.1 Introduction

The study of the atomic nucleus and its properties plays a crucial role in understanding nuclear physics and radioactivity. This section explores key concepts such as nuclear stability, the neutron-to-proton (n/p) ratio, and the various modes of radioactive decay that govern the transformation of unstable nuclei. Additionally, the principles of nuclear reactions—including fusion, fission, and spallation—are examined, along with their applications in energy production and scientific research. Fundamental concepts such as mass defect, packing fraction, and binding energy help explain the forces that hold the nucleus together. The significance of magic numbers in nuclear stability is also highlighted. By the end of this section, learners will have a strong foundation in nuclear physics, enabling them to analyse nuclear processes and their practical implications.

14.2 Atomic Nucleus

The atomic nucleus is the dense central core of an atom, composed of protons and neutrons, collectively known as nucleons. The nucleus determines the identity and many properties of an element. The forces that bind the nucleus together are governed by the strong nuclear force, which overcomes electrostatic repulsion between protons to maintain stability.

Structure of the Atomic Nucleus

1. **Protons** (p^+): Positively charged particles that determine the atomic number (Z) of an element.
2. **Neutrons** (n): Electrically neutral particles that contribute to the mass of the nucleus but do not affect its charge.
3. **Nuclear Force**: A strong attractive force binds protons and neutrons together, overcoming the electrostatic repulsion between protons.

Properties of the Nucleus

- **Size**: The nuclear radius is approximately $r = r_0 A^{1/3}$, where $r_0 \approx 1.2$ fm (femtometers) and A is the mass number (total nucleons).
- **Mass**: Nearly the entire mass of an atom is concentrated in the nucleus.
- **Charge**: Equal to $+Ze$, where e is the elementary charge.

14.3 Artificial Radioactivity

Artificial Radioactivity, also known as induced radioactivity, refers to the phenomenon where a normally stable element is made radioactive by bombarding it with nuclear particles, such as neutrons, protons, or alpha particles. This process was first discovered by Irène Joliot-Curie and Frédéric Joliot-Curie in 1934, when they bombarded aluminum with alpha particles, producing radioactive phosphorus.

Key Aspects of Artificial Radioactivity:

1. Process: A stable nucleus absorbs a high-energy particle, leading to the formation of an unstable (radioactive) isotope.
2. Decay: The newly formed radioactive isotope undergoes beta decay, gamma decay, or other nuclear transformations to become stable.
3. Commonly Used Particles:

  - Neutrons (e.g., in nuclear reactors)
  - Protons (e.g., in cyclotrons)
  - Alpha particles (e.g., from radioactive sources)
  - Gamma rays (sometimes used to induce nuclear reactions)

Applications of Artificial Radioactivity:

- Medicine: Production of radioisotopes like Cobalt-60 (used in cancer therapy) and Technetium-99m (used in diagnostic imaging).
- Industry: Non-destructive testing (radiography), thickness measurement, and material analysis.
- Agriculture: Development of better crop varieties using radiation-induced mutations.
- Nuclear Power: Fission reactions in nuclear reactors produce artificial radioactivity as by-products.

Examples of Artificially Created Radioactive Isotopes:

Phosphorus-32 (used in medical treatments)
Cobalt-60 (used in sterilization and radiation therapy)
Carbon-14 (used in radiocarbon dating)

Some important equations demonstrating artificial radioactivity:

1. Discovery by Joliot-Curie: Artificial Production of Phosphorus-30

When aluminum-27 (^{27}Al) is bombarded with alpha particles (^{4}He), it produces phosphorus-30 (^{30}P), which is radioactive and undergoes beta decay.

$$^{27}_{13}Al +^{4}_{2} He \rightarrow^{30}_{15} P +^{1}_{0} n$$

The phosphorus-30 isotope then undergoes **beta decay**:

$$^{30}_{15}P \rightarrow^{30}_{14} Si + \beta^{+}$$

2. Neutron-Induced Artificial Radioactivity: Cobalt-60 Production

Cobalt-60 is an important artificial radioisotope used in cancer treatment. It is produced by neutron bombardment of cobalt-59:

$$^{59}_{27}Co +^{1}_{0} n \rightarrow^{60}_{27} Co$$

Cobalt-60 undergoes **beta decay**, emitting gamma radiation:

$$^{60}_{27}Co \rightarrow^{60}_{28} Ni + \beta^{-} + \gamma$$

3. Proton Bombardment: Production of Fluorine-18

Fluorine-18 is used in **PET (Positron Emission Tomography) scans**. It is created by bombarding oxygen-18 with protons:

$$^{18}_{8}O +^{1}_{1} p \rightarrow^{18}_{9} F + \gamma$$

Fluorine-18 undergoes **positron emission**:

$$^{18}_{9}F \rightarrow^{18}_{8} O + \beta^{+}$$

14.4Nuclear Stability & n/p Ratio

Nuclear Stability

Nuclear stability refers to the ability of a nucleus to remain intact without undergoing radioactive decay. It is influenced by factors such as the neutron-to-proton (n/p) ratio, nuclear forces, and shell effects. Stable nuclei do not spontaneously emit radiation, while unstable ones decay to achieve a more stable configuration.

