UNIT 1: ATOMIC AND MOLECULAR STRUCTURE & ADVANCED MATERIALS

This unit covers core concepts in atomic and molecular structure, properties of advanced materials, and an introduction to green chemistry.

1. ATOMIC AND MOLECULAR STRUCTURE

This section primarily deals with the **Molecular Orbital Theory** (MOT) and its applications to diatomic molecules.

- **Molecular Orbital Theory (MOT) - Introduction and Postulates**
  - **Definition:** MOT, proposed by R.S. Mulliken and F. Hund, postulates that the valence electrons in a molecule are associated with **all the nuclei** in the molecule, rather than being localized to individual atoms.
  - **Combination of Atomic Orbitals:** According to MOT, atomic orbitals with similar energy and symmetry combine to form new molecular orbitals. This combination occurs via the **Linear Combination of Atomic Orbitals (LCAO)** method.
  - **Types of Molecular Orbitals:** When atomic orbitals combine, they form two types of molecular orbitals:
    - **Bonding Molecular Orbitals (BMOs):** Formed by the additive overlap of atomic orbitals, resulting in increased electron density between the nuclei and lower energy.
    - **Antibonding Molecular Orbitals (ABMOs):** Formed by the subtractive overlap of atomic orbitals, resulting in decreased electron density between the nuclei, higher energy, and a nodal plane between nuclei.
- **Bond Order**
  - **Definition:** Bond order is a quantitative measure of the number of chemical bonds between two atoms in a molecule.
  - **Calculation:** It is calculated as half the difference between the number of electrons in bonding molecular orbitals (Nb) and antibonding molecular orbitals (Na).
    - **Formula:** Bond Order = ½ (Nb - Na)

- **Significance:** A higher bond order generally indicates greater bond strength and shorter bond length. A bond order of zero suggests that a stable molecule does not form.
- **Magnetic Characters (Paramagnetic vs. Diamagnetic)**
    - **Paramagnetic:** Substances are paramagnetic if they contain **unpaired electrons** in their molecular orbitals. These substances are attracted to a magnetic field.
    - **Diamagnetic:** Substances are diamagnetic if **all their electrons are paired** in their molecular orbitals. These substances are weakly repelled by a magnetic field.
- **Applications to Diatomic Molecules and Numerical Problems:**
    - **CO (Carbon Monoxide):** Its molecular energy level diagram can be drawn to calculate its bond order and explain its magnetic behavior.
    - **N2, O2, F2:** Molecular orbital diagrams for these homonuclear diatomic molecules can be used to determine their bond order and magnetic properties. For example, O2 is typically paramagnetic due to unpaired electrons, while N2 and F2 are diamagnetic.
    - **H2, H22+, H22-:** These species are used to illustrate paramagnetism based on their electron configurations in molecular orbitals.
    - **NO, NO+, NO-:** The molecular orbital diagram for NO can be used to calculate the bond order and predict the magnetic behavior of NO, NO+, and NO-.

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2. CHEMISTRY OF ADVANCED MATERIALS

This section explores various advanced materials, including liquid crystals, solids, graphite, fullerenes, and nanomaterials.

- **Liquid Crystals**
    - **Introduction:** Liquid crystals are a state of matter that possesses properties intermediate between those of conventional isotropic liquids and solid crystalline materials. They exhibit both liquid-like fluidity and solid-like optical and electrical anisotropy.
    - **Types of Liquid Crystals:**
        - **Nematic Liquid Crystals:** Characterized by molecules that have no positional order but tend to maintain a long-range orientational order, aligning themselves along a common director axis. They are less viscous and respond faster to electric fields.

