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Ans to the Question No - 05

(a) Defects of Rutherford's Model and Bohr's Suggestions

Rutherford's nuclear model, based on his gold foil experiment, was a groundbreaking step in understanding the atom. It correctly proposed a small, dense, positively charged nucleus at the center with electrons orbiting around it. However, it suffered from some significant defects:

- Stability of the Atom: According to classical electromagnetic theory, an accelerating charged particle (like an electron orbiting the nucleus) should continuously radiate energy in the form of electromagnetic radiation. As it loses energy, the electron would spiral into the nucleus, causing the atom to collapse. Rutherford's model couldn't explain the stability of atoms; why don't electrons simply fall into the nucleus?
- **Atomic Spectra:** When elements are heated or subjected to electrical discharge, they emit light of specific wavelengths, forming a line spectrum. Rutherford's model predicted a continuous spectrum because electrons could orbit at any radius and thus emit radiation of any wavelength. It failed to explain the discrete line spectra observed experimentally.

To address these shortcomings, Niels Bohr proposed his model of the atom, incorporating quantum ideas:

- Postulate 1: Quantized Energy Levels: Bohr suggested that electrons can only exist in specific,
 discrete energy levels or orbits around the nucleus. These orbits are stationary states, and
 electrons in these orbits do not radiate energy, even though they are accelerating. Each orbit is
 associated with a fixed amount of energy.
- **Postulate 2: Emission and Absorption of Energy:** Electrons can transition between these allowed energy levels by absorbing or emitting energy in the form of photons. When an electron jumps from a higher energy level (E2) to a lower energy level (E1), it emits a photon with energy equal to the difference between the two levels (hv=E2–E1), where h is Planck's constant and v is the frequency of the emitted radiation. Conversely, an electron can jump to a higher energy level by absorbing a photon of the correct energy.
- **Postulate 3: Quantized Angular Momentum:** Bohr postulated that the angular momentum of an electron in an allowed orbit is quantized and is an integral multiple of $2\pi h$ (denoted as \hbar). Mathematically, mvr= $n\hbar$, where m is the mass of the electron, v is its velocity, r is the radius of the orbit, and n is a positive integer (the principal quantum number, n=1,2, 3...).

Bohr's model successfully explained the stability of the atom by postulating quantized energy levels where electrons don't radiate energy. It also beautifully accounted for the discrete line spectra of hydrogen by relating the specific wavelengths of emitted light to the transitions between these quantized energy levels.

(b) Quantum Numbers and Their Significance

The term "quantum number" refers to a set of numbers that describe the properties of an electron in an atom, such as its energy, shape of its orbital, and spatial orientation of the orbital. An electron in an orbital is described by **four** quantum numbers:

1. Principal Quantum Number (n):

- Symbol: n
- Values: Positive integers (n=1,2, 3...)
- o Significance: It primarily determines the **energy level** of the electron and the **size** of the orbital. Higher values of n indicate higher energy levels and larger orbitals (further from the nucleus). These energy levels are often referred to as shells (n=1 is the K shell, n=2 is the L shell, n=3 is the M shell, and so on).

2. Angular Momentum or Azimuthal Quantum Number (I):

- o Symbol: I
- Values: Integers ranging from 0 to n−1 (l=0,1,2,...,n−1)
- Significance: It determines the shape of the electron's orbital and also contributes to the angular momentum of the electron. Different values of I correspond to different subshells within a principal energy level. These subshells are designated by letters:
 - I=0: s orbital (spherical shape)
 - l=1: p orbital (dumbbell shape)
 - I=2: d orbital (more complex shapes)
 - I=3: f orbital (even more complex shapes)

3. Magnetic Quantum Number (ml):

- o Symbol: ml
- Values: Integers ranging from -l to +l, including 0 (ml=-l,-l+1,...,0,...,+l-1,+l)
- Significance: It determines the spatial orientation of an atomic orbital in three-dimensional space relative to an applied magnetic field. For a given value of I, there are
 2l+1 possible values of mI, indicating the number of orbitals with that particular shape

within a subshell. For example, a p subshell (l=1) has three p orbitals (ml=-1,0,+1) oriented along the x, y, and z axes.

4. Spin Quantum Number (ms):

o Symbol: ms

o Values: +1/2 or −1/2

 Significance: It describes the intrinsic angular momentum of the electron, which is also quantized and is called spin angular momentum. This spin creates a magnetic dipole moment, and in an external magnetic field, the electron can have one of two spin orientations, often referred to as "spin up" (+1/2) and "spin down" (-1/2).