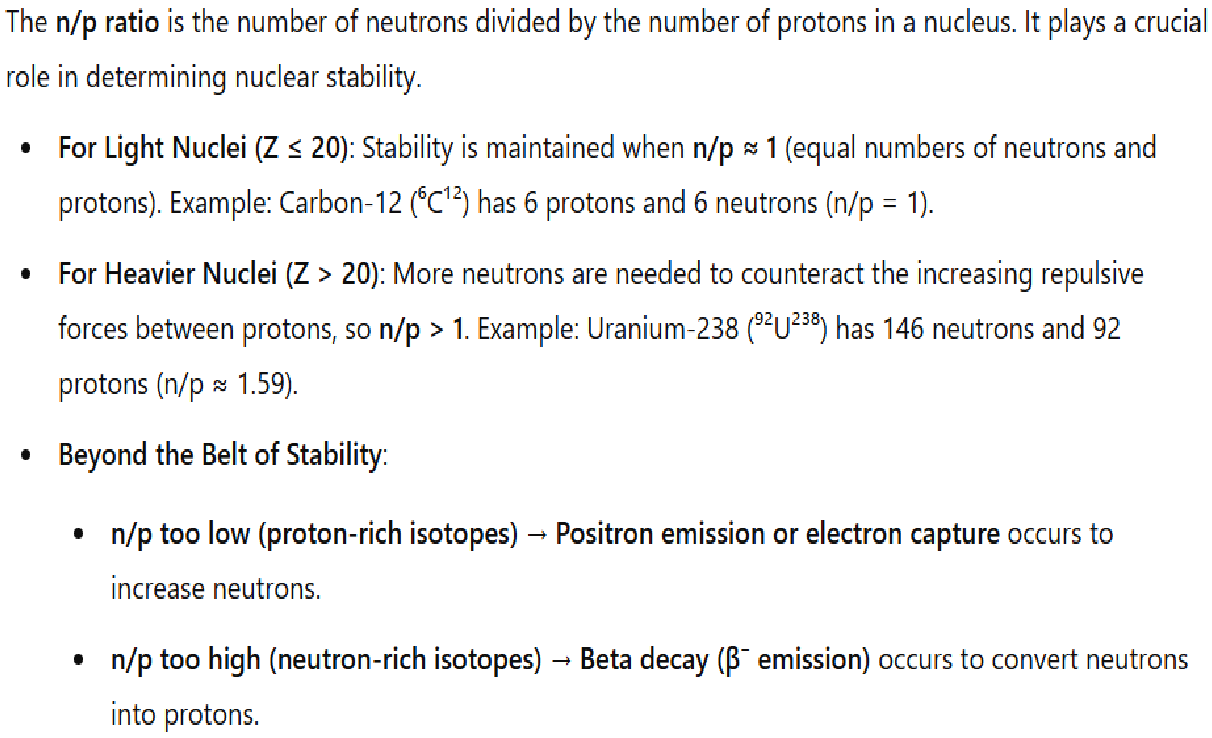
Key factors affecting nuclear stability:

Binding Energy: Higher binding energy per nucleon means greater stability.

Even-Odd Rule: Nuclei with even numbers of protons and neutrons tend to be more stable.

Magic Numbers: Nuclei with proton or neutron numbers equal to 2, 8, 20, 28, 50, 82, and 126 exhibit extra stability.

Neutron-to-Proton (n/p) Ratio



The **n/p ratio** is the number of neutrons divided by the number of protons in a nucleus. It plays a crucial role in determining nuclear stability.

- **For Light Nuclei ($Z \leq 20$)**: Stability is maintained when **$n/p \approx 1$** (equal numbers of neutrons and protons). Example: Carbon-12 ($^{6}\text{C}^{12}$) has 6 protons and 6 neutrons ($n/p = 1$).
- **For Heavier Nuclei ($Z > 20$)**: More neutrons are needed to counteract the increasing repulsive forces between protons, so **$n/p > 1$**. Example: Uranium-238 ($^{92}\text{U}^{238}$) has 146 neutrons and 92 protons ($n/p \approx 1.59$).
- **Beyond the Belt of Stability**:
    - **n/p too low (proton-rich isotopes) → Positron emission or electron capture** occurs to increase neutrons.
    - **n/p too high (neutron-rich isotopes) → Beta decay (β^- emission)** occurs to convert neutrons into protons.

14.5 Different Modes of Decay

Several decay mechanisms help unstable nuclei attain stability:

Alpha (α) Decay: The nucleus emits an alpha particle (two protons and two neutrons), reducing both atomic and mass numbers.

Beta (β) Decay: A neutron converts into a proton (β^- decay) or a proton into a neutron (β^+ decay), accompanied by the emission of electrons or positrons and neutrinos.

Gamma (γ) Decay: Excited nuclei release excess energy in the form of high-energy photons without changing their composition.

Electron Capture: The nucleus captures an orbital electron, converting a proton into a neutron and emitting a neutrino.

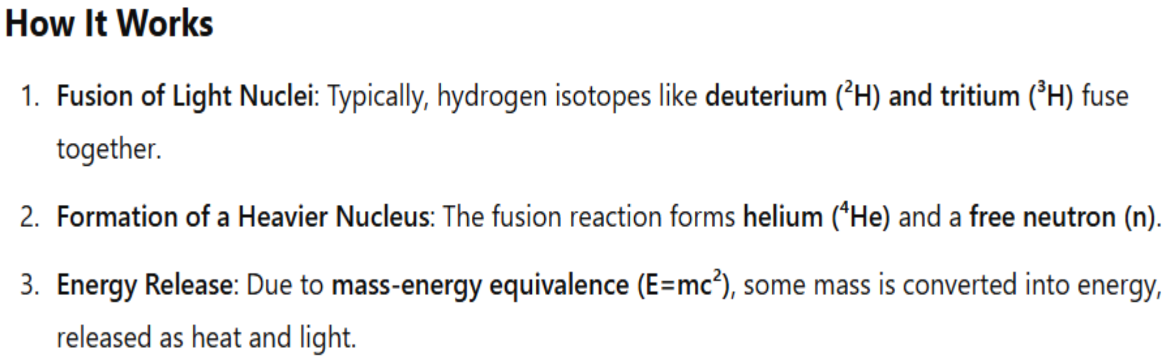
Spontaneous Fission: Some heavy nuclei split into smaller fragments, emitting neutrons and energy.

14.6 Nuclear Reactions

Nuclear reactions involve changes in the composition of atomic nuclei. They can be categorized into several types:

