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 compounds characterized by a fundamental structural unit consisting of a silicon atom tetrahedrally coordinated to four oxygen atoms (SiO4 tetrahedron), with Si-O bond lengths of approximately 1.6 Å and O-Si-O bond angles close to 109.5°. The overall structure depends on the degree of polymerization through shared oxygen atoms (bridging oxygens), leading to classifications such as nesosilicates (isolated tetrahedra, e.g., olivine), sorosilicates (two tetrahedra sharing one oxygen), cyclosilicates (cyclic arrangements), inosilicates (single or double chains, e.g., pyroxenes), phyllosilicates (layered sheets, e.g., micas), and tectosilicates (three-dimensional frameworks, e.g., quartz). Bonding within the silicate framework is predominantly covalent, with partial ionic character due to the electronegativity difference between silicon and oxygen. The negative charge from non-bridging oxygen atoms is balanced by cations such as Na^+, K^+, or Ca^{2+}, while in fully polymerized tectosilicates, all oxygen atoms are bridging, resulting in a neutral framework. The stability of silicates arises from the strong covalent Si-O network, with cation coordination influencing structural diversity and physical properties.

Question 2

What is a borane? Classification of boranes

STUDENT RESPONSE:

Boranes are electron-deficient compounds consisting solely of boron and hydrogen atoms, characterized by multi-center bonding, including three-center two-electron bonds. They are classified according to Wade's rules into structural types: closo (closed polyhedral structures with the general formula $[B_nH_n]^{2-}$, e.g., $[B_6H_6]^{2-}$), nido (nest-like structures derived from closo by removal of one vertex, formula B_nH_{n+4}, e.g., B_5H_9), arachno (web-like structures with two vertices removed, formula B_nH_{n+6}, e.g., B_4H_{10}), and hypho (structures with three vertices removed, formula B_nH_{n+8}, e.g., B_5H_{11}). Neutral boranes such as diborane (B_2H_6) and tetraborane (B_4H_{10}) are common examples, while anionic boranes include the closo-borane dianions.

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 in the synthesis of various inorganic polymers through ring-opening polymerization or thermal processes. For example, hexachlorophosphazene ($N_3P_3Cl_6$), a phosphorus-nitrogen heterocycle, undergoes ring-opening polymerization to form polyphosphazenes, which are tailored for biomedical and flame-retardant applications by substituting chloride groups. Tetrasulfur tetranitride (S_4N_4), a sulfur-nitrogen heterocycle, thermally polymerizes to yield polythiazyl ($(SN)_x$), a one-dimensional metallic conductor. Additionally, cyclic siloxanes such as octamethylcyclotetrasiloxane (D_4) undergo ring-opening polymerization to produce polysiloxanes (silicones), widely used in sealants and insulating materials due to their thermal stability and flexibility. These examples illustrate the critical role of inorganic heterocycles in constructing functional polymeric frameworks.

Question 4

Crystalline defects

STUDENT RESPONSE:

Crystalline defects are deviations from the ideal periodic arrangement of atoms in a crystal lattice, classified into four main categories based on dimensionality. Point defects (0D) include vacancies, interstitial atoms, substitutional impurities, and intrinsic defects such as Frenkel (a vacancy-interstitial pair) and Schottky (paired cation-anion vacancies in ionic compounds). Line defects (1D), or dislocations, consist of edge dislocations (extra half-plane of atoms) and screw dislocations (helical atomic displacement). Planar defects (2D) encompass grain boundaries (interfaces between crystal domains), stacking faults (irregular layer sequences), and twin boundaries (symmetrical misorientations). Volume defects (3D) involve voids, precipitates, or foreign inclusions. These defects critically influence material properties, including mechanical strength, electrical conductivity, and reactivity, and are fundamental to understanding non-stoichiometric compounds and solid-state reactions.

Question 5

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

STUDENT RESPONSE:

The polymerization of vanadates (VO_4^{3-}) is highly dependent on pH and concentration. At high pH (alkaline conditions, $pH > 12$), VO_4^{3-} remains predominantly monomeric due to electrostatic repulsion and deprotonation. As pH decreases (pH 10–7), partial protonation forms HVO_4^{2-} and $H_2VO_4^-$, enabling condensation reactions via dehydration to yield oligomeric species such as divanadate ($V_2O_7^{4-}$) and trivanadate ($V_3O_9^{3-}$). At pH 6–4 and moderate to high vanadate concentrations, decavanadate ($V_{10}O_{28}^{6-}$) becomes the dominant species, stabilized by its cyclic structure. Further acidification ($pH < 4$) promotes the formation of larger polyvanadates or amorphous V_2O_5, especially at elevated concentrations. Higher vanadate concentrations favor polymerization by shifting the equilibrium toward condensed species, while dilute solutions inhibit extensive polymerization even at lower pH due to reduced ion collision frequency. The process is reversible, with depolymerization occurring upon alkalinization.