Ans to the Question No -06

(a) Comparison of Ionic and Covalent Compounds

lonic and covalent compounds represent two primary types of chemical bonds that hold atoms together. They exhibit distinct properties due to the fundamental differences in the nature of their bonding. Here's a comparison:

Property	Ionic Compounds	Covalent Compounds
Bond Formation	Transfer of electrons from one atom to another, resulting in the formation of ions (cations and anions) held together by electrostatic attraction.	Sharing of electrons between atoms to achieve a stable electron configuration.
Type of Elements	Typically formed between a metal (low ionization energy) and a nonmetal (high electron affinity).	Typically formed between two or more nonmetals.
Physical State	Usually crystalline solids at room temperature.	Can exist as solids, liquids, or gases at room temperature.
Melting and Boiling Points	Generally high due to strong electrostatic forces between ions.	Generally low due to weaker intermolecular forces.
Solubility in Water	Many are soluble in polar solvents like water because the polar water molecules can interact with and separate the ions (hydration).	Generally insoluble in water, but some polar covalent compounds can dissolve (e.g., sugars, alcohols). Often soluble in nonpolar solvents.

Electrical Conductivity	Conduct electricity when molten or dissolved in water because the ions are free to move and carry charge. Do not conduct in the solid state because ions are held in fixed positions in the crystal lattice.	Generally poor conductors of electricity because there are no free ions or mobile electrons. Some exceptions exist (e.g., graphite).
Hardness and Brittleness	Typically hard and brittle. The strong electrostatic forces make them difficult to scratch, but a sharp blow can cause layers of ions to shift, leading to repulsion between similarly charged ions and causing the crystal to fracture.	Hardness varies greatly (e.g., diamond is very hard, while waxes are soft). Solids are often more malleable or ductile than ionic compounds.
Nature of Bond	Strong electrostatic forces (ionic bonds are strong).	Relatively weaker intermolecular forces compared to ionic bonds, although the covalent bonds within molecules are strong.
Crystal Structure	Form crystal lattices with a regular arrangement of ions.	Often form discrete molecules that may or may not arrange themselves in a regular crystal lattice in the solid state.

(b) Co-ordinate Covalent Bond

A **co-ordinate covalent bond**, also known as a dative bond or polar covalent bond, is a type of covalent bond in which **both** of the shared electrons are contributed by **one** of the bonding atoms. The other atom involved in the bond provides an empty orbital to accommodate the electron pair. Once formed, a co-ordinate covalent bond is indistinguishable from a normal covalent bond in terms of its properties (bond length, bond strength, etc.).

Difference from a Normal Covalent Bond:

In a **normal covalent bond**, each of the bonding atoms contributes one electron to the shared pair. For example, in the formation of a hydrogen molecule (H₂), each hydrogen atom contributes one electron to form the covalent bond.

In contrast, the formation of a co-ordinate covalent bond involves one atom with a lone pair of electrons (a Lewis base or donor) donating this pair to another atom or ion that has an empty valence orbital (a Lewis acid or acceptor).

Examples of Co-ordinate Covalent Bonds:

• Formation of the Ammonium Ion (NH₄⁺): Ammonia (NH₃) has a lone pair of electrons on the nitrogen atom. This lone pair can be donated to a proton (H⁺), which has an empty 1s orbital, forming a co-ordinate covalent bond.

```
    H H
    \ /
    N: + H<sup>+</sup> → [H-N-H]<sup>+</sup>
    / \ |
    H (empty) H
```

• Formation of the Hydronium Ion (H₃O⁺): A water molecule (H₂O) has two lone pairs of electrons on the oxygen atom. One of these lone pairs can be donated to a proton (H⁺), forming a coordinate covalent bond.

```
    H
    H-O: + H<sup>+</sup> → [H-O-H]<sup>+</sup>
    \
    H
    H
```

• Formation of Metal Complexes: Many transition metal complexes involve co-ordinate covalent bonds between the metal ion (Lewis acid) and ligands (Lewis bases) that donate electron pairs to the metal's empty d orbitals. For example, in the tetraamminecopper(II) ion, [Cu(NH3)4]2+, each ammonia molecule donates a lone pair of electrons to the copper(II) ion.

Ans to the question No -07

(a) Hydrogen Bonds

Hydrogen bonds are a special type of intermolecular force that occurs when a hydrogen atom is bonded to a highly electronegative atom (such as oxygen, nitrogen, or fluorine) and is attracted to another electronegative atom in a different molecule (or a different part of the same large molecule) that has a lone pair of electrons. The hydrogen atom acts as a bridge between the two electronegative atoms.

Classification of Hydrogen Bonds with Examples:

Hydrogen bonds can be classified into two main types:

1. **Intermolecular Hydrogen Bonds:** These occur between different molecules. They are responsible for many of the unique properties of substances like water, ammonia, and hydrogen fluoride.