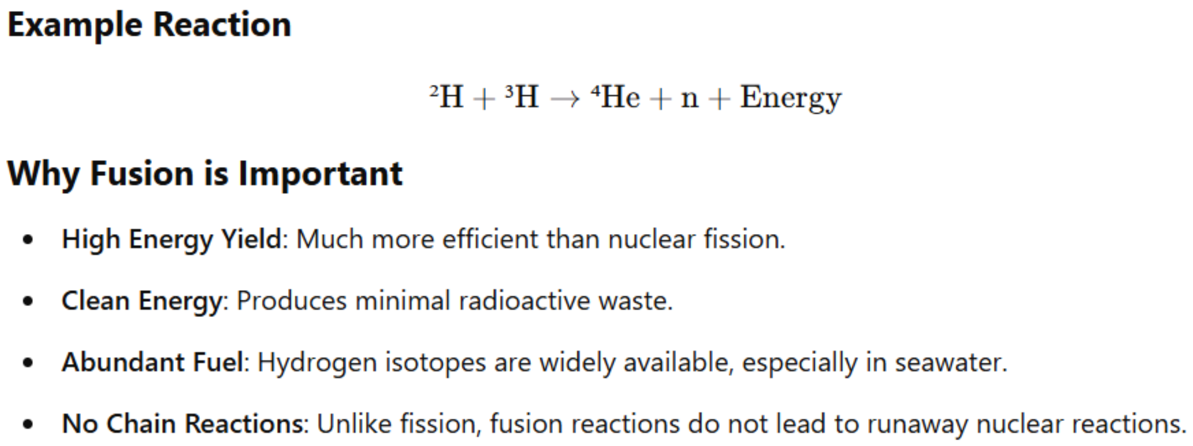
14.6.1 Fusion

Nuclear fusion is a process where two light atomic nuclei combine to form a heavier nucleus, releasing a tremendous amount of energy. This is the same reaction that powers the Sun and other stars.



How It Works

1. **Fusion of Light Nuclei**: Typically, hydrogen isotopes like **deuterium (^{2}H) and tritium (^{3}H)** fuse together.
2. **Formation of a Heavier Nucleus**: The fusion reaction forms **helium (^{4}He)** and a **free neutron (n)**.
3. **Energy Release**: Due to **mass-energy equivalence ($E=mc^2$)**, some mass is converted into energy, released as heat and light.



Example Reaction

$$^2\mathrm{H} + {}^3\mathrm{H} \rightarrow {}^4\mathrm{He} + \mathrm{n} + \mathrm{Energy}$$

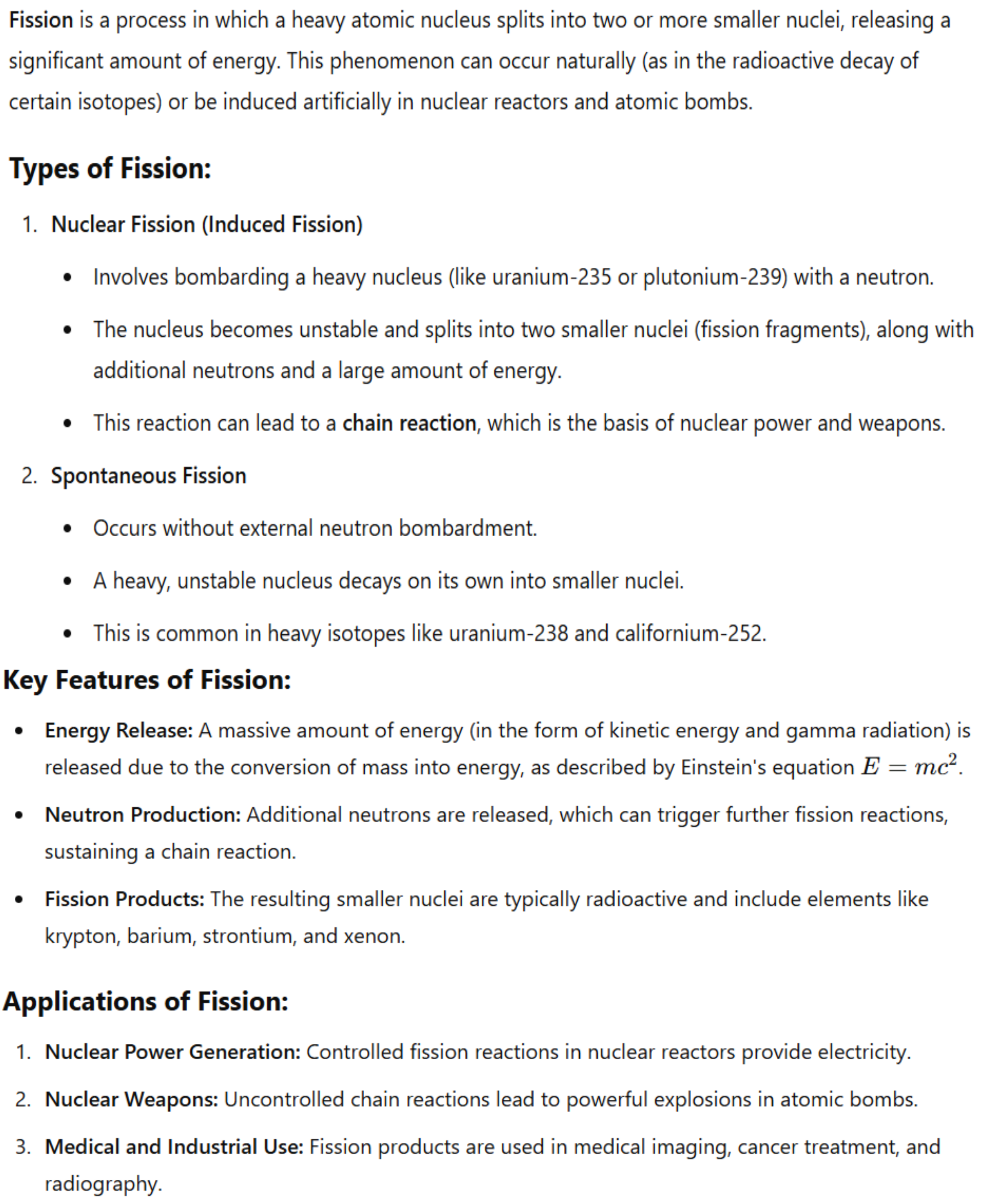
Why Fusion is Important

- **High Energy Yield**: Much more efficient than nuclear fission.
- **Clean Energy**: Produces minimal radioactive waste.
- **Abundant Fuel**: Hydrogen isotopes are widely available, especially in seawater.
- **No Chain Reactions**: Unlike fission, fusion reactions do not lead to runaway nuclear reactions.

Current Research and Future Prospects

Projects like ITER (International Thermonuclear Experimental Reactor) and NIF (National Ignition Facility) are leading the way toward commercial fusion energy, with hopes of a sustainable fusion power plant within the next few decades.

14.6.2 Fission



Fission is a process in which a heavy atomic nucleus splits into two or more smaller nuclei, releasing a significant amount of energy. This phenomenon can occur naturally (as in the radioactive decay of certain isotopes) or be induced artificially in nuclear reactors and atomic bombs.