        - **Smectic Liquid Crystals:** Possess both orientational order and a degree of positional order, where molecules are arranged in layers. Within these layers, molecules can be ordered in various ways. They are more viscous than nematics.
    - **Applications:**
        - **Liquid Crystal Displays (LCDs):** A primary application due to their optical properties and ability to reorient in an electric field.
        - **Reinforced Materials:** Copolymers like those formed from p-hydroxy benzoic acid, phthalic acid, and ethylene glycol can create reinforced materials, providing strength and stiffness to thermotropic polymers. They are also used as reinforcing fillers in thermoplastic materials.
        - **Temperature Sensors and Thermometers:** Some liquid crystals are used in these applications due to their sensitivity to temperature changes.
        - **Optical Devices:** Used in various optical devices.
        - **Industrially Important Materials:** Their unique properties, such as switching time, viscosity, dielectric anisotropy, and refractive index, are crucial for LC displays.
- **Band Theory of Solids**
    - **Concept:** The band theory explains the electrical conductivity of materials (conductors, semiconductors, and insulators) based on the formation of energy bands from atomic orbitals.
        - **Valence Band:** The highest energy band completely filled with electrons at absolute zero temperature.
        - **Conduction Band:** The lowest energy band that is empty or partially filled with electrons.
        - **Band Gap (Forbidden Energy Gap):** The energy difference between the valence band and the conduction band.
    - **Applications to Metals:** In metals, the valence band and conduction band either overlap or are very close, allowing electrons to move freely, making them excellent conductors.
    - **Effect of Doping on Conductance:** Doping, the intentional introduction of impurities into a semiconductor, can significantly alter its electrical conductivity by creating more charge carriers (electrons or holes).
- **Point Defects in Solids**
    - **Introduction:** These are localized disruptions in the crystal lattice of a solid material.
    - **Types:** The sources mention "Zero Dimensional defects". (Without

further detail in the sources, specific types like vacancies, interstitial atoms, or substitutional impurities are not elaborated.)

- **Graphite and Fullerenes (Allotropes of Carbon)**
  - **Graphite:**
    - **Structure:** Graphite has a unique layered structure, with carbon atoms arranged in hexagonal rings within each layer. The layers are held together by weak Van der Waals forces, allowing them to slide past each other easily.
    - **Applications:**
      - **Lubricant:** Due to its layered structure, it acts as a good lubricant.
      - **Pencils:** Used in pencil leads.
      - **Electrodes:** Utilized in dry cells and for electroplating due to its electrical conductivity.
      - **Crucibles:** Used for making high-grade steel.
      - **Moderator:** Acts as a moderator in nuclear reactors by absorbing fast-moving neutrons.
      - **Conductive Ink:** Used as a conductive ink for screen printing.
  - **Fullerene (e.g., C60 Buckminsterfullerene or Bucky Ball):**
    - **Introduction:** Fullerenes are allotropes of carbon discovered by Kroto and Smalley. The most well-known fullerene is C60, which has an icosahedral symmetry, resembling a soccer ball.
    - **Structure:** C60 has a **truncated icosahedron geometry** consisting of 20 hexagons and 12 pentagons. It possesses an electronic structure similar to graphene.
    - **Preparation:** Fullerenes can be prepared by evaporating graphite rods in an inert atmosphere (like Helium gas) at low pressure (0.05 to 0.1 atm). This process yields fullerene soot, a light and fluffy dust containing 5-15% fullerenes. Pure C60 can then be isolated from this mixture using techniques like column chromatography with alumina and hexane, followed by sublimation.
    - **Properties:**
      - Typically a mustard-colored solid, appearing brown to black with increasing thickness.
      - Primarily **semiconductors**, but they can become **superconductors** when doped with alkali metals.
      - High thermal stability and high strength.

        - **Applications:**
            - **Antioxidants:** Possess powerful antioxidant properties, making them useful in health and personal care products.
            - **Catalysts:** C60 shows catalytic activity.
            - **Drug Delivery Agents:** Can act as effective drug delivery agents.
            - **HIV Inhibitors:** Derivatives of C60 show potential as inhibitors for HIV.
            - **Superconductors:** Used in the preparation of superconductors.
            - **Optical Devices:** Applied in optical devices.
            - **Soft Ferromagnets:** Used in the preparation of soft ferromagnets.
            - **Batteries:** Can function as charge carriers in batteries.
- **Nanomaterials**
    - **Concepts and Introduction:**
        - **Nanomaterials:** Materials where at least one of their dimensions is in the **nanometer scale (1 nm = 10-9 m)**.
        - **Nanotechnology:** The technology involving the manipulation of materials and their properties at the nanoscale (atomic or molecular level) to achieve specific applications.
        - **Nanostructured Materials:** Can be classified by their dimensions:
            - **0D (Zero-dimensional):** All dimensions are at the nanoscale (e.g., **Fullerene**, Nanoparticles).
            - **1D (One-dimensional):** Two dimensions are at the nanoscale (e.g., **Carbon Nanotubes**, Nanowires, Nanorods).
            - **2D (Two-dimensional):** One dimension is at the nanoscale (e.g., **Graphene**).
            - **3D (Three-dimensional):** All dimensions are larger than the nanoscale, but they may contain nanoscale features (e.g., Bulk Graphite).
    - **Properties/Characteristics of Nanomaterials:**
        - **Size-Dependent Properties:** Their properties (physical and chemical) are highly dependent on their size, composition, and structure.
        - **Increased Surface Area:** Nano size dramatically increases the surface area to volume ratio.

