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Chemistry Assignment Answers

Question 5

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

Defects of Rutherford's Model:

- 1. Electromagnetic Radiation Instability: According to classical electromagnetic theory, an electron orbiting the nucleus should continuously emit radiation due to its centripetal acceleration. This energy loss would cause the electron to spiral inward and collapse into the nucleus within a fraction of a second, making the atom unstable.
- 2. Continuous Emission Spectrum: The model predicted that orbiting electrons would emit a continuous spectrum of electromagnetic radiation as they lose energy. However, experimental observations (e.g., line spectra of hydrogen) showed discrete spectral lines, contradicting the model.
- 3. No Explanation for Electron Positioning: Rutherford's model did not specify the positions or energies of electrons in their orbits, failing to account for the quantized nature of atomic spectra.

Bohr's Suggestions to Remove Defects: Niels Bohr proposed the following modifications in his atomic model for hydrogen-like atoms:

1. Quantized Orbits: Electrons orbit the nucleus in fixed, circular orbits with specific energies, and they do not radiate energy while in these stationary states. The angular momentum of an electron in an orbit is quantized:

$$mvr = n\frac{h}{2\pi}$$

where m is the electron's mass, v is its velocity, r is the radius of the orbit, n is the principal quantum number (n = 1, 2, 3, ...), and h is Planck's constant.

2. **Energy Transitions**: Electrons can jump between orbits by absorbing or emitting a photon with energy equal to the difference between the two energy levels:

$$\Delta E = E_2 - E_1 = h\nu$$

where ΔE is the energy difference, h is Planck's constant, and ν is the frequency of the emitted or absorbed photon. This explains the discrete line spectra.

3. **Stable Orbits**: Electrons in quantized orbits are stable and do not spiral into the nucleus, resolving the instability issue.

(b) Quantum Numbers and Their Significance

Definition of Quantum Number: A quantum number is a set of numerical values that describe the unique quantum state of an electron in an atom, specifying its energy, position, and orientation in an orbital.

Number of Quantum Numbers: An electron in an orbital is fully described by **four quantum numbers**:

- 1. Principal Quantum Number (n):
 - **Definition**: Specifies the energy level or shell of the electron.
 - Values: $n = 1, 2, 3, \dots$ (positive integers).
 - **Significance**: Determines the size of the orbital and the energy of the electron. Higher *n* indicates higher energy and larger orbitals. For hydrogen, the energy is given by:

$$E_n = -\frac{13.6}{n^2} \,\text{eV}$$

- 2. Azimuthal Quantum Number (l):
 - **Definition**: Describes the shape of the orbital (subshell).
 - Values: l = 0, 1, 2, ..., (n-1), corresponding to s (l = 0), p (l = 1), d (l = 2), f (l = 3), etc.
 - **Significance**: Defines the subshell type and orbital shape (e.g., spherical for s, dumbbell for p).
- 3. Magnetic Quantum Number (m_l) :
 - **Definition**: Specifies the orientation of the orbital in space.
 - Values: $m_l = -l, -l+1, \ldots, 0, \ldots, +l$.
 - Significance: Determines the number of orbitals in a subshell and their spatial orientation (e.g., p_x, p_y, p_z for l = 1).
- 4. Spin Quantum Number (m_s) :
 - **Definition**: Describes the intrinsic spin of the electron.
 - Values: $m_s = +\frac{1}{2}$ (spin-up) or $-\frac{1}{2}$ (spin-down).
 - Significance: Accounts for the electron's magnetic moment and ensures that no two electrons in the same orbital have identical quantum numbers (Pauli Exclusion Principle).

Question 6

(a) Comparison of Ionic and Covalent Compounds

Comparison of Properties:

Examples:

- Ionic Compounds: Sodium chloride (NaCl), Magnesium oxide (MgO).
- Covalent Compounds: Water (H₂O), Carbon dioxide (CO₂).

