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 characterized by the tetrahedral arrangement of one silicon atom covalently bonded to four oxygen atoms (SiO_4^{4-}). This tetrahedral unit forms the fundamental building block of all silicate structures. Bonding within the tetrahedral unit is strong and primarily covalent due to the high charge density and small size of silicon.

Silicate structures arise from the different ways these tetrahedra can be linked and arranged in three dimensions. These arrangements lead to several main structural classifications:

- **Nesosilicates (Isolated Tetrahedra):** Tetrahedra are not linked, bonded by cations. Example: Olivine $(Mg,Fe)_2SiO_4$.
- **Sorosilicates (Double Tetrahedra):** Two tetrahedra share one oxygen atom. Example: Epidote $Ca_2(Al,Fe)_3(SiO_4)_3(OH)$.
- **Cyclosilicates (Ring Silicates):** Tetrahedra are linked in rings. Example: Beryl $Be_3Al_2Si_6O_{18}$.
- **Inosilicates (Chain Silicates):** Tetrahedra are linked in chains.
- Single chain: Example: Pyroxenes (e.g., Enstatite $MgSiO_3$).
- Double chain: Example: Amphiboles (e.g., Hornblende).
- **Phyllosilicates (Sheet Silicates):** Tetrahedra are linked in sheets. Example: Micas (e.g., Muscovite $KAl_2(AlSi_3O_{10})(OH)_2$), Talc $Mg_3Si_4O_{10}(OH)_2$. Weak van der Waals forces between sheets.
- **Tectosilicates (Framework Silicates):** Tetrahedra are linked in a three-dimensional network.
- Example: Quartz SiO_2, Feldspars (e.g., Albite $NaAlSi_3O_8$), Zeolites.

Bonding between tetrahedra involves the sharing of oxygen atoms, creating bridging oxygen. The overall charge balance is achieved through the incorporation of cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}) into the structure. The nature of the cation influences the properties of the silicate.

The degree of polymerization (the extent of tetrahedral linkage) dictates the dimensionality and resulting physical properties of the silicate. Increasing polymerization generally leads to increased structural rigidity and decreased reactivity. Aluminum can isomorphically substitute silicon in the tetrahedral network, creating a charge imbalance that is compensated by the inclusion of cations.

Question 2

What is a borane? Classification of boranes

STUDENT RESPONSE:

Boranes are compounds of boron and hydrogen, generally represented by the formula BnHm. They are characterized by non-classical bonding, deviating from the octet rule, and possessing unique structures.

Boranes are classified based on the number of boron atoms in their structure:

- **Monoboranes:** Contain a single boron atom, such as BH_3, which exists as the dimer diborane (B_2H_6).
- **Diboranes:** Contain two boron atoms, the most well-known being diborane (B_2H_6).
- **Triboranes:** Contain three boron atoms, e.g., B_3H_7.
- **Tetraboranes:** Contain four boron atoms, e.g., B_4H_{10}.
- **Pentaboranes:** Contain five boron atoms, e.g., B_5H_{11}.
- **Higher Boranes:** Containing six or more boron atoms, such as B_6H_{12}, B_7H_{13}, etc.

Further classification within these groups is based on structural isomers, denoted by Greek letters (α, β, γ, etc.). These isomers differ in the arrangement of hydrogen atoms on the boron cluster. For example, diborane has two main isomers: α-diborane (B_2H_6, the common form) and β-diborane (B_2H_6 with a different bonding arrangement).

Additionally, boranes can be categorized as:

- **Cloose Boranes:** Follow the general formula BnHm where $n > m/2$.
- **Nido Boranes:** Follow the general formula BnHm where $n = m/2$.
- **Arachno Boranes:** Follow the general formula BnHm where $n < m/2$.

These classifications relate to the degree of completion of the boron-hydrogen cluster and its structural similarity to 'cloos', 'nido' (nest-like) and 'arachno' (spider-web-like) shapes.

Question 3

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

STUDENT RESPONSE:

Inorganic heterocycles serve as versatile building blocks for constructing polymeric structures through various polymerization strategies. Examples include:

1. Polysilazanes from Tris(dimethylamino)silane: Cyclic silazanes, such as tris(dimethylamino)silane, undergo ring-opening polymerization, often initiated by moisture or heat, to yield polysilazanes [-(Si(CH3)2NH)-]n. These polymers exhibit ceramic properties upon pyrolysis.