- o Example 1: Water (H₂O): Each water molecule can form hydrogen bonds with up to four other water molecules. The partially positive hydrogen atoms of one water molecule are attracted to the lone pairs of electrons on the oxygen atom of a neighboring water molecule. This extensive network of hydrogen bonds is responsible for water's high boiling point, surface tension, and its ability to act as a solvent.
- Example 2: Ammonia (NH₃): Similar to water, ammonia molecules can form intermolecular hydrogen bonds between the partially positive hydrogen atoms and the lone pair of electrons on the nitrogen atom of adjacent ammonia molecules. These hydrogen bonds are weaker than those in water due to the lower electronegativity of nitrogen compared to oxygen.
- Example 3: Hydrogen Fluoride (HF): Hydrogen fluoride exhibits strong intermolecular hydrogen bonding due to the high electronegativity of fluorine. The hydrogen bond in HF is particularly strong, leading to its relatively high boiling point compared to other hydrogen halides.
- H δ+ F δ- ··· H δ+ F δ-
- 2. **Intramolecular Hydrogen Bonds:** These occur within the same molecule when a hydrogen atom bonded to an electronegative atom is close to another electronegative atom with a lone pair of electrons within the same molecule. This often occurs in large organic molecules.
 - o **Example 1: o-Nitrophenol:** In o-nitrophenol, the hydrogen atom of the hydroxyl (-OH) group is close to the oxygen atom of the nitro (-NO₂) group within the same molecule, allowing for the formation of an intramolecular hydrogen bond. This intramolecular hydrogen bonding affects the physical properties of o-nitrophenol, such as its lower boiling point compared to its para and meta isomers, as the intramolecular hydrogen bond reduces intermolecular interactions.
 - Example 2: DNA: Intramolecular hydrogen bonds are crucial for the structure of DNA.
 Hydrogen bonds form between the nitrogenous bases on opposite strands (adenine with thymine, and guanine with cytosine), holding the double helix together.

Why Water Has Abnormally High Boiling Point:

Water (H_2O) has an abnormally high boiling point (100 °C) compared to other hydrides of Group 16 elements (like H_2S , H_2Se , and H_2Te) due to the extensive and strong intermolecular hydrogen bonding between water molecules.

• **High Electronegativity of Oxygen:** Oxygen is highly electronegative, creating a significant partial positive charge (δ +) on the hydrogen atoms and a partial negative charge (δ -) on the oxygen atom in a water molecule.

- Small Size of Hydrogen and Oxygen: The small size of hydrogen and oxygen allows for a close approach between water molecules, leading to stronger dipole-dipole interactions and effective hydrogen bond formation.
- Two Lone Pairs on Oxygen: Each oxygen atom in a water molecule has two lone pairs of
 electrons, which can each attract a partially positive hydrogen atom from another water
 molecule. Similarly, each water molecule has two hydrogen atoms that can participate in
 hydrogen bonding with the lone pairs of electrons on oxygen atoms of neighboring water
 molecules.

This results in a vast, three-dimensional network of hydrogen bonds in liquid water. To convert liquid water to gaseous water (steam), a significant amount of energy is required to overcome these strong intermolecular hydrogen bonds and separate the water molecules. This is why water has a much higher boiling point than expected based on its molecular weight and compared to other similar hydrides where hydrogen bonding is weaker or absent. For instance, H₂S (which cannot form strong hydrogen bonds) has a boiling point of around -60 °C.

(b) Bond Angles of H₂O and NH₃

The bond angles of H₂O (104.5°) and NH₃ (107°) are less than the ideal tetrahedral angle of 109.5° expected for molecules with a central atom that is sp3 hybridized. This deviation is primarily attributed to the **lone pair-lone pair and lone pair-bond pair repulsions**, which are stronger than bond pair-bond pair repulsions according to the VSEPR (Valence Shell Electron Pair Repulsion) theory.

Water (H₂O):

- The central oxygen atom in water is sp3 hybridized, resulting in four electron pairs around it: two bond pairs with the two hydrogen atoms and two lone pairs of electrons.
- According to VSEPR theory, electron pairs around a central atom arrange themselves to minimize repulsion. The order of repulsion strength is: lone pair-lone pair > lone pair-bond pair > bond pair-bond pair.
- In water, there are two lone pairs, and the repulsion between these two lone pairs is the strongest. This repulsion forces the bond pairs (O-H bonds) closer together, resulting in a smaller bond angle of 104.5°. The two lone pairs occupy more space around the central oxygen atom than the two bond pairs, effectively "squeezing" the H-O-H angle.

