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 solids built from the tetrahedral oxyanion unit [SiO4]4−. Their structures arise from the ability of Si(IV) (small, high charge density) to form four strong, directional Si–O bonds in approximately tetrahedral geometry; polymerization occurs by sharing tetrahedron corners through bridging oxygen atoms.

1. Fundamental structural unit and polymerization
- Basic unit: SiO4 tetrahedron with O–Si–O angles close to 109.5°.
- Two types of oxygen in silicates:
- Non-bridging oxygen (NBO): bonded to one Si; carries more negative charge and is typically coordinated to extra-framework cations (M+, M2+, etc.).
- Bridging oxygen (BO): shared by two tetrahedra, giving Si–O–Si linkages.
- Polymerization principle: tetrahedra link almost exclusively by corner sharing (Si–O–Si). Edge- or face-sharing would bring Si4+ centers too close, increasing electrostatic repulsion and destabilizing the lattice.
- Degree of polymerization is described by Qn notation, where n is the number of bridging oxygens per tetrahedron:
- Q0: isolated tetrahedra
- Q1: end groups in dimers/chain ends
- Q2: chains/rings
- Q3: sheets
- Q4: 3D frameworks

2. Bonding in silicates
- Si–O bonding is polar covalent:
- Strong σ bonding from overlap of O 2p with Si sp3 hybrids.
- Significant ionic character due to electronegativity difference; negative charge is largely on oxygen, especially on NBO.
- Bridging vs non-bridging Si–O bond lengths:
- Si–O(BO) is typically slightly longer than Si–O(NBO) because electron density is shared between two Si centers in BO, whereas NBO has greater localized negative charge and stronger single Si–O interaction.
- Si–O–Si angles vary widely (commonly ~120–180°) depending on composition and network constraints; this flexibility enables many silicate topologies.
- Charge balance and extra-framework species:
- Pure SiO2 frameworks (Q4) are neutral (all O are bridging).
- When NBO are present, the anionic framework is balanced by cations in interstitial sites; cations also influence polymerization (high field-strength cations favor higher polymerization).
- Isomorphic substitution (aluminosilicates):
- Replacement of Si4+ by Al3+ in tetrahedral sites creates a net negative charge per substitution, requiring charge-compensating cations (Na+, K+, Ca2+, etc.).
- This is central to feldspars, zeolites, many clays; it modifies acidity, ion-exchange capacity, and framework topology.

3. Structural classification of silicates (by tetrahedral connectivity)
- Nesosilicates (orthosilicates, Q0): isolated [SiO4]4− tetrahedra.
- General feature: highest proportion of NBO; require many charge-balancing cations.
- Sorosilicates (Q1): paired tetrahedra sharing one oxygen, [Si2O7]6−.

- Cyclosilicates (Q2): rings of corner-sharing tetrahedra, [SinO3n]2n− (e.g., n = 3, 4, 6).
- Inosilicates:
- Single chains (Q2): [SinO3n]2n−; each tetrahedron shares two oxygens.
- Double chains (mixed Q2/Q3): more polymerized; typical anion motif [Si4O11]6− repeated.
- Phyllosilicates (sheet silicates, Q3): infinite 2D sheets, idealized composition [Si2O5]2− layers; one NBO per tetrahedron points out of the sheet, often bonded to interlayer cations or hydroxylated (common in clays, micas).
- Tectosilicates (framework silicates, Q4): 3D networks with all oxygens bridging; composition SiO2 or aluminosilicate frameworks when Al substitutes for Si.
- Open frameworks (e.g., zeolites) contain channels/cavities hosting water and exchangeable cations; bonding remains corner-sharing Si/Al–O tetrahedra.

Overall, the structure and bonding of silicates are governed by the strong, directional, polar-covalent Si–O bonds in tetrahedra and by corner-sharing through bridging oxygens, with the connectivity (Qn) controlling charge distribution, required counter-cations, and the resulting one-, two-, or three-dimensional architectures.

Question 2

What is a borane? Classification of boranes

STUDENT RESPONSE:

A borane is a molecular hydride of boron, i.e., a compound consisting only of boron and hydrogen with general formula BnHm. Because boron is electron-deficient, boranes are predominantly covalent and their structures are based on multicenter bonding (notably 3-center–2-electron B–H–B bridges), giving rise to polyhedral cluster frameworks.

Classification of boranes

1. By structural type (polyhedral cluster class; Wade–Mingos scheme)
- Closo-boranes: closed, complete deltahedral clusters with formula [BnHn]2− (all vertices occupied; maximum skeletal connectivity).
- Nido-boranes: one vertex missing relative to the corresponding closo deltahedron; typical neutral formula BnHn+4.
- Arachno-boranes: two vertices missing; typical neutral formula BnHn+6.
- Hypho-boranes: three vertices missing; typical neutral formula BnHn+8 (less common).
- Conjuncto boranes (fused clusters): species formed by fusion of two or more borane subclusters (e.g., linked/fused polyhedra).

