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CHEMISTRY

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1. Atomic Structure

Atomic Orbitals (Shapes and energies of s, p, d, f orbitals, nodal surfaces)

- Quantum Numbers:
  - Principal Quantum Number (n): Determines the main energy level and size of the orbital. Values: 1, 2, 3...
  - Azimuthal/Angular Momentum Quantum Number (l): Determines the shape of the orbital and subshell. Values: 0 to n-1.
    - l=0: s orbital (spherical)
    - l=1: p orbital (dumbbell)
    - l=2: d orbital (double dumbbell, except d_{z^2})
    - l=3: f orbital (complex)
  - Magnetic Quantum Number (m_l): Determines the orientation of the orbital in space. Values: -l to +l.
- Orbital Shapes:
  - s-orbitals: Spherically symmetric. Example: 1s, 2s.
  - p-orbitals: Dumbbell-shaped along axes. Three orientations: p_x, p_y, p_z.
  - d-orbitals: Five orientations. Four are double-dumbbell (d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$) and one is dumbbell with a collar (d_{z^2}).
  - f-orbitals: Seven complex orientations.
- Orbital Energies (Multi-electron atoms):
  - Energy depends on both 'n' and 'l'.
  - For a given principal quantum number 'n', the order of increasing energy is: s < p < d < f (due to varying penetration and shielding effects).
  - General filling order (Aufbau principle, (n+l) rule): 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p.
- Nodal Surfaces (Nodes): Regions where the probability of finding an electron is zero.
  - Total number of nodes = n - 1.
  - Angular Nodes (Nodal Planes): Equal to 'l'. These define regions where the probability density is zero due to orbital shape/orientation.
    - For p-orbitals (l=1): 1 angular node.

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        - For d-orbitals (l=2): 2 angular nodes.
        - d_{xy} orbital: Has 2 nodal planes (xz and yz planes).
    - Radial Nodes (Spherical Nodes): Equal to n - l - 1. These define spherical regions of zero probability.
    - For a 4d orbital (n=4, l=2):
        - Angular nodes = l = 2.
        - Radial nodes = n - l - 1 = 4 - 2 - 1 = 1.
- Stability of Electron Configurations: Atoms achieve extra stability with half-filled or completely-filled subshells.
    - Europium (Eu, Z=63): Electronic configuration is [Xe] $4f^7$ $6s^2$ (half-filled 4f orbital).
    - Gadolinium (Gd, Z=64): Electronic configuration is [Xe] $4f^7$ $5d^1$ $6s^2$ (half-filled 4f orbital, with an additional electron in 5d for stability).
- Pi (π) bond: Formed by the lateral (sideways) overlap of parallel p-orbitals.

Atomic Spectra (Origin, Types, Fine Structure - brief)

- Origin of Atomic Spectra: Arises from electron transitions between discrete energy levels within an atom. When an electron gains energy, it moves to a higher energy state; when it returns to a lower state, it emits electromagnetic radiation (photon) with energy `E = hν = E*final - Einitial*`.
- *Emission Spectra: Produced when excited atoms release energy by emitting photons as electrons fall to lower energy levels. Appears as bright lines on a dark background, unique for each element.*
- *Absorption Spectra: Produced when atoms absorb specific wavelengths of incident radiation, causing electrons to jump to higher energy levels. Appears as dark lines on a bright background at the same wavelengths as the emission lines.*
- *Line Spectra: Characteristic of individual atoms in the gaseous state, consisting of distinct, discrete lines due to quantized energy levels.*
- *Types of Transitions & Spectroscopic Regions:*
    - *Electronic Transitions: Involve electron jumps between different electronic energy levels. High energy. Occur primarily in the Ultraviolet (UV) and Visible regions of the electromagnetic spectrum. (Relevant to UV spectrometer)*
    - *Vibrational Transitions: Involve changes in molecular vibrational energy levels (not typically for isolated atoms, but relevant for comparison). Medium energy. Occur in the Infrared (IR) region.*
    - *Rotational Transitions: Involve changes in molecular rotational energy levels (not for isolated atoms). Low energy. Occur in the Microwave and Far-IR regions.*
- *Fine Structure: The splitting of main spectral lines into multiple, closely spaced lines. Primarily caused by spin-orbit coupling, which is the interaction between the electron's spin angular momentum and its orbital angular momentum. Relativistic corrections also contribute.*

