

NATIONAL UNIVERSITY OF DISTANCE EDUCATION

Compuestos Inorgánicos de Estructura Compleja

Idioma: EN

INSTRUCTIONS:

No general instructions specified in the form, but there are 5 questions in the exam.

Question 1

Structure and bonding of silicates

STUDENT RESPONSE:

Silicates are inorganic polymers based on the silicon-oxygen (Si-O) bond, forming the most abundant class of minerals in the Earth's crust. Their structure and bonding are governed by the following key features:

1. **Basic Structural Unit:** The fundamental building block is the $[\text{SiO}_4]^{4-}$ tetrahedron, where a central silicon atom is coordinated to four oxygen atoms in a tetrahedral arrangement. The Si-O bond has significant covalent character due to the overlap of silicon sp^3 hybrid orbitals with oxygen 2p orbitals, though ionic contributions also exist due to the electronegativity difference.

2. **Polymerization and Connectivity:** Silicate structures arise from the condensation of $[\text{SiO}_4]^{4-}$ tetrahedra through shared oxygen atoms (bridging oxygens, BO), forming Si-O-Si linkages. The degree of polymerization determines the structural classification:

- **Nesosilicates:** Isolated $[\text{SiO}_4]^{4-}$ tetrahedra (e.g., olivine, $(\text{Mg,Fe})_2\text{SiO}_4$).
- **Sorosilicates:** Two tetrahedra sharing one oxygen (e.g., hemimorphite, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$).
- **Cyclosilicates:** Rings of tetrahedra sharing two oxygens per unit (e.g., beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$).
- **Inosilicates:** Single or double chains of tetrahedra (e.g., pyroxenes (single chain) or amphiboles (double chain)).
- **Phyllosilicates:** Sheets of tetrahedra sharing three oxygens per unit (e.g., clays, micas).
- **Tectosilicates:** Three-dimensional frameworks where all four oxygens are shared (e.g., quartz, feldspars).

3. Bonding Characteristics:

- The Si-O bond length ($\sim 1.6 \text{ \AA}$) and bond angle (Si-O-Si $\sim 140\text{--}180^\circ$) vary with structure due to steric and electronic effects.
- Bridging oxygens (BO) exhibit stronger covalent bonding than non-bridging oxygens (NBO), which are often associated with cations (e.g., Na^+ , Ca^{2+}) to balance charge.
- The bond strength and stability increase with polymerization, as seen in the high melting points of tectosilicates (e.g., quartz, $\sim 1700^\circ\text{C}$).

4. **Role of Cations:** Alkali and alkaline earth metals (e.g., Na^+ , K^+ , Ca^{2+}) or transition metals (e.g., Al^{3+} , Fe^{3+}) can substitute for Si^{4+} in tetrahedral sites (isomorphic substitution), altering charge balance and requiring additional cations for neutrality. Aluminosilicates (e.g., feldspars) are common examples where Al^{3+} replaces Si^{4+} , creating a negative framework charge.

5. **Thermodynamic Stability:** Silicate structures are stabilized by the high bond energy of Si-O ($\sim 452 \text{ kJ/mol}$) and the efficient packing of tetrahedra in three dimensions. The polymerization degree correlates with thermodynamic stability, with tectosilicates being the most stable under ambient conditions.

Question 2

What is a borane? Classification of boranes

STUDENT RESPONSE:

A borane is a chemical compound composed of boron and hydrogen, with the general formula B_xH_y . These compounds are characterized by their electron-deficient nature, as boron has only three valence electrons, leading to the formation of multicenter bonds (such as two-electron three-center bonds) to achieve stability. Boranes exhibit unique structural and bonding properties, including deltahedral geometries and cluster-like arrangements.

Boranes are classified based on their stoichiometry and structure into the following categories:

- **Closo-boranes:** Closed polyhedral structures with the general formula $B_nH_n^{2-}$, where n ranges from 5 to 12. These are the most stable boranes, with all boron atoms forming a complete polyhedron (e.g., $B_6H_6^{2-}$, $B_{12}H_{12}^{2-}$).
- **Nido-boranes:** Derived from closo-boranes by the removal of one boron vertex, resulting in a nest-like structure with the formula B_nH_{n+4} (e.g., B_2H_6 , B_5H_9 , $B_{10}H_{14}$).
- **Arachno-boranes:** Obtained by removing two boron vertices from a closo-borane, leading to a web-like structure with the formula B_nH_{n+6} (e.g., B_4H_{10} , B_5H_{11}).
- **Hypso-boranes:** Derived from the removal of three boron vertices from a closo-borane, forming very open structures with the formula B_nH_{n+8} (e.g., B_8H_{16}).
- **Conjuncto-boranes:** Formed by the fusion of two or more borane clusters through shared boron atoms (e.g., $B_{10}H_{16}$, which consists of two B_5H_8 units).

Additionally, boranes can be classified as neutral (e.g., B_2H_6 , diborane) or anionic (e.g., $B_{12}H_{12}^{2-}$), depending on their charge.