Types of Fission:

1. **Nuclear Fission (Induced Fission)**
   - Involves bombarding a heavy nucleus (like uranium-235 or plutonium-239) with a neutron.
   - The nucleus becomes unstable and splits into two smaller nuclei (fission fragments), along with additional neutrons and a large amount of energy.
   - This reaction can lead to a **chain reaction**, which is the basis of nuclear power and weapons.
2. **Spontaneous Fission**
   - Occurs without external neutron bombardment.
   - A heavy, unstable nucleus decays on its own into smaller nuclei.
   - This is common in heavy isotopes like uranium-238 and californium-252.

Key Features of Fission:

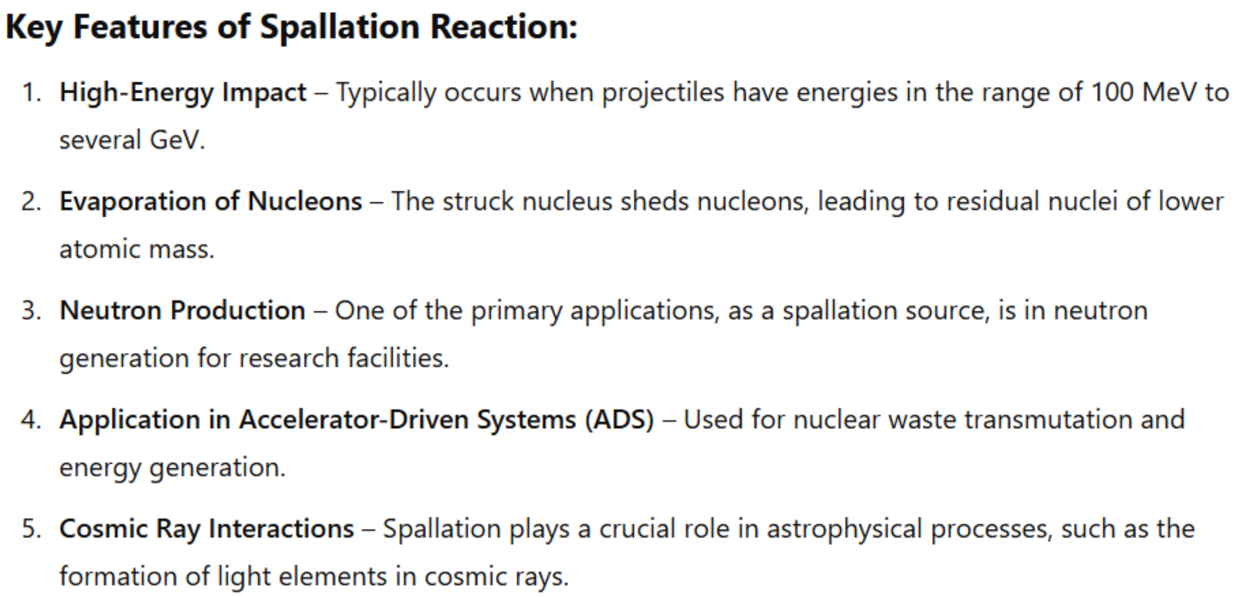
- **Energy Release:** A massive amount of energy (in the form of kinetic energy and gamma radiation) is released due to the conversion of mass into energy, as described by Einstein's equation $E = mc^2$.
- **Neutron Production:** Additional neutrons are released, which can trigger further fission reactions, sustaining a chain reaction.
- **Fission Products:** The resulting smaller nuclei are typically radioactive and include elements like krypton, barium, strontium, and xenon.

Applications of Fission:

1. **Nuclear Power Generation:** Controlled fission reactions in nuclear reactors provide electricity.
2. **Nuclear Weapons:** Uncontrolled chain reactions lead to powerful explosions in atomic bombs.
3. **Medical and Industrial Use:** Fission products are used in medical imaging, cancer treatment, and radiography.

14.6.3 Spallation Reaction

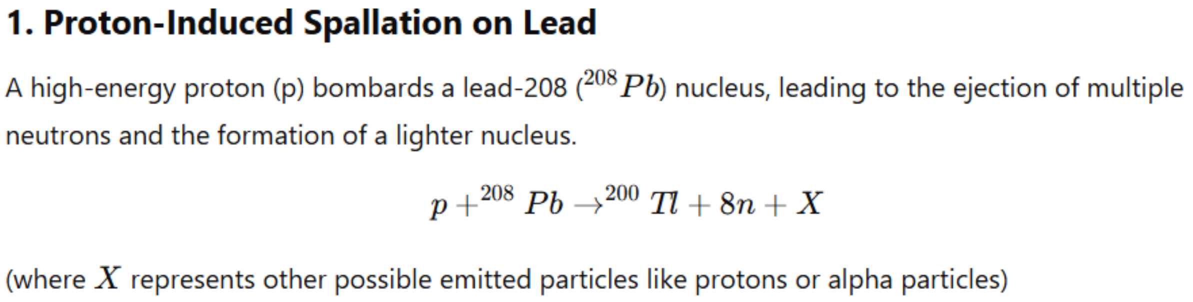
A **spallation reaction** is a high-energy nuclear reaction in which a heavy nucleus (such as lead, tungsten, or uranium) is bombarded by high-energy particles, typically protons, neutrons, or light ions (like deuterons or alpha particles). This collision results in the ejection of multiple nucleons (protons and neutrons) and sometimes lighter fragments from the target nucleus. The process is distinct from fission because it does not involve the splitting of the nucleus into two major fragments but rather the emission of many smaller particles.



Key Features of Spallation Reaction:

1. **High-Energy Impact** – Typically occurs when projectiles have energies in the range of 100 MeV to several GeV.
2. **Evaporation of Nucleons** – The struck nucleus sheds nucleons, leading to residual nuclei of lower atomic mass.
3. **Neutron Production** – One of the primary applications, as a spallation source, is in neutron generation for research facilities.
4. **Application in Accelerator-Driven Systems (ADS)** – Used for nuclear waste transmutation and energy generation.
5. **Cosmic Ray Interactions** – Spallation plays a crucial role in astrophysical processes, such as the formation of light elements in cosmic rays.