2. By charge (formal acid–base forms)
- Neutral boranes: BnHm (often nido/arachno types).
- Anionic boranes (borate clusters): [BnHm]q− (frequently closo; also nido/arachno anions).
- Cationic boranes: [BnHm]q+ (rare; strongly electrophilic).

3. By nuclearity (size)
- Lower boranes: small clusters (typically n = 2–4).
- Higher boranes: larger polyhedral clusters (typically n ≥ 5), where the closo/nido/arachno patterns are most clearly developed.

4. By hydrogen bonding mode (descriptive)
- Boranes with terminal hydrogens (B–H).
- Boranes containing bridging hydrogens (B–H–B) in addition to terminal hydrogens (very common in electron-deficient clusters).

Question 3

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

STUDENT RESPONSE:

Examples in which an inorganic heterocycle is used as the monomer (or key precursor) to obtain the corresponding inorganic polymer include:

- Phosphazene heterocycles → polyphosphazenes
- Monomer: cyclic phosphazenes, typically hexachlorocyclotriphosphazene, $(NPCl_2)_3$, and/or octachlorocyclotetraphosphazene, $(NPCl_2)_4$.
- Polymer obtained: linear poly(dichlorophosphazene), $[NPCl_2]_n$, formed by thermal ring-opening polymerization (ROP) of the cyclic oligomer; subsequent nucleophilic substitution of Cl gives functional poly(organophosphazenes) $[NP(OR)_2]_n$, $[NP(NR_2)_2]_n$, etc.

- Siloxane heterocycles → polysiloxanes (silicones)
- Monomer: cyclic siloxanes such as hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4), i.e., $(Me_2SiO)_3$ and $(Me_2SiO)_4$.
- Polymer obtained: polydimethylsiloxane (PDMS), $[–SiMe_2–O–]_n$, by acid- or base-catalyzed ring-opening polymerization/equilibration of D3/D4; analogous routes from substituted cyclic siloxanes afford functional polysiloxanes.

- Sulfur–nitrogen heterocycles → polythiazyl
- Monomer/precursor: disulfur dinitride, S_2N_2, a cyclic S–N heterocycle (commonly generated from S_4N_4).
- Polymer obtained: polythiazyl, $(SN)_x$, by polymerization (ring-opening/condensation) of S_2N_2 to give the one-dimensional conjugated inorganic polymer.

- Boron–nitrogen heterocycles → polyborazylene / polymeric BN precursors
- Monomer: borazine, $B_3N_3H_6$ (“inorganic benzene”), and substituted borazines.
- Polymer obtained: polyborazylene (a B–N polymeric network) via thermal polymerization/condensation of borazine (often with H_2 evolution); this polymer is a typical preceramic polymer that can be converted on pyrolysis into boron nitride (BN) materials.

Question 4

Crystalline defects

STUDENT RESPONSE:

Crystalline defects are any deviation from the ideal periodic arrangement of atoms/ions in a crystal lattice. Real solids are imperfect due to thermodynamic reasons (finite temperature gives a nonzero equilibrium defect concentration) and kinetic/synthetic factors (growth conditions, quenching, irradiation, mechanical deformation). Defects can be classified by their dimensionality:

1. Point defects (0D)
a) Intrinsic point defects (in pure crystals)
- Vacancy: missing atom/ion at a lattice site.
- Interstitial: extra atom/ion in an interstitial site.
- Schottky defect (ionic crystals): paired cation and anion vacancies that preserve electroneutrality; decreases density; typical in highly ionic, high-coordination lattices (e.g., alkali halides).
- Frenkel defect (ionic crystals): an ion (usually a small cation) leaves its lattice site and occupies an interstitial position, creating a vacancy–interstitial pair; density approximately unchanged; common in lattices with significant interstitial space.
- Antisite defect (ordered compounds): atom/ion occupies the “wrong” sublattice site (important in ordered oxides and intermetallics).

b) Extrinsic point defects (impurities/dopants)
- Substitutional impurity: foreign atom replaces a host atom at a lattice site.
- Interstitial impurity: foreign atom sits in an interstitial site.

Charge compensation mechanisms in ionic solids:
- If a dopant has different charge than the host ion, electroneutrality is maintained by creating compensating defects (vacancies or interstitials) and/or by changing oxidation states of neighboring ions. This is central to defect chemistry in oxides (acceptor vs donor doping).

c) Electronic defects and color centers
- Localized electrons or holes associated with lattice imperfections (e.g., oxygen vacancies trapping electrons in oxides; F-centers in halides). These defects can modify optical absorption (color), magnetic behavior, and electrical conductivity.