Question 3

Give examples of the use of inorganic heterocycles in the synthesis of the corresponding polymers

STUDENT RESPONSE:

Inorganic heterocycles serve as key precursors or structural units in the synthesis of various inorganic polymers. Examples include:

- **Cyclic phosphazenes (e.g., hexachlorocyclotriphosphazene, $[\text{NPCl}_2]_3$):**

These heterocycles undergo ring-opening polymerization (ROP) under thermal or catalytic conditions to form linear polyphosphazenes, $[\text{N}=\text{PR}_2]_n$, which exhibit high thermal stability and flexibility. Substitution of chlorine atoms with organic or inorganic groups (e.g., alkoxy, aryloxy, or amino) tailors the polymer's properties.

- **Cyclic siloxanes (e.g., octamethylcyclotetrasiloxane, D_4 , $[\text{Si}(\text{CH}_3)_2\text{O}]_4$):**

These silicon-oxygen heterocycles undergo anionic or cationic ROP to produce polysiloxanes (silicones), $[\text{Si}(\text{CH}_3)_2\text{O}]_n$, which are widely used for their hydrophobicity, thermal resistance, and biocompatibility.

- **Borazines (e.g., $\text{B}_3\text{N}_3\text{H}_6$):** Analogous to benzene, borazines can be polymerized via dehydrocoupling or thermolysis to form boron nitride (BN) polymers or ceramics, which exhibit high thermal and chemical stability.

- **Cyclic thiazyl compounds (e.g., S_4N_4):** These sulfur-nitrogen heterocycles can be polymerized under controlled conditions to yield polythiazyl, $(\text{SN})_n$, a metallic polymer with intrinsic conductivity and superconductivity at low temperatures.

- **Cyclic boroxines (e.g., trialkylboroxines, $[\text{RBO}]_3$):** These boron-oxygen heterocycles can be used as precursors for borate-based polymers or ceramics through condensation reactions, often employed in flame-retardant materials.

- **Cyclic silazanes (e.g., hexamethylcyclotrisilazane, $[\text{Si}(\text{CH}_3)_2\text{NH}]_3$):** These silicon-nitrogen heterocycles undergo ROP to form polysilazanes, which are precursors for silicon nitride (Si_3N_4) ceramics via pyrolysis.

Question 4

Crystalline defects

STUDENT RESPONSE:

Crystalline defects are imperfections in the regular arrangement of atoms, ions, or molecules within a crystal lattice. These deviations from ideal periodicity can be classified based on their dimensionality:

- **Point defects (0D):**

- *Vacancies*: Missing atoms or ions at lattice sites.
- *Interstitial defects*: Atoms or ions occupying positions between regular lattice sites.
- *Substitutional defects*: Foreign atoms replacing host atoms in the lattice.
- *Frenkel defects*: A combination of a vacancy and an interstitial defect, where an atom or ion moves from its lattice site to an interstitial position.
- *Schottky defects*: Paired vacancies of cations and anions to maintain electrical neutrality in ionic crystals.

- **Line defects (1D):**

- *Dislocations*: Linear defects where atoms are misaligned, including edge dislocations (extra half-plane of atoms) and screw dislocations (spiral arrangement around a dislocation line).

- **Planar defects (2D):**

- *Grain boundaries*: Interfaces between crystallites with different orientations.
- *Twin boundaries*: Mirror planes where the crystal lattice is symmetrically reflected.
- *Stacking faults*: Errors in the sequence of atomic planes, common in close-packed structures.

- **Bulk defects (3D):**

- *Voids*: Three-dimensional empty spaces within the crystal.
- *Precipitates*: Clusters of impurity atoms or secondary phases.
- *Inclusions*: Foreign particles embedded in the crystal.

These defects influence physical properties such as mechanical strength, electrical conductivity, diffusion, and optical behavior, playing a crucial role in materials science and solid-state chemistry.

Question 5

Explain the polymerization of vanadates, VO_4^{3-} as a function of concentration and pH

STUDENT RESPONSE:

The polymerization of vanadate ions (VO_4^{3-}) is highly dependent on both concentration and pH, leading to the formation of different polyoxovanadate species through condensation reactions.

At very low concentrations (below $\sim 10^{-5}$ M) and high pH (pH > 13), the dominant species is the monomeric orthovanadate ion, VO_4^{3-} . As the pH decreases (pH 12–9), protonation occurs, forming HVO_4^{2-} and H_2VO_4^- , which can condense to form dimeric ($\text{V}_2\text{O}_7^{4-}$) and tetrameric ($\text{V}_4\text{O}_{12}^{4-}$) species through the elimination of water.

At intermediate pH (pH 9–6) and higher concentrations, further condensation leads to the formation of decavanadate ions ($\text{V}_{10}\text{O}_{28}^{6-}$), which are stable in acidic conditions. The decavanadate structure consists of edge- and corner-sharing VO_6 octahedra.

At even lower pH (pH < 6), protonation continues, and the decavanadate species ($\text{HV}_{10}\text{O}_{28}^{5-}$, $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$) dominate until precipitation of hydrated V_2O_5 occurs. In highly acidic conditions (pH < 2), the vanadium exists primarily as the cationic VO_2^+ species.

In summary, increasing concentration and decreasing pH favor polymerization, progressing from monomeric to oligomeric and eventually to large polyoxovanadate clusters before precipitation.