Some examples of **spallation reactions** along with their respective nuclear equations:



1. Proton-Induced Spallation on Lead

A high-energy proton (p) bombards a lead-208 (^{208}Pb) nucleus, leading to the ejection of multiple neutrons and the formation of a lighter nucleus.

$$p + ^{208}Pb \rightarrow ^{200}Tl + 8n + X$$

(where X represents other possible emitted particles like protons or alpha particles)

2. Neutron Spallation on Tungsten

High-energy neutrons interact with tungsten-184 (^{184}W), resulting in neutron ejection:

$$n +^{184} W \rightarrow^{175} Lu + 9n + X$$

This type of reaction is commonly used in **spallation neutron sources** for scientific research.

3. Cosmic Ray Spallation (Astrophysical Example)

Cosmic-ray protons striking interstellar carbon-12 (^{12}C) can lead to spallation reactions that form lighter elements such as lithium, beryllium, and boron:

$$p +^{12} C \rightarrow^{10} B + 2p + n$$

This process explains the abundance of light elements in cosmic rays.

4. Accelerator-Driven Thorium Spallation

A high-energy proton interacts with thorium-232 (^{232}Th):

$$p +^{232} Th \rightarrow^{207} Pb + 10n + X$$

This type of reaction is explored in **Accelerator-Driven Systems (ADS)** for nuclear waste transmutation.

14.7 Mass Defect

The mass of a nucleus is always less than the sum of its constituent protons and neutrons. This difference, called mass defect, corresponds to the binding energy of the nucleus according to Einstein's equation: where is the binding energy, is the mass defect, and is the speed of light**.**

The **mass defect** (ΔM) is calculated as:

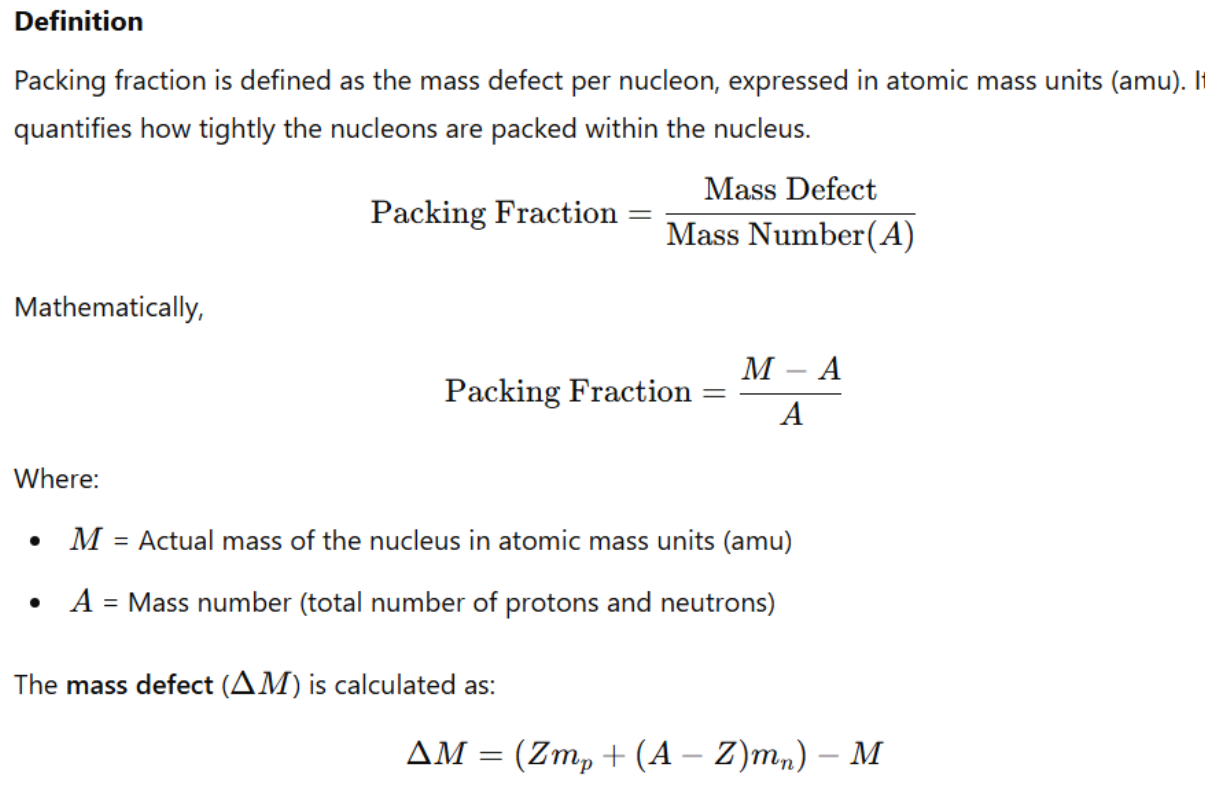
$$\Delta M = (Zm_p + (A - Z)m_n) - M$$

Where:

- Z = Number of protons
- m_p = Mass of a proton (1.007825 amu)
- m_n = Mass of a neutron (1.008665 amu)
- M = Actual mass of the nucleus

14.8 Packing Fraction

In nuclear chemistry, the packing fraction refers to the difference between the actual mass of a nucleus and the sum of the masses of its individual nucleons (protons and neutrons). It provides insights into nuclear stability and binding energy.



Definition

Packing fraction is defined as the mass defect per nucleon, expressed in atomic mass units (amu). I
quantifies how tightly the nucleons are packed within the nucleus.