Electronic Configuration Principles (Aufbau Principle, Pauli's Exclusion Principle, Hund's Rule)

- *Electronic Configuration Principles: Rules governing the distribution of electrons in atomic orbitals.*
- *1. Aufbau Principle:*
    - *Electrons occupy atomic orbitals in order of increasing energy.*
    - *Lowest energy orbitals are filled first.*
    - *General order of filling: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.*
- *2. Pauli's Exclusion Principle:*
    - *No two electrons in an atom can have all four quantum numbers identical.*
    - *An atomic orbital can hold a maximum of two electrons, and these two electrons must have opposite spins (↑↓).*

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- *3. Hund's Rule of Maximum Multiplicity:*
  - *For degenerate orbitals (orbitals of the same energy level, e.g., p, d, f subshells), electron pairing in an orbital does not occur until all orbitals of that subshell are singly occupied.*
  - *All singly occupied electrons in degenerate orbitals must have parallel spins.*
- *Electron Shell Capacities ($2n^2$ Rule): The maximum number of electrons a main energy shell (n) can hold is `$2n^2$`.*
  - *K-shell (n=1): Max 2 electrons (21^2).*
  - *L-shell (n=2): Max 8 electrons (22^2).*
  - *M-shell (n=3): Max 18 electrons (23^2).*
  - *N-shell (n=4): Max 32 electrons (24^2).*
- *Valence Electrons:*
  - *Electrons located in the outermost main energy shell of an atom.*
  - *Primarily determine an atom's chemical properties and reactivity.*
  - *For an element with Z=35 (Bromine), configuration is [Ar] $3d^{10}$ $4s^2$ $4p^5$. The outermost shell is n=4, thus valence electrons = 2 (from 4s) + 5 (from 4p) = 7.*

Electronic Configurations of Multi-electron Atoms and Ions

- *Electronic Configuration (EC) describes the distribution of electrons in an atom's orbitals.*
- *Aufbau Principle: Electrons fill atomic orbitals of the lowest energy first.*
- *Pauli Exclusion Principle: An orbital holds a maximum of two electrons with opposite spins.*
- *Hund's Rule of Maximum Multiplicity: For degenerate orbitals, electrons fill each orbital singly with parallel spins before pairing up.*
- *Shells and Subshells:*
  - *Shells (n=1, 2, 3...) or (K, L, M...). Maximum electrons in a shell (n) = $2n^2$. E.g., M shell (n=3) accommodates 18 electrons. (MCQ 11)*
  - *Subshells: s (max $2e^-$), p (max $6e^-$), d (max $10e^-$), f (max $14e^-$).*
- *Valence Electrons: Electrons in the outermost shell. They determine an element's chemical properties and valency. (MCQ 1, 8, 25, 59)*
- *Chemical Properties: Primarily determined by the number of valence electrons. (MCQ 1, 8, 25)*
- *Valency: Combining capacity, based on electrons gained, lost, or shared to achieve a stable octet/duet.*
  - *Silicon (Z=14): Valency 4.*
  - *Fluorine (Z=9): Valency 1.*
  - *Aluminium (Z=13): Valency 3.*
  - *Sulphur (Z=16): Valency 2.*
  - *Nitrogen (Z=7): Valency 3. (MCQ 33)*
  - *Magnesium (Z=12): Valency 2.*
  - *Sodium (Z=11): Valency 1.*
  - *Oxygen (Z=8): Valency 2. (Gains 2 electrons to form an octet; MCQ 30)*
  - *Neon (Z=10): Valency 0. (MCQ 9, 27, 28)*
  - *In CaO, Ca atom transfers its two valence electrons to the oxygen atom. (MCQ 23)*
- *Stability: Half-filled (e.g., d^5, p^3) and fully-filled (e.g., d^{10}, p^6, s^2) subshells confer extra stability.*
- *Exceptions to Aufbau Principle:*
  - *Chromium (Cr, Z=24): [Ar] $3d^5$ $4s^1$ (not [Ar] $3d^4$ $4s^2$) due to half-filled d-subshell stability. (MCQ 15)*
  - *Copper (Cu, Z=29): [Ar] $3d^{10}$ $4s^1$ (not [Ar] $3d^9$ $4s^2$) due to fully-filled d-subshell stability. (MCQ 14, 62)*
  - *Vanadium (V, Z=23): [Ar] $3d^3$ $4s^2$. (MCQ 49)*
- *Unpaired Electrons: Electrons occupying an orbital singly. For $1s^2 2s^2 2p^5$ (Fluorine, Z=9), there is 1 unpaired electron. (MCQ 34)*
- *Ions: Formed by gaining (anions) or losing (cations) electrons.*
  - *Cations: Smaller than parent atom. (MCQ 57)*
  - *Anions: Larger than parent atom.*
  - *Example: Cl (Z=17, $17e^-$). Cl^- has 18 electrons (7 valence + 1 gained = 8 valence electrons). (MCQ 10, 38)*
  - *Example: An ion with +3 charge, mass number 27, 14 neutrons: Protons = 27-14=13. Neutral atom has 13 elec-*

