

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,  $\text{VO}_4^{3-}$  as a function of concentration and pH

## Question 1

### Structure and bonding of silicates

#### STUDENT RESPONSE:

Silicates are a large and diverse group of inorganic polymers that are fundamentally composed of silicon and oxygen atoms, often in combination with various metals. The basic building block of silicate structures is the  $\text{SiO}_4$  tetrahedron, where a silicon atom is bonded to four oxygen atoms in a tetrahedral arrangement. These tetrahedra can be isolated or linked together in various ways, leading to a wide range of silicate structures.

The Si-O bond is a key factor in the structure and stability of silicates. It is a relatively strong bond with a significant degree of covalent character, although the degree of covalency can vary depending on the specific silicate and the other elements present. The linking of  $\text{SiO}_4$  tetrahedra occurs through the sharing of oxygen atoms, a process known as condensation or polymerization. This sharing can result in a variety of structural motifs, including isolated tetrahedra, pairs, rings, chains, sheets, and three-dimensional frameworks.

The classification of silicates is based on the manner in which the  $\text{SiO}_4$  tetrahedra are linked. For example:

- Nesosilicates have isolated  $\text{SiO}_4$  tetrahedra.
- Sorosilicates have pairs of tetrahedra sharing one oxygen.
- Cyclosilicates have rings of tetrahedra.
- Inosilicates have chains of tetrahedra, which can be single or double.
- Phyllosilicates have sheet structures.
- Tectosilicates have three-dimensional frameworks.

The bonding within silicates involves a combination of covalent Si-O bonds within and between the tetrahedra, and ionic or covalent interactions between the silicate anions and the metal cations present. The specific arrangement and the type of metal cations can significantly influence the properties of the silicate, including its stability, solubility, and potential applications.

Silicates are ubiquitous in nature, forming a major component of the Earth's crust, and they have numerous industrial applications, ranging from ceramics and glass to cement and zeolites used in catalysis and ion exchange.

## Question 2

What is a borane? Classification of boranes

### STUDENT RESPONSE:

Boranes are a class of compounds that consist of boron and hydrogen atoms. They are also known as boron hydrides. The simplest borane is  $\text{BH}_3$ , but it is not stable as a monomer and exists as a dimer,  $\text{B}_2\text{H}_6$ . Boranes can be classified into several categories based on their structure and composition.

Classification of boranes:

- closo-boranes:  $\text{B}_n\text{H}_n^{2-}$  ( $n = 5-12$ )
- nido-boranes:  $\text{B}_n\text{H}_n^{+4}$
- arachno-boranes:  $\text{B}_n\text{H}_n^{+6}$
- hypho-boranes:  $\text{B}_n\text{H}_n^{+8}$

They are classified based on their structure, which is related to the number of vertices in a polyhedron that the borane occupies, with closo having a complete polyhedron, nido having one missing vertex, arachno having two missing vertices, and hypho having three missing vertices.

## Question 3

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

### STUDENT RESPONSE:

Inorganic heterocycles have been utilized as precursors or monomers in the synthesis of various polymers. Examples include the use of cyclophosphazenes in the synthesis of polyphosphazenes, which are a class of inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms. These polymers have diverse applications due to their unique properties, such as thermal stability and flame retardancy.

Cyclosiloxanes are another example of inorganic heterocycles used in polymerization reactions, resulting in the formation of polysiloxanes, also known as silicones. These polymers are known for their flexibility, thermal stability, and resistance to chemicals.

Additionally, certain sulfur-nitrogen (S-N) rings, such as  $(\text{SN})_4$  or  $(\text{S}_3\text{N}_3)\text{Cl}_3$  derivatives, can be used as precursors to  $(\text{SN})_x$  polymers, which exhibit electrical conductivity.

Examples of these inorganic heterocycles and their corresponding polymers demonstrate the importance of these compounds in the development of advanced materials.

## Question 4

### Crystalline defects

#### **STUDENT RESPONSE:**

Crystalline defects refer to the imperfections or irregularities in the crystal lattice of a solid. These defects can be classified into several types based on their dimensionality.

\* Point defects (0-dimensional):

- Vacancies: absence of an atom or ion at a lattice site
- Interstitials: presence of an atom or ion at a non-lattice site
- Impurities: presence of a foreign atom or ion at a lattice site or interstitial site

\* Line defects (1-dimensional):

- Edge dislocations: a line defect where an extra row of atoms is present
- Screw dislocations: a line defect where the lattice is twisted

\* Planar defects (2-dimensional):

- Grain boundaries: interfaces between two crystalline regions with different orientations
- Stacking faults: errors in the stacking sequence of layers in a crystal

\* Volume defects (3-dimensional):

- Inclusions: presence of a foreign phase or particle within the crystal
- Voids: presence of empty space within the crystal

These defects can significantly affect the physical and chemical properties of a material, such as its electrical conductivity, mechanical strength, and reactivity. They can also influence the material's behavior in various applications, including its performance in catalytic reactions, its resistance to corrosion, and its optical properties.

### Question 5

Explain the polymerization of vanadates,  $\text{VO}_4^{3-}$  as a function of concentration and pH

**STUDENT RESPONSE:**

The vanadate ion,  $\text{VO}_4^{3-}$ , undergoes polymerization as a function of concentration and pH due to the ability of vanadium to expand its coordination sphere and form polyvanadates. At high pH and low concentration,  $\text{VO}_4^{3-}$  exists as a monomeric orthovanadate. As the concentration increases or the pH decreases,  $\text{VO}_4^{3-}$  polymerizes to form various polyvanadate species.

At lower pH, protonation of  $\text{VO}_4^{3-}$  occurs, leading to the formation of  $\text{HVO}_4^{2-}$  and  $\text{H}_2\text{VO}_4^-$ , which then condense to form divanadate ( $\text{V}_2\text{O}_7^{4-}$ ) and subsequently higher polyvanadates such as  $\text{V}_3\text{O}_9^{3-}$ ,  $\text{V}_4\text{O}_{12}^{4-}$ , and  $\text{V}_5\text{O}_{15}^{3-}$ . Further decrease in pH leads to the formation of decavanadate ( $\text{V}_{10}\text{O}_{28}^{6-}$ ), which is a major species at pH around 6-7 and consists of a complex structure with  $\text{VO}_6$  octahedra sharing edges and corners.

The degree of polymerization increases with decreasing pH and increasing concentration of vanadium. The polymerization process involves the condensation of vanadate units with the elimination of water, resulting in the formation of a variety of polyvanadate anions with different structures and charges.