$$\text{Packing Fraction} = \frac{\text{Mass Defect}}{\text{Mass Number}(A)}$$

Mathematically,

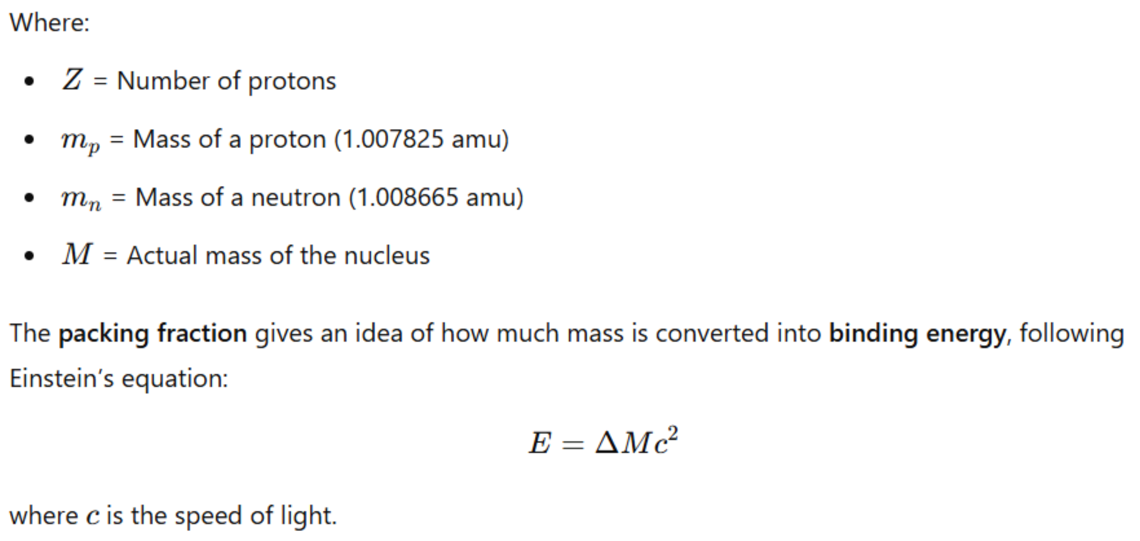
$$\text{Packing Fraction} = \frac{M - A}{A}$$

Where:

- M = Actual mass of the nucleus in atomic mass units (amu)
- A = Mass number (total number of protons and neutrons)

The **mass defect** (ΔM) is calculated as:

$$\Delta M = (Zm_p + (A - Z)m_n) - M$$



Where:

- Z = Number of protons
- m_p = Mass of a proton (1.007825 amu)
- m_n = Mass of a neutron (1.008665 amu)
- M = Actual mass of the nucleus

The **packing fraction** gives an idea of how much mass is converted into **binding energy**, following Einstein's equation:

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

where c is the speed of light.

Significance of Packing Fraction in Nuclear Stability

1. Lower Packing Fraction → Higher Stability

   - A lower or negative packing fraction means that nucleons are strongly bound, indicating a stable nucleus.
   - Example: Iron-56 (^{56}Fe) has a very small packing fraction, making it one of the most stable nuclei.
2. Higher Packing Fraction → Less Stability
   - A higher or positive packing fraction means the nucleus is less tightly bound and more unstable.
   - Example: Lighter elements (like hydrogen) and very heavy elements (like uranium) have higher packing fractions, making them less stable and more prone to nuclear reactions.
3. Variation in Packing Fraction and Nuclear Fission/Fusion
   - For light nuclei, fusion occurs to achieve lower packing fraction.
   - For heavy nuclei, fission occurs to break into smaller nuclei with lower packing fractions.
   - The binding energy curve shows that iron and nickel are the most stable elements.

14.5Nuclear Binding Energy

The nuclear binding energy (NBE) of a nucleus is defined as the energy needed to disassemble a nucleus into its constituent protons and neutrons, overcoming the strong nuclear force that holds them together. It is also equivalent to the energy released during the formation of the nucleus from free nucleons.

This energy arises due to the mass defect, which is the difference between the total mass of the nucleons when free and the actual mass of the nucleus.Iron-56 and nickel-62 are among the most stable nuclei due to their high binding energy per nucleon.

Mass Defect and Energy Calculation:

a) Mass Defect (Δm)

The mass defect is given by:

$$\Delta m = Zm_p + Nm_n - m_{\text{nucleus}}$$

where:

- Z = Number of protons
- N = Number of neutrons
- m_p = Mass of a proton
- m_n = Mass of a neutron
- m_{nucleus} = Observed mass of the nucleus

Since the nucleus weighs **less** than the sum of its free nucleons, this missing mass is converted into binding energy according to Einstein's famous equation:

$$E = \Delta mc^2$$

where:

- E = Nuclear binding energy
- c = Speed of light (3.0×10^8 m/s)
- Δm = Mass defect (in kg or atomic mass units, amu)

Using atomic mass units (1 amu = 931.5 MeV/c^2), the binding energy in MeV is:

$$E = \Delta m \times 931.5\ \text{MeV}$$

Binding Energy per Nucleon

The **binding energy per nucleon (BE/A)** is obtained by dividing the total binding energy by the number of nucleons (A):

$$BE/A = \frac{E}{A}$$

This value helps in understanding the stability of a nucleus:

- **Higher BE/A → More stable nucleus** (e.g., Iron-56)
- **Lower BE/A → Less stable nucleus** (e.g., Uranium-238)

Applications of Nuclear Binding Energy

1. Nuclear Power Plants: Energy from fission is used to generate electricity.
2. Nuclear weapons: Uncontrolled fission and fusion release massive amounts of energy.
3. Astrophysics: Stellar nucleosynthesis in stars relies on fusion reactions governed by nuclear binding energy.
4. Medical Applications: Radioisotopes produced from nuclear reactions are used in cancer treatment and diagnostics.

14.6Magic Numbers

In nuclear physics, magic numbers are specific numbers of protons or neutrons in an atomic nucleus that make it exceptionally stable. These numbers correspond to fully filled energy levels (or shells) within the nucleus, similar to how electrons in an atom follow the shell model in quantum mechanics.

The nuclear magic numbers are:2, 8, 20, 28, 50, 82, and 126.

These numbers indicate that nuclei with these proton or neutron counts exhibit higher binding energy, greater stability, and lower natural radioactivity compared to nearby elements.

The Shell Model and Magic Numbers

The concept of nuclear magic numbers is explained by the nuclear shell model, proposed by Maria Goeppert Mayer and J. Hans D. Jensen in 1949. It suggests that:Protons and neutrons in a nucleus occupy discrete energy levels, similar to electrons in atomic orbitals.