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trons. Ion has 13-3=10 electrons. (MCQ 36)

- *Isoelectronic Species: Atoms or ions with the same total number of electrons.*
  - *Cl^- ($18e^-$) is isoelectronic with K^+ ($18e^-$), S^{2-} ($18e^-$), P^{3-} ($18e^-$). (MCQ 6, 12, 26)*
  - *O^{2-} ($10e^-$) is isoelectronic with F^- ($10e^-$), Ne ($10e^-$), Na^+ ($10e^-$), Mg^{2+} ($10e^-$), Al^{3+} ($10e^-$). (MCQ 26, 35, 63)*
  - *N^- ($8e^-$) is NOT isoelectronic with F^- ($10e^-$). (MCQ 32)*
  - *S ($16e^-$) is NOT isoelectronic with Cl^- ($18e^-$). (MCQ 29)*
- *Atomic Number (Z): The most fundamental characteristic of an element. (MCQ 31)*
- *Atomic Radius (AR):*
  - *Decreases across a period (increasing effective nuclear charge).*
  - *Increases down a group (increasing number of shells). (MCQ 22)*
  - *Order of AR: Na > Li > Be > O. (MCQ 3)*
  - *Order of AR: C < B < Si < Al. (MCQ 13)*
  - *Correct comparisons: Mg > Be, I > Br, K > Na. Rb < Cs (Cs has larger radius than Rb). (MCQ 42)*
  - *Ionic Radii (Isoelectronic Series): For isoelectronic species, radius decreases with increasing positive nuclear charge (Z). E.g., $Mg^{2+} < Na^+ < F^- < O^{2-}$ (all $10e^-$). (MCQ 41)*
  - *Lanthanide Contraction: Gradual decrease in atomic/ionic radii across lanthanides due to poor shielding by 4f electrons. Order of increasing ionic size: $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$. (MCQ 50)*
- *Ionization Energy (IE): Energy required to remove an electron from a gaseous atom/ion.*
  - *Generally increases across a period and decreases down a group.*
  - *Exceptions: IE_1 of Be ([He] $2s^2$) > IE_1 of B ([He] $2s^22p^1$) due to stable $2s^2$; IE_1 of N ([He] $2s^22p^3$) > IE_1 of O ([He] $2s^22p^4$) due to stable half-filled $2p^3$.*
  - *Order for 2nd period elements (IE_1): Li < B < Be < C < O < N < F. (MCQ 48)*
  - *Successive IE: $IE_1 < IE_2 < IE_3$... (removing electrons from a positive ion requires more energy). Mg^{2+} has the highest IE among Mg, Mg^+, Mg^{2+}. (MCQ 24)*
  - *Highest IE: Configuration $1s^22s^22p^3$ (Nitrogen) has highest IE among options due to stable half-filled 2p subshell. (MCQ 39)*
- *Electron Gain Enthalpy (EGE): Energy change when an electron is added to a neutral gaseous atom.*
  - *Generally more negative (energy released) across a period and less negative down a group.*
  - *Exceptions: Noble gases have positive EGE (energy required).*
  - *High negative EGE: Halogens (e.g., F, Cl).*
  - *EGE Matching: Ne ($1s^22s^22p^6$): +48 kJ/mol; Na ($1s^22s^22p^63s^1$): -53 kJ/mol; F ($1s^22s^22p^5$): -328 kJ/mol; O ($1s^22s^22p^4$): -141 kJ/mol. (MCQ 47)*
  - *Assertion: Electron affinity (EGE) does NOT always increase from top to bottom in a group; it generally decreases (becomes less negative). (MCQ 37)*
- *Diamagnetism and Paramagnetism:*
  - *Paramagnetic: Contains one or more unpaired electrons (attracted to magnetic field).*
  - *Diamagnetic: All electrons are paired (weakly repelled by magnetic field).*
  - *Example (via MO theory): O_2^+, O_2^-, O_2 are paramagnetic. O_2^{2-} (18 electrons) is diamagnetic. (MCQ 56, 58)*
- *Bond Order (BO) from Molecular Orbital Theory (for diatomic molecules):*
  - *BO = ½ (Number of bonding electrons - Number of antibonding electrons).*
  - *Higher BO indicates greater bond strength.*
  - *Calculations: O_2 (BO=2.0), O_2^+ (BO=2.5), O_2^- (BO=1.5), O_2^{2-} (BO=1.0). (MCQ 53, 61)*
  - *Order: $O_2^+ > O_2 > O_2^- > O_2^{2-}$. (MCQ 44)*
  - *Transformations: N_2 (BO=3.0) -> N_2^+ (BO=2.5): BO decreases. O_2 (BO=2.0)*

