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 based on silicon and oxygen whose fundamental structural unit is the tetrahedral anion $[SiO_4]^{4-}$. In this unit, the silicon atom is sp^3-hybridized and covalently bonded to four oxygen atoms arranged at the corners of a regular tetrahedron. The Si–O bond has a strong covalent character due to orbital overlap, but also a significant ionic contribution arising from the difference in electronegativity between Si and O.

Silicate structures arise from the ability of $[SiO_4]$ tetrahedra to share one or more oxygen atoms (bridging oxygens) with neighboring tetrahedra. When an oxygen atom is shared, it is bonded to two silicon atoms (Si–O–Si), and its effective charge is reduced. Non-bridging oxygens are bonded to only one silicon atom and usually coordinate to metal cations to maintain electroneutrality. The degree of polymerization of the tetrahedra determines the structure and properties of the silicate.

Based on the number of shared oxygen atoms per tetrahedron, silicates are classified structurally into several types. In nesosilicates (orthosilicates), the tetrahedra are isolated and do not share oxygen atoms; the anionic unit remains $[SiO_4]^{4-}$, and charge balance is achieved by metal cations. In sorosilicates, two tetrahedra share one oxygen atom, forming $[Si_2O_7]^{6-}$ units. In cyclosilicates, each tetrahedron shares two oxygen atoms, generating ring structures with general formula $[Si_nO_{3n}]^{2n-}$. In inosilicates, each tetrahedron shares two or three oxygens, giving rise to single chains ($[SiO_3]_n^{2n-}$) or double chains ($[Si_4O_{11}]_n^{6n-}$). In phyllosilicates, each tetrahedron shares three oxygen atoms, forming two-dimensional sheets with composition $[Si_2O_5]_n^{2n-}$. In tectosilicates, all four oxygen atoms are shared, producing three-dimensional frameworks with an overall neutral composition of SiO_2 or with charge-compensating cations when Al^{3+} substitutes for Si^{4+}.

Bonding in silicates is characterized by strong directional Si–O bonds, which confer high thermal and chemical stability. The Si–O–Si bond angle is flexible, allowing a wide variety of structures. The presence of metal cations interacting ionically with non-bridging oxygens influences lattice energy, melting point, and mechanical properties. Substitution of Si^{4+} by Al^{3+} introduces negative charge into the framework, which is balanced by alkali or alkaline earth cations and is fundamental to the chemistry of aluminosilicates such as feldspars and zeolites.

Question 2

What is a borane? Classification of boranes

STUDENT RESPONSE:

A borane is an inorganic compound composed exclusively of boron and hydrogen, generally with the formula BnHm, characterized by electron-deficient multicenter bonding (three-center two-electron B–H–B bonds) and polyhedral cluster structures that cannot be described by classical two-center two-electron bonds.

Classification of boranes:

- According to structural type (Wade–Mingos rules):
- Closo-boranes: closed, deltahedral clusters with formula [BnHn]2− or neutral derivatives; all vertices occupied.
- Nido-boranes: open clusters derived from closo structures missing one vertex; general formula BnHn+4.
- Arachno-boranes: more open clusters derived from closo structures missing two vertices; general formula BnHn+6.
- Hypho-boranes: highly open clusters missing three vertices; rare and poorly represented.

- According to nuclearity:
- Lower boranes: small clusters, typically n ≤ 4.
- Higher boranes: larger polyhedral clusters, n ≥ 5.

- According to charge:
- Neutral boranes: BnHm.
- Anionic boranes: borane clusters carrying negative charge, often more stable than their neutral counterparts.

- According to substitution:
- Parent boranes: containing only boron and hydrogen.
- Substituted boranes: hydrogen atoms partially replaced by organic or inorganic substituents.

Question 3

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

STUDENT RESPONSE:

Inorganic heterocycles are frequently used as well-defined molecular precursors for the synthesis of inorganic polymers through ring-opening or condensation processes. Representative examples include:

- Phosphazenes: cyclic phosphazenes such as hexachlorocyclotriphosphazene, (NPCl2)3, and octachlorocyclotetraphosphazene, (NPCl2)4, undergo thermal or catalytic ring-opening polymerization to give linear poly(dichlorophosphazene), (NPCl2)n, which can be further substituted to obtain functional polyphosphazenes with elastomeric or fire-resistant properties.