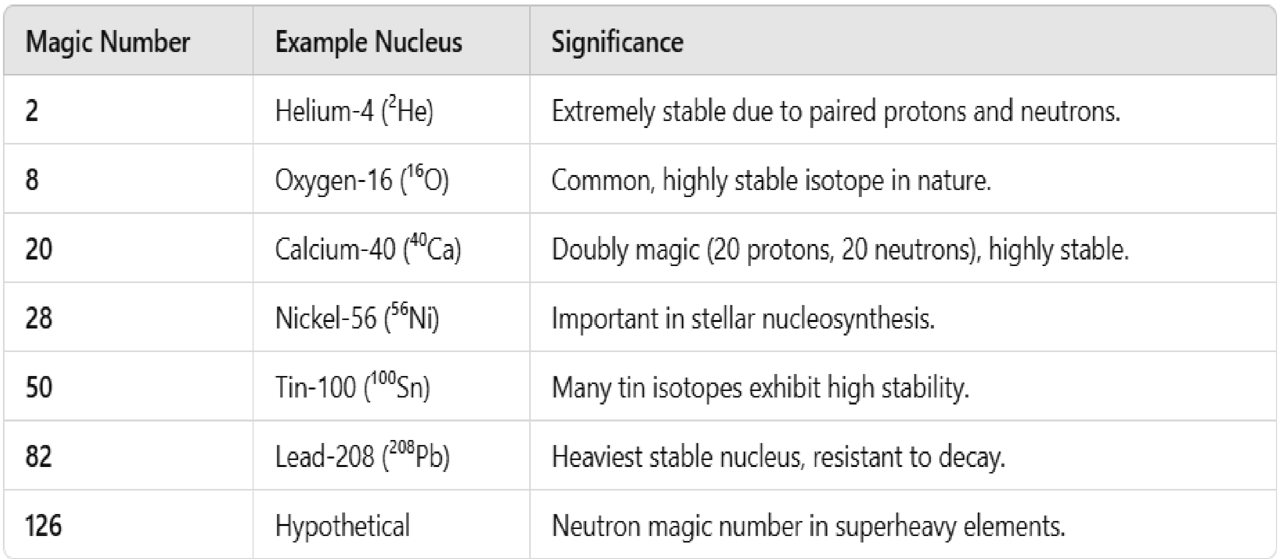
When a shell is completely filled, the nucleus becomes more stable.The observed magic numbers arise due to specific gaps in nuclear energy levels, where adding another proton or neutron requires significantly more energy.

Energy Level Splitting and Spin-Orbit Coupling

The splitting of nuclear energy levels is influenced by spin-orbit coupling, where the interaction between a nucleon's spin and its motion within the nucleus creates stability at specific numbers.

This leads to "magic" configurations where nuclei have completely filled shells and are less likely to undergo radioactive decay.

List of Nuclear Magic Numbers and Their Significance



Magic Number	Example Nucleus	Significance
2	Helium-4 (^{2}He)	Extremely stable due to paired protons and neutrons.
8	Oxygen-16 (^{16}O)	Common, highly stable isotope in nature.
20	Calcium-40 (^{40}Ca)	Doubly magic (20 protons, 20 neutrons), highly stable.
28	Nickel-56 (^{56}Ni)	Important in stellar nucleosynthesis.
50	Tin-100 (^{100}Sn)	Many tin isotopes exhibit high stability.
82	Lead-208 (^{208}Pb)	Heaviest stable nucleus, resistant to decay.
126	Hypothetical	Neutron magic number in superheavy elements.

Doubly Magic Nuclei:

A doubly magic nucleus contains both a magic number of protons and neutrons, making it extremely stable. Examples:

- **Helium-4 (^{2}He)** (2 protons, 2 neutrons)
- **Oxygen-16 (^{16}O)** (8 protons, 8 neutrons)
- **Calcium-40 (^{4} □Ca)**(20 protons, 20 neutrons)

- **Lead-208 (^{2}□□Pb)** (82 protons, 126 neutrons)

These nuclei exhibit very low radioactive decay rates and are commonly found in nature.

Experimental Confirmation of Magic Numbers

Magic numbers were discovered through:

1. Binding Energy Studies – Magic-number nuclei have higher binding energy, making them more stable.
2. Nuclear Reaction Cross-Sections – Magic-number nuclei show lower cross-sections, meaning they are less likely to undergo nuclear reactions.
3. Alpha Decay Chains – Nuclei with magic numbers show longer half-lives, as seen in lead-208 (^{2}□□Pb).
4. Mass Spectrometry – Helps determine shell closures based on neutron-proton ratios.

Beyond Traditional Magic Numbers

With advancements in **radioactive ion beam experiments**, physicists have observed **island of stability** regions where additional magic numbers may exist, especially for neutron-rich or proton-deficient isotopes.

- **Possible new magic numbers:N = 14, 16, 32, 34, 54, 70, etc.**
- **Exotic nuclei like Nickel-78 (^{78}Ni) and Calcium-54 (^{54}Ca)** exhibit characteristics of new magic numbers.

Applications of Magic Numbers

1. **Nuclear Reactor Design** – Understanding magic numbers helps in fuel selection for stable and efficient nuclear fission reactions.
2. **Nuclear Medicine** – Magic-number isotopes like Technetium-99m (^{99}mTc) are used in medical imaging.
3. **Astrophysics & Stellar Evolution** – Elements with magic numbers play key roles in supernova nucleosynthesis and neutron star composition.

4. **Nuclear Waste Management** – Identifying stable isotopes helps in designing long-lived nuclear storage solutions.
5. **Superheavy Element Research** – Searching for new elements beyond uranium ($Z > 92$) involves finding stable nuclei using new magic numbers.

14.7Summary

- Artificial radioactivity refers to the process by which stable nuclei are transformed into radioactive isotopes by bombarding them with particles such as neutrons, protons, or alpha particles. This phenomenon was first discovered by Irène and Frédéric Joliot-Curie. It is widely used in medical applications, industry, and scientific research.
- The stability of a nucleus is determined by the neutron-to-proton (n/p) ratio. Lighter elements have a nearly equal number of neutrons and protons, while heavier elements require more neutrons for stability. If the n/p ratio deviates significantly from the ideal range, the nucleus becomes unstable, leading to radioactive decay.
- Unstable nuclei undergo decay to achieve stability.
- Nuclear reactions involve changes in the nucleus due to collisions or decays, leading to the formation of new elements and energy release.
- Fusion: The process in which two light nuclei combine to form a heavier nucleus, releasing a tremendous amount of energy. This powers stars, including the Sun.
- Fission: The splitting of a heavy nucleus (e.g., Uranium-235) into smaller nuclei, accompanied by the release of energy and neutrons, which can induce a chain reaction. Used in nuclear reactors and weapons.
- Spallation Reaction: High-energy particles (like cosmic rays or accelerated protons) strike a heavy nucleus, causing it to eject multiple smaller fragments. Used in particle physics and isotope production.