2. Polysiloxanes from Cyclic Siloxanes: Octamethylcyclotetrasiloxane (D4) and other cyclic siloxanes are polymerized via ring-opening polymerization catalyzed by acids or bases, creating polydimethylsiloxane (PDMS) and related polysiloxanes. The ring strain in the heterocycle drives the polymerization.

3. Polyphosphazenes from Phosphazene Heterocycles: Linear or cyclic phosphazene heterocycles, like (NPCl2)n, can be polymerized through substitution of the chlorine atoms with various nucleophiles (e.g., alkoxides, amines) to generate polyphosphazenes with diverse properties depending on the substituent.

4. Polytiazoles from Thiazole Derivatives: Thiazole monomers containing polymerizable substituents can undergo condensation or addition polymerization to form polytiazoles. These polymers demonstrate interesting electronic and optical characteristics.

5. Boron-containing Polymers from Borole Derivatives: Borole rings, though less common, can be incorporated into polymer backbones through reactions involving the boron atoms, leading to polymers with unique boron-related properties.

6. Coordination Polymers utilizing Heterocyclic Ligands: Heterocyclic ligands containing nitrogen or sulfur atoms (e.g., bipyridine, terpyridine, thiophene) coordinate to metal ions, forming coordination polymers with varying dimensionalities (1D chains, 2D layers, 3D networks). The heterocycle provides the binding site for metal coordination.

Question 4

Crystalline defects

STUDENT RESPONSE:

Crystalline defects are deviations from the ideal periodic arrangement of atoms in a crystal lattice. They are broadly classified into point defects, line defects (dislocations), planar defects (grain boundaries, stacking faults, twin boundaries), and volume defects (voids, inclusions).

Point defects include: vacancies (missing atoms), interstitial atoms (extra atoms in the interstices), substitutional impurities (foreign atoms replacing host atoms), and Frenkel defects (vacancy-interstitial pair of the same atom), and Schottky defects (pairs of vacancies maintaining charge neutrality).

Line defects, or dislocations, are one-dimensional defects. Edge dislocations involve an extra half-plane of atoms inserted into the lattice, creating a strain field. Screw dislocations result from a shear stress, creating a spiral-like distortion. Mixed dislocations combine edge and screw components.

Planar defects are two-dimensional. Grain boundaries separate regions of different crystallographic orientation. Stacking faults are errors in the stacking sequence of atomic planes. Twin boundaries are mirror images of the crystal structure across a plane.

Volume defects are three-dimensional. Voids are empty spaces within the crystal. Inclusions are precipitates of a different phase.

The formation of defects is thermodynamically favored at higher temperatures. Defects influence mechanical properties (strength, ductility), electrical conductivity, diffusion rates, and chemical reactivity. Point defects increase with temperature according to the Boltzmann distribution. Dislocations allow plastic deformation. Defects can be introduced by plastic deformation, irradiation, or chemical reactions. Characterization techniques include X-ray diffraction (broadening of diffraction peaks), electron microscopy (direct observation of defects), and positron annihilation spectroscopy.

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 strongly dependent on both concentration and pH, leading to a series of polyoxovanadates with varying structures. At low concentrations and high pH (pH > 7), the predominant species is the isolated tetrahedral vanadate ion, VO_4^{3-}. As the concentration increases, and pH remains high, these tetrahedral units begin to share corners, forming linear chains of VO_3^-. Further condensation, with increasing concentration, leads to the formation of sheets, where tetrahedra share corners in two dimensions.

At intermediate pH values (pH ≈ 5-7), the polymerization process is more complex. Condensation of VO_4^{3-} units continues to form chains, but protonation of the vanadate ion to HVO_4^{2-} and $H_2VO_4^-$ becomes significant. This protonation alters the charge and coordination preferences, influencing the resulting structures. Dimers, such as $[V_2O_7]^{4-}$, become prevalent.

At low pH (pH < 3), extensive protonation to $H_2VO_4^-$ dominates. This species favors the formation of polymeric structures through corner-sharing, resulting in complex, three-dimensional networks. These networks often exhibit disordered structures with varying degrees of hydration. The final product under strongly acidic conditions is often a hydrated vanadium pentoxide ($V_2O_5 \cdot nH_2O$) precipitate. The specific polymeric species formed are highly sensitive to the exact pH and vanadium concentration, leading to a diverse range of polyoxovanadates.