- Sulfur–nitrogen heterocycles: the heterocycle S4N4 serves as the classical precursor of the one-dimensional inorganic conductor polythiazyl, (SN)x, obtained by controlled decomposition and polymerization of the ring, yielding a conjugated polymer with metallic conductivity.

- Boron–nitrogen heterocycles: borazine, B3N3H6, the inorganic analogue of benzene, can be thermally polymerized or cross-linked to form polyborazylene, a precursor polymer for boron nitride ceramics.

- Silicon–nitrogen heterocycles: cyclic silazanes, such as hexamethylcyclotrisilazane, (Si(CH3)2NH)3, can undergo ring-opening polymerization to form polysilazanes, which are important preceramic polymers for the preparation of Si–N-based materials.

These examples illustrate how inorganic heterocycles act as key molecular building blocks that enable controlled synthesis of inorganic polymers with specific structural and functional properties.

Question 4

Crystalline defects

STUDENT RESPONSE:

Crystalline defects are deviations from the ideal periodic arrangement of atoms or ions in a crystal lattice. Real crystals are always imperfect, and these imperfections strongly influence their physical, chemical and mechanical properties.

According to their dimensionality, defects are classified as point, line, planar and volume defects.

Point defects involve one or a few lattice sites. In ionic and covalent solids the most important point defects are vacancies, where a lattice site is unoccupied, and interstitials, where an atom or ion occupies a normally empty position. In ionic crystals, point defects must preserve electrical neutrality. Schottky defects consist of paired cation and anion vacancies and are typical of highly ionic compounds such as alkali halides. Frenkel defects involve the displacement of an ion, usually a small cation, from its normal site to an interstitial position, generating a vacancy–interstitial pair. Substitutional defects occur when foreign atoms replace host atoms in the lattice, giving rise to doped or solid solution materials.

Line defects are dislocations, which correspond to a misalignment of atomic planes along a line. Edge dislocations involve the termination of an extra half-plane of atoms inside the crystal, whereas screw dislocations arise from a helical distortion of the lattice. Dislocations are responsible for plastic deformation and strongly affect mechanical strength and ionic or electronic transport.

Planar defects affect two-dimensional regions of the crystal. These include grain boundaries, which separate crystals of different orientation in polycrystalline materials, stacking faults, due to errors in the stacking sequence of atomic planes, and twin boundaries, where two regions of the crystal are related by a symmetry operation.

Volume defects are three-dimensional imperfections such as pores, cracks, inclusions of foreign phases or precipitates, and extended regions of disorder. They often arise during crystal growth or solid-state reactions.

Crystalline defects play a crucial role in non-stoichiometric compounds, diffusion processes, electrical conductivity, catalytic activity and mechanical behavior, and are therefore fundamental to understanding the properties and applications of inorganic solids.

Question 5

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

STUDENT RESPONSE:

In aqueous solution the vanadate system shows a strong dependence of its degree of polymerization on both pH and total vanadium concentration. At very high pH ($pH \geq 12$) and low concentration, the predominant species is the isolated orthovanadate tetrahedron, VO_4^{3-}, which is stable under strongly basic conditions and remains essentially unpolymerized.

As the pH is lowered from strongly basic to mildly basic or neutral conditions, protonation of VO_4^{3-} occurs, generating HVO_4^{2-} and $H_2VO_4^-$ species. Protonation reduces the negative charge and favors condensation reactions through shared oxygen atoms, leading to polymerization. At moderate concentrations and pH values around 7–10, equilibrium mixtures of oligovanadates are formed, mainly divanadate ($V_2O_7^{4-}$) and tetravanadate species, produced by condensation reactions with elimination of water.

Further decrease in pH and/or increase in vanadium concentration strongly promotes polymerization. In slightly acidic solutions, extensive condensation leads to the formation of larger isopolyanions, such as metavanadate chains $(VO_3^-)_n$ and cyclic or cage-like polyvanadates. Under sufficiently acidic conditions, highly condensed species such as decavanadate, $V_{10}O_{28}^{6-}$, become the dominant form. These species are stabilized by extensive V–O–V bridging and are favored by both higher concentration and lower pH.

Therefore, vanadate polymerization increases with decreasing pH and increasing concentration: isolated orthovanadate tetrahedra dominate at high pH and low concentration, while progressively larger and more condensed polyvanadate ions form as the solution becomes more acidic and concentrated.