2. Line defects (1D): dislocations
Dislocations are one-dimensional defects characterized by a Burgers vector b, controlling plastic deformation and many mechanical properties.
- Edge dislocation: insertion of an extra half-plane; b is perpendicular to the dislocation line.
- Screw dislocation: helical mismatch; b is parallel to the dislocation line.
- Mixed dislocation: general case combining edge and screw character.

Dislocations interact with point defects (pinning), influence diffusion (pipe diffusion), and can act as nucleation sites for reactions and phase transformations.

3. Planar defects (2D)
- Grain boundaries: interfaces between crystallites of different orientation

in polycrystals; high defect density; affect diffusion, corrosion, ionic transport, and mechanical strength.
- Twin boundaries: special, mirror-symmetry related boundaries (growth twins or deformation twins).
- Stacking faults: local errors in the stacking sequence of close-packed planes (e.g., ABCABC → ABCABABC); can be intrinsic or extrinsic; relevant in fcc/hcp-related structures and layered solids.
- Antiphase boundaries: in ordered solids when regions are shifted by a lattice translation, disrupting long-range order.

4. Volume defects (3D)
- Voids/pores, precipitates, inclusions, second-phase particles, and cracks. These arise from processing, segregation, or incomplete densification and strongly influence mechanical, transport, and catalytic properties.

Relation to non-stoichiometry (especially in inorganic solids)
Many inorganic solids (notably transition-metal oxides) tolerate deviations from ideal stoichiometry through point defects coupled to variable oxidation states:
- Oxygen deficiency (anion vacancies) or oxygen excess (cation vacancies/interstitial oxygen), with accompanying changes in metal oxidation state.
- Such defect equilibria control ionic/electronic conductivity, reactivity in solid-state processes, and properties of mixed oxides (e.g., semiconducting behavior, catalytic activity).

Question 5

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

STUDENT RESPONSE:

In aqueous solution the tetrahedral orthovanadate unit, VO4^3−, undergoes stepwise protonation and acid-catalysed condensation (olation/oxolation) to give polyoxovanadates through formation of V–O–V bridges with elimination of water. The distribution of species is therefore controlled mainly by (i) pH (degree of protonation, which activates terminal V–OH groups toward condensation) and (ii) total vanadium concentration (mass-action favouring higher nuclearity aggregates).

1. High pH (strongly basic; dilute solutions): predominance of monomeric orthovanadate
VO4^3− is stable and largely depolymerised. As pH decreases slightly but remains basic, protonation occurs without extensive condensation:
VO4^3− + H+ ⇌ HVO4^2−
HVO4^2− + H+ ⇌ H2VO4−
At sufficiently low total [V], these monomeric species dominate over a wide pH window because dilution shifts equilibria toward smaller units.

2. Mildly basic to near-neutral pH and/or higher concentration: onset of condensation to small polyvanadates and metavanadates
Protonated monomers condense by sharing oxygen atoms:
2 HVO4^2− ⇌ V2O7^4− + H2O   (pyrovanadate, dimer; promoted by lower pH and higher [V])
Further condensation yields higher oligomers and metavanadates (chains/rings built from corner-sharing VO4 units), generically:
n H2VO4− ⇌ (VO3−)n + n H2O   (metavanadate polymerisation)
In this region, increasing total vanadium concentration at fixed pH shifts the speciation from predominantly monomeric HxVO4(3−x)− toward dimers/trimers and then to polymeric metavanadate species.

3. Moderately acidic pH (typically around pH 2–6, especially at higher concentration): formation of isopolyvanadates, notably decavanadate
As pH is lowered, multiple protonation steps strongly favour condensation to compact polyoxovanadate clusters. The characteristic species is decavanadate:
10 VO4^3− + 24 H+ ⇌ V10O28^6− + 12 H2O
(Equivalently expressed starting from H2VO4−/HVO4^2−, depending on pH.)
At a given acidic pH, higher total [V] favours V10O28^6− (and related protonated forms) over smaller oligomers; dilution shifts back toward smaller units.

4. Strongly acidic conditions (very low pH): depolymerisation to small cationic/neutral oxovanadium(V) aquo species
At sufficiently high acidity, polyvanadates can break down and the dominant vanadium(V) forms are small oxo/aquo species (often represented as dioxovanadium(V) species, VO2+, in strongly acidic media), with polymeric anions becoming less stable.

Overall trend:
Decreasing pH (more protonation) and increasing vanadium concentration both promote polymerisation/condensation of VO4^3− into V–O–V linked oligomers

and polyoxovanadate clusters; increasing pH and/or dilution promotes depolymerisation back to monomeric orthovanadate/protonated orthovanadate.