- Mass Defect:The mass defect is the difference between the total mass of a nucleus and the sum of the individual masses of its protons and neutrons.
- Packing fraction is a measure of nuclear stability, defined as the difference between the actual nuclear mass and the mass number, divided by the mass number. A low or negative packing fraction indicates higher binding energy and stability.
- Nuclear binding energy is the energy required to separate a nucleus into its individual nucleons. It determines the stability of the nucleus—the higher the binding energy per nucleon, the more stable the nucleus. Iron-56 has the highest binding energy per nucleon, making it the most stable element.
- Magic numbers are specific numbers of protons or neutrons (2, 8, 20, 28, 50, 82, 126) that result in exceptionally stable nuclei. These numbers correspond to complete nuclear shells, similar to electron shells in atoms. The study of atomic nuclei and nuclear reactions provides essential insights into the forces governing matter at a fundamental level. Applications of nuclear physics range from energy generation to medical diagnostics and treatment. Understanding nuclear stability, decay processes, and energy release mechanisms continues to drive advancements in science and technology.

14.12 Sample Questions

A. Multiple Choice Type Questions

1. What is the primary composition of an atomic nucleus?
   a) Electrons and neutrons
   b) Protons and electrons
   c) Protons and neutrons
   d) Neutrons and positrons

2. Which force holds the nucleons together inside the nucleus?
   a) Gravitational force

b) Electromagnetic force

c) Weak nuclear force

d) Strong nuclear force

3. Artificial radioactivity was first discovered by:

a) Marie Curie

b) Henri Becquerel

c) Irene Joliot-Curie and Frédéric Joliot-Curie

d) Ernest Rutherford

4. Which of the following isotopes is commonly used in artificial radioactivity?

a) Carbon-12

b) Uranium-238

c) Phosphorus-32

d) Oxygen-16

5. The stability of a nucleus primarily depends on its:

a) Electron-to-proton ratio

b) Neutron-to-proton (n/p) ratio

c) Total number of electrons

d) Atomic volume

6. For stable light nuclei ($Z < 20$), the ideal n/p ratio is approximately:

a) 1:2

b) 2:1

c) 1:1

d) 3:1

7. In beta decay, a neutron is converted into:

a) A proton and an electron

b) An alpha particle

c) A positron

d) A neutron remains unchanged

8. Alpha decay results in:
   a) An increase in atomic number by 1
   b) A decrease in atomic number by 2
   c) No change in atomic number
   d) An increase in mass number
9. Which of the following is an example of a nuclear fusion reaction?
   a) Splitting of uranium-235
   b) The combination of deuterium and tritium
   c) Radioactive decay of carbon-14
   d) Fission of plutonium-239
10. In nuclear fission, a heavy nucleus splits into:
    a) A single larger nucleus
    b) Two or more smaller nuclei
    c) A neutron and a photon
    d) An electron and a positron

11. Spallation reactions involve:
    a) The combination of light nuclei
    b) The ejection of multiple neutrons and protons from a heavy nucleus
    c) The decay of a nucleus into smaller fragments
    d) The emission of alpha particles

12. The mass defect of a nucleus is the difference between:
    a) The sum of individual nucleon masses and actual nucleus mass
    b) The neutron mass and proton mass
    c) The nucleus mass and electron mass
    d) The total nuclear charge and mass number

13. Packing fraction is defined as:
    a) The ratio of nuclear mass to atomic mass
    b) The binding energy per nucleon
    c) The difference between atomic mass and mass number per nucleon
    d) The ratio of binding energy to atomic number

14. The nuclear binding energy is responsible for:

    a) Holding protons together inside the nucleus

    b) Keeping electrons in orbit around the nucleus

    c) The radioactivity of an element

    d) Increasing the atomic mass

15. Magic numbers refer to:

    a) The total number of electrons in a stable atom

    b) The specific numbers of protons or neutrons that lead to extra nuclear stability

    c) The neutron-to-proton ratio for stable elements

    d) The energy levels in an atom

16. Which of the following is NOT a magic number?

    a) 2

    b) 8

    c) 15

    d) 126

B. Short Type Questions

1. What is the mass defect of a nucleus?
2. Define artificial radioactivity with an example.
3. What is the neutron-to-proton (n/p) ratio for stable nuclei?
4. Name two elements commonly used in nuclear fission reactions.
5. What is the difference between nuclear fusion and nuclear fission?
6. Define spallation reaction with an example.
7. What is meant by the term "packing fraction" in nuclear chemistry?
8. How is nuclear binding energy related to nuclear stability?
9. List any four magic numbers in nuclear chemistry.
10. What are the different modes of radioactive decay?

C. Assay Type Questions

1. Explain the concept of mass defect and its significance in nuclear binding energy.

2. Discuss artificial radioactivity. How is it different from natural radioactivity? Provide suitable examples.
3. Describe the role of the neutron-to-proton (n/p) ratio in determining the stability of a nucleus.
4. Explain the different modes of radioactive decay (alpha, beta, and gamma) with suitable equations.
5. Compare and contrast nuclear fission and nuclear fusion. Discuss their applications in energy production.
6. Describe the spallation reaction and its importance in nuclear chemistry.
7. What is the packing fraction? How does it influence the stability of an atomic nucleus?
8. Define nuclear binding energy and explain its relationship with the concept of mass defect. How does it affect nuclear stability?
9. Explain the concept of magic numbers in nuclear chemistry. Why are certain nuclei with magic numbers more stable?
10. Discuss the applications of nuclear reactions in medicine, industry, and power generation.

14.13 References

1. "Nuclear and Radiochemistry" – Gerhart Friedlander, Joseph W. Kennedy, Edward S. Macias, and James M. Miller, ISBN: 978-0471115325
2. "Radiochemistry and Nuclear Chemistry" – Gregory R. Choppin, Jan-Olov Liljenzin, Jan Rydberg, ISBN: 978-0124058972
3. "Nuclear Chemistry" – Arnikar H.J. ISBN: 978-8122434539
4. "Essentials of Nuclear Chemistry" – H.J. Arnikar, ISBN: 978-8122434539□

5. "The Chemistry of Nuclear Fuel Waste Disposal" – Donald R. Wiles, ISBN: 978-0198526374
6. "Nuclear Chemistry: Fundamentals and Applications" – M. Satake, ISBN: 978-0136111027