Property	Ionic Compounds	Covalent Compounds
Bond Formation	Electrostatic attraction between	Sharing of electron pairs between
	oppositely charged ions (cation	atoms.
	and anion).	
Structure	Crystalline lattice (e.g., NaCl	Discrete molecules or network
	forms a cubic lattice).	solids (e.g., diamond).
Melting/Boiling Points	High due to strong ionic bonds	Low for molecular compounds
	(e.g., NaCl melts at 801°C).	(e.g., H_2O boils at $100^{\circ}C$); high
		for network solids (e.g., SiO_2).
Solubility	Soluble in polar solvents like wa-	Non-polar compounds soluble in
	ter (e.g., NaCl dissolves in water).	non-polar solvents; polar covalent
		compounds may dissolve in water.
Electrical Conductivity	Conduct electricity when molten	Non-conductive (except network
	or in aqueous solution due to free	solids like graphite).
	ions.	
Physical State	Solids at room temperature.	Can be gases, liquids, or solids.

(b) Coordinate Covalent Bond vs. Normal Covalent Bond

Definition of Coordinate Covalent Bond: A coordinate covalent bond (or dative bond) is a type of covalent bond in which both electrons in the shared pair come from one atom (the donor), rather than one electron from each atom. The bond is formed between a Lewis base (electron-pair donor) and a Lewis acid (electron-pair acceptor).

Example: In the formation of the ammonium ion (NH_4^+) :

$$NH_3 + H^+ \longrightarrow NH_4^+$$

The nitrogen in NH₃ donates a lone pair to H⁺, forming a coordinate covalent bond. Differences from Normal Covalent Bond:

Feature	Coordinate Covalent Bond	Normal Covalent Bond
Electron Contribution	Both electrons come from one	Each atom contributes one elec-
	atom (e.g., NH_3 in NH_4^+).	tron (e.g., H_2).
Bond Formation	Involves a Lewis acid and base in-	Involves mutual electron sharing
	teraction.	between atoms.
Notation	Often represented with an arrow	Represented with a line (A-B).
	$(A \longrightarrow B)$ to indicate the donor.	
Stability	Once formed, behaves like a nor-	Stable with equal sharing.
	mal covalent bond.	

Question 7

(a) Hydrogen Bonds and High Boiling Point of Water

Definition of Hydrogen Bonds: A hydrogen bond is a strong intermolecular force of attraction between a hydrogen atom covalently bonded to a highly electronegative atom (e.g., O, N, F) and a lone pair of electrons on another electronegative atom in a neighboring molecule.

Classification of Hydrogen Bonds:

1. Intermolecular Hydrogen Bonds:

- Occur between different molecules.
- Example: Water (H₂O):

$$O-H \cdots O$$

The hydrogen of one water molecule is attracted to the oxygen lone pair of another.

• Example: Ammonia (NH₃):

$$N-H \cdot \cdot \cdot N$$

2. Intramolecular Hydrogen Bonds:

- Occur within the same molecule when hydrogen and an electronegative atom are appropriately positioned.
- **Example**: o-Nitrophenol, where the hydroxyl group (-OH) forms a hydrogen bond with the nitro group $(-NO_2)$.

Why Water Has an Abnormally High Boiling Point: Water's boiling point (100°C) is significantly higher than expected for a molecule of its molecular weight (18 g/mol), compared to similar molecules like H_2S (boiling point -60°C). This is due to:

- 1. **Strong Hydrogen Bonding**: Each water molecule can form up to four hydrogen bonds (two via its H atoms and two via its O lone pairs), creating a network that requires significant energy to break.
- 2. **High Electronegativity of Oxygen**: Oxygen's electronegativity (3.44) makes the O-H bond highly polar, strengthening hydrogen bonds.
- 3. **Energy Requirement**: The energy to overcome hydrogen bonds during boiling is high, increasing the boiling point.

(b) Bond Angles in H₂O and NH₃

Bond Angles:

- Water (H_2O) : Bond angle is 104.5° .
- Ammonia (NH₃): Bond angle is 107°.