        - **Surface Energy:** Leads to a change in surface energy (often higher).
        - **Electronic Properties:** Changes in electronic properties and optical band gap.
        - **Electrical Conductivity:** Altered electrical conductivity.
        - **Catalytic Activity:** Exhibit higher and specific catalytic activity.
        - **Thermal and Mechanical Stabilities:** Changes in thermal and mechanical stabilities.
    - **Preparation/Fabrication of Nanomaterials:**
        - **Top-Down Approach (e.g., Chemical Vapor Deposition - CVD):** Involves reducing larger materials to nanoscale dimensions.
        - **Bottom-Up Approach (e.g., Sol-Gel method):** Involves building materials from atomic or molecular components.
    - **Carbon Nanotubes (CNTs):**
        - **Introduction:** One of the most important nanomaterials.
        - **Features/Properties:**
            - High tensile strength (100 times stronger than steel).
            - Chemically stable and **resistant to corrosion**.
            - High thermal conductivity.
        - **Types:**
            - **Single-Walled Carbon Nanotubes (SWCNTs):** Consist of a single layer of graphene rolled into a cylinder. They have diameters typically ranging from 0.5 to 2.5 nm and lengths up to 2 µm, often possessing an aspect ratio greater than 10,000. They can exhibit both metallic and semiconducting behavior, with band gaps from 0 to 2 eV. SWCNTs are used in electronics.
            - **Multi-Walled Carbon Nanotubes (MWCNTs):** Comprise multiple concentric tubes of graphene.
        - **Applications:**
            - **Electronics:** Used in nano transistors, field-effect transistors, and nano electrodes.
            - **Field Emission:** Applications in field emission technologies.
            - **Sensors:** Utilized in chemical, biological, pressure, and thermal sensors, including those for sensing greenhouse gases (CO_2, CH_4).
            - **Nano Devices:** For various nano-scale devices.
            - **Medicine:** Applied in nano medicine, drug delivery systems, and disease diagnosis.

- **General Applications of Nanomaterials:**
    - Electronics
    - Medicine
    - Engineering and Technology
    - Industries
    - Environment
    - Catalysis

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3. GREEN CHEMISTRY

This section focuses on the principles and applications of environmentally benign chemical practices.

- **Introduction/Definition:**
    1. **Green Chemistry (Sustainable Chemistry):** It is a branch of chemistry focused on designing and optimizing chemical processes and products to **minimize or eliminate the production and use of hazardous substances**. It is distinct from environmental chemistry, which studies environmental pollutants.
- **12 Principles of Green Chemistry:** These principles guide chemists in designing greener chemical processes.
    1. **Prevention of Waste:** It is preferable to prevent waste formation rather than treating or cleaning up waste after it has been created.
    2. **Atom Economy:** Synthetic methods should be designed to maximize the incorporation of all raw materials into the final product, minimizing waste.
    3. **Less Hazardous Chemical Syntheses:** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
    4. **Designing Safer Chemicals:** Chemical products should be designed to achieve their desired function while minimizing their toxicity.
    5. **Safer Solvents and Auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents) should be avoided wherever possible, and if used, they should be innocuous.
    6. **Design for Energy Efficiency:** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
    7. **Use of Renewable Feedstocks:** A raw material or feedstock should be

renewable rather than depleting whenever technically and economically practicable.

8. **Reduce Derivatives:** Unnecessary derivatization (e.g., blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, as such steps require additional reagents and can generate waste.
9. **Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation:** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-time Analysis for Pollution Prevention:** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention:** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

- **Importance of Green Synthesis and Green Chemicals:** These methods and chemicals contribute to a more sustainable and environmentally friendly chemical industry by reducing pollution and resource depletion.
- **Synthesis of Typical Organic Compounds (Adipic acid and Paracetamol):** Green chemistry promotes the synthesis of such compounds through conventional and green routes, comparing their environmental impacts. For instance, paracetamol is a key pharmaceutical.
- **Environmental Impact on Society:** Green chemistry aims to mitigate negative environmental impacts by designing processes that are safer for human health and the planet.
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