Ammonia (NH₃):

- The central nitrogen atom in ammonia is also sp3 hybridized, resulting in four electron pairs around it: three bond pairs with the three hydrogen atoms and one lone pair of electrons.
- In ammonia, there is one lone pair. The repulsion between this lone pair and the three bond pairs (N-H bonds) is stronger than the repulsion between the bond pairs themselves.

 This lone pair repulsion compresses the bond angles, resulting in a bond angle of 107°, which is smaller than the ideal tetrahedral angle but larger than that in water. This is because ammonia has only one lone pair, leading to less overall repulsion compared to water with two lone pairs.

Ans to the question No -08

(a) Ionization Potential

The **ionization potential** (also known as ionization energy) of an element is the minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom in its ground state. It is usually expressed in units of kilojoules per mole (kJ/mol) or electron volts (eV).

The process can be represented by the following equation for the first ionization:

 $X(g)+Energy \rightarrow X+(g)+e-$

Why the First Ionization Potential is Less Than the Second Ionization Potential:

The first ionization potential refers to the energy needed to remove the *first* electron from a neutral atom. The second ionization potential is the energy required to remove the *second* electron from the resulting positively charged ion (X+):

 $X+(g)+Energy \rightarrow X2+(g)+e-$

The second ionization potential is always greater than the first ionization potential for the following reasons:

- Increased Nuclear Attraction: When the first electron is removed, the remaining electrons are
 now held more tightly by the same number of protons in the nucleus. This is because the
 effective nuclear charge experienced by each remaining electron increases. With a stronger
 positive pull from the nucleus and fewer electrons to repel each other, more energy is required
 to remove the second electron.
- 2. Smaller Ionic Size: After the removal of the first electron, the resulting positive ion has a smaller ionic radius compared to the neutral atom. This is because the remaining electrons are pulled closer to the nucleus due to the increased effective nuclear charge. Removing an electron from a smaller, more compact ion where the remaining electrons are held more tightly requires more energy.

Variation of Ionization Potential with Atomic Volume:

Atomic volume is related to the size of an atom. Generally, ionization potential shows an inverse relationship with atomic volume:

• Larger Atomic Volume (Larger Atomic Size): Elements with larger atomic volumes have their outermost electrons located farther away from the nucleus. The attraction between the nucleus and these valence electrons is weaker due to the increased distance and increased shielding

- effect from the inner electrons. Consequently, it requires less energy to remove these outermost electrons, resulting in a **lower ionization potential**.
- Smaller Atomic Volume (Smaller Atomic Size): Elements with smaller atomic volumes have their outermost electrons located closer to the nucleus. The nuclear attraction on these valence electrons is stronger due to the shorter distance and less effective shielding. Therefore, more energy is needed to remove these electrons, leading to a higher ionization potential.

(b) f-Block Elements and Inner Transition Elements

f-block elements are a group of elements in the periodic table where the last electron added to the atom enters the f-subshell of the antepenultimate (n-2) energy level. These elements are located in two series at the bottom of the periodic table:

- 1. **Lanthanide Series (Atomic numbers 57-71):** These elements follow lanthanum (La, atomic number 57). Their electronic configurations involve the filling of the 4f orbitals.
- 2. **Actinide Series (Atomic numbers 89-103):** These elements follow actinium (Ac, atomic number 89). Their electronic configurations involve the filling of the 5f orbitals.

Why f-Block Elements are Called Inner Transition Elements:

The term "inner transition elements" is used to describe the f-block elements because of their position and electronic configuration within the periodic table. Here's why:

- 1. **Transition Element Characteristics:** Transition elements are generally defined as elements that have partially filled d-subshells in their elemental or common oxidation states. The f-block elements are positioned *within* the d-block transition elements. The lanthanides occur after lanthanum (a d-block element), and the actinides occur after actinium (also a d-block element).
- 2. **Electronic Configuration:** The general electronic configuration of transition elements involves the filling of the (n-1)d subshell. For the f-block elements, the differentiating electron enters the (n-2)f subshell. This means that the f-orbitals being filled are two energy levels inside the outermost shell. This "inner" filling of the f-orbitals distinguishes them from the "outer" d-orbital filling in typical transition elements.
- 3. Placement in the Periodic Table: To maintain the organization of the periodic table based on chemical properties and electron configurations, the lanthanide and actinide series are typically placed separately at the bottom. If they were placed within the main body of the table according to their atomic numbers, they would interrupt the d-block transition metal series. Their placement "inside" the transition metals, conceptually between the s-block and the d-block elements of periods 6 and 7, further justifies the term "inner transition elements."