Explanation: Both H_2O and NH_3 have central atoms (O and N) that are sp^3 hybridized, leading to a tetrahedral electron geometry with an ideal bond angle of 109.5°. However, the actual bond angles are reduced due to lone pair repulsion:

- 1. **VSEPR Theory**: The Valence Shell Electron Pair Repulsion (VSEPR) theory states that electron pairs around the central atom repel each other, with lone pairs exerting greater repulsion than bonding pairs.
- 2. Water (H₂O):

- Oxygen has two bonding pairs (to H atoms) and two lone pairs.
- Lone pair-lone pair repulsion is stronger than lone pair-bonding pair or bonding pair-bonding pair repulsion, compressing the H-O-H bond angle to 104.5°.

3. Ammonia (NH_3) :

- Nitrogen has three bonding pairs (to H atoms) and one lone pair.
- The single lone pair exerts less repulsion than the two lone pairs in water, resulting in a bond angle of 107°, closer to the tetrahedral ideal.

4. Comparison:

- Water's two lone pairs cause greater compression of the bond angle compared to ammonia's single lone pair.
- Electronegativity also plays a role: Oxygen (3.44) is more electronegative than nitrogen (3.04), pulling bonding electrons closer and enhancing lone pair repulsion in water.

Question 8

(a) Ionization Potential and Its Trends

Definition of Ionization Potential: Ionization potential (or ionization energy) is the minimum energy required to remove the most loosely bound electron from a neutral gaseous atom in its ground state to form a positive ion:

$$M(g) \longrightarrow M^+(g) + e^-, \quad \Delta E = IE_1$$

It is typically measured in kJ/mol or eV.

Why First Ionization Potential is Less Than Second:

- First Ionization Energy (IE₁): Removes an electron from a neutral atom. The electron is relatively loosely bound, shielded by other electrons.
- Second Ionization Energy (IE₂): Removes an electron from a positively charged ion (M⁺). The ion has a higher effective nuclear charge due to reduced electron shielding, and the remaining electrons are held more tightly, requiring more energy.
- Example: For sodium:

$$Na \longrightarrow Na^+ + e^-, \quad IE_1 \approx 496 \, kJ/mol$$

 $Na^+ \longrightarrow Na^{2+} + e^-, \quad IE_2 \approx 4562 \, kJ/mol$

Variation with Atomic Volume:

- Atomic Volume: The volume occupied by an atom, related to its atomic radius.
- Trend:

- As atomic volume (or radius) increases, the outermost electron is farther from the nucleus, experiencing less nuclear attraction due to increased shielding by inner electrons.
- This reduces the ionization potential (easier to remove the electron).
- **Example**: In Group 1 (alkali metals), ionization energy decreases down the group (Li \rightarrow Cs) as atomic volume increases:

 $Li: 520 \, kJ/mol$, $Cs: 376 \, kJ/mol$

• Periodic Trend:

- Across a period (left to right), atomic volume decreases due to increasing nuclear charge, increasing ionization potential.
- Down a group, atomic volume increases, decreasing ionization potential.

(b) f-Block Elements and Inner Transition Elements

Definition of f-Block Elements: f-Block elements are elements in which the last electron enters the f-orbitals of the penultimate (n-2) shell. They are located in two rows at the bottom of the periodic table:

- Lanthanides: Atomic numbers 58–71 (Ce to Lu), filling the 4f orbitals.
- Actinides: Atomic numbers 90–103 (Th to Lr), filling the 5f orbitals.

Why f-Block Elements Are Called Inner Transition Elements:

- Transition Elements: Elements where the last electron enters the d-orbitals (d-block) are called transition elements due to their partially filled d-orbitals and variable oxidation states.
- Inner Transition Elements: f-Block elements are called inner transition elements because:
 - 1. The f-orbitals being filled are in the (n-2) shell, "inner" to the valence (n) shell.
 - 2. They exhibit properties similar to d-block transition elements (e.g., multiple oxidation states, colored compounds), but the f-orbital filling occurs in a deeper energy level.
 - 3. The 4f and 5f electrons are shielded by outer s and p electrons, leading to unique properties like lanthanide contraction.
- Example: In cerium (Ce, Z=58), the electron configuration is [Xe] 4f¹ 5d¹ 6s², with the 4f orbital being filled, making it an inner transition element.