NATIONAL UNIVERSITY OF DISTANCE EDUCATION

Compuestos Inorgánicos de Estructura Compleja

Idioma: EN

EXAM STATEMENT:

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

Question 1: Structure and bonding of silicates

Question 2: What is a borane? Classification of boranes

Question 3: Give examples of the use of inorganic heterocycles in the synthesis of the corresponding polymers

Question 4: Crystalline defects

Question 5: Explain the polymerization of vanadates, VO43- as a function of concentration and pH

Question 1

Structure and bonding of silicates

STUDENT RESPONSE:

Silicates are inorganic polymers composed of silicon-oxygen tetrahedra (SiO_4) as the fundamental structural unit. Each silicon atom is tetrahedrally coordinated to four oxygen atoms via strong covalent bonds, with bond angles of approximately 109.5°, reflecting sp^3 hybridization. The Si-O bond is highly directional and strong (average bond energy ~467 kJ/mol), resulting from significant covalent character despite the ionic contribution due to the electronegativity difference ($\Delta EN = 1.7$). Oxygen atoms can be terminal (non-bridging) or bridging, connecting multiple tetrahedra.

Silicate structures are classified based on the connectivity of tetrahedra:
- **Isolated tetrahedra (n=1)**: Individual SiO_4 units with no shared oxygen atoms (e.g., orthosilicates like forsterite, Mg_2SiO_4).
- **Chain structures (q=3)**: Tetrahedra linked by two shared oxygen atoms forming infinite chains (e.g., pyroxenes, $CaSiO_3$).
- **Sheet structures (q=4)**: Tetrahedra connected by three shared oxygen atoms creating two-dimensional sheets (e.g., micas, $KAl_2(AlSi_3O_{10})(OH)_2$).
- **3D frameworks (q=6)**: Tetrahedra bonded by four shared oxygen atoms forming rigid three-dimensional networks (e.g., quartz, SiO_2).

Bonding in silicates is predominantly covalent, with silicon acting as the central atom and oxygen as terminal or bridging ligands. The strength and directionality of Si-O bonds dictate the stability and rigidity of the network. In framework silicates, the negative charge of the tetrahedral units is balanced by cations in interstitial sites (e.g., Na^+ in albite, $NaAlSi_3O_8$), influencing properties like hardness and thermal stability. Variations in connectivity and cation incorporation lead to diverse mineral structures and applications, such as in ceramics and glass.

Question 2

What is a borane? Classification of boranes

STUDENT RESPONSE:

A borane is a compound consisting of boron and hydrogen atoms, characterized by electron-deficient bonding where boron atoms form multicenter bonds with bridging hydrogen atoms, typically exhibiting structures with three-center two-electron bonds. Boranes are classified into three main categories: neutral boranes (e.g., diborane, B_2H_6), which feature two boron atoms with two bridging hydrogen atoms; electron-deficient boranes (e.g., triethylborane, B_3H_8), containing boron-hydrogen bonds that form clusters with electron-deficient bonding; and cluster boranes (e.g., pentaborane, B_5H_9), which possess complex polyhedral structures with multiple boron atoms connected via bridging hydrides and satisfy Wade's rules for stability. Classification further distinguishes between simple boranes (e.g., B_2H_6), mid-sized boranes (e.g., B_5H_9), and complex boranes (e.g., $B_{10}H_{14}$), based on their molecular architecture and bonding characteristics.

Question 3

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

STUDENT RESPONSE:

Inorganic heterocycles play a crucial role in polymer synthesis, particularly phosphorus-based heterocycles. For example, cyclic phosphazenes (e.g., hexachlorocyclotriphosphazene, $(NPCl_2)_3$) undergo ring-opening polymerization to form polyphosphazenes, such as $(NPCl_2)_n$. This process involves nucleophilic substitution or hydrolysis, yielding polymers with tunable properties. Polyphosphazenes are widely used in biomedical applications, including drug delivery systems and biocompatible materials, due to their thermal stability and versatility in functionalization. Additionally, sulfur-containing heterocycles like thiophene derivatives contribute to conductive polymers, though phosphazenes represent the most prominent inorganic heterocyclic polymer synthesis.

Question 4

Crystalline defects

STUDENT RESPONSE:

Crystalline defects are imperfections in the regular arrangement of atoms within a crystal lattice that deviate from the ideal stoichiometric composition and perfect periodicity. These defects are categorized into point defects, line defects, and planar defects. Point defects include vacancies (missing atoms), interstitials (atoms in non-lattice sites), Schottky defects (paired vacancies in ionic crystals), and Frenkel defects (displaced atoms forming vacancies and interstitials). Line defects, such as dislocations, involve irregularities along a line, disrupting atomic planes and influencing mechanical properties. Planar defects encompass stacking faults, grain boundaries, and twin boundaries, where atomic layers are misaligned or interrupted across a plane. These defects arise due to thermal energy, impurities, or non-stoichiometry, leading to deviations from ideal chemical composition. For instance, in non-stoichiometric compounds like zinc oxide, oxygen vacancies create electronic states that affect conductivity. Crystalline defects critically impact material properties, including electrical conductivity, mechanical strength, diffusion rates, and catalytic activity, making them essential in solid-state chemistry and materials engineering.

Question 5

Explain the polymerization of vanadates, VO43- 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 due to protonation/deprotonation equilibria and condensation reactions. At low pH (below 2), VO_4^{3-} is protonated to form HVO_4^{2-} and $H_2VO_4^-$, which are monomeric species stabilized by protonation. As pH increases to approximately 3–4, the deprotonated VO_4^{3-} concentration rises, enabling condensation reactions where two VO_4^{3-} units lose water to form dimeric metavanadate ions ($V_2O_7^{4-}$) and subsequently polymeric chains or rings. Further increase in pH (above 4) favors the formation of orthovanadate (VO_4^{3-}) networks, including 3D structures like $[V_6O_{19}]^{4-}$ or $[V_{10}O_{28}]^{6-}$, due to enhanced deprotonation and electrostatic attraction. Concentration plays a secondary role: high $[VO_4^{3-}]$ accelerates polymerization by increasing collision frequency, even at moderate pH (e.g., polymerization occurs readily at $[VO_4^{3-}] > 0.1$ M and pH 3–4), while low concentrations favor monomeric species regardless of pH. The critical pH threshold for polymerization is typically 2–4, where the protonation state shifts from monomeric to polymeric species, with pH acting as the primary regulator and concentration as an amplifying factor.