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-> O_2^+ (BO=2.5): BO increases. (MCQ 46)
- C_2 molecule consists of only pi (π) bonds. (MCQ 51)

Historical Development of Atomic Models (Dalton, Thomson, Rutherford)

- Dalton's Atomic Theory (1808):
  - Matter consists of indivisible particles called atoms.
  - Atoms of a given element are identical in mass and properties.
  - Atoms are the smallest particles that participate in chemical reactions.
  - Proposed unique symbols for elements; e.g., Phosphorus: A circle with three lines radiating from the center to the circumference.
- Thomson's Atomic Model (1904) - "Plum Pudding Model":
  - Proposed after discovery of electron (1897).
  - Atom is a uniform sphere of positive charge with negatively charged electrons embedded in it, like plums in a pudding.
  - Overall electrically neutral.
- Rutherford's Atomic Model (1911) - "Nuclear Model":
  - Gold Foil Experiment (Alpha-scattering): Most alpha particles passed through, some deflected at small angles, very few bounced back.
  - Conclusions:
    - Most of the atom's space is empty.
    - A tiny, dense, positively charged region at the center called the nucleus contains nearly all the atom's mass.
    - Electrons revolve around the nucleus in distinct orbits.
    - An atom is electrically neutral: The positive charge on the nucleus is exactly balanced by the total negative charge of the orbiting electrons.
  - Limitations: Failed to explain the stability of the atom and the discrete atomic spectra.

Isotopes, Isobars, and Isotones

1. Atomic Number (Z):
   - Number of protons in an atom's nucleus.
   - Defines the identity of an element (its most characteristic property).
   - In a neutral atom, Z = number of electrons.
2. Mass Number (A):
   - Total number of protons and neutrons (collectively called nucleons) in the nucleus.
   - A = Z + N (where N = number of neutrons).
   - Number of neutrons (N) = A - Z.
3. Atomic Particles & Charge:
   - Protons (p^+): Positive charge, negligible mass relative to nucleus, located in nucleus.
   - Neutrons (n^0): No charge (neutral), located in nucleus.
   - Electrons (e^-): Negative charge, negligible mass, orbit the nucleus.
   - A neutral atom has an equal number of protons and electrons, making it electrically neutral.
   - Ions are formed when atoms gain or lose electrons, resulting in a net charge (e.g., Fe^{3+} has 3 fewer electrons than protons).
4. Isotopes:
   - Atoms of the same element.
   - Have the same atomic number (Z) (same number of protons).
   - Have different mass numbers (A) (different number of neutrons).
   - Exhibit similar chemical properties (due to same Z and electron configuration).
   - Exhibit different physical properties (due to different masses).