**INORGANIC CHEMISTRY CUMULATIVE EXAM**
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**Silicon and sulfur chemistry in the earth system**

The inorganic chemistry of the earth system is important in many respects, including some involving life and environmental science. This cumulative exam considers some examples of basic inorganic chemistry that one might encounter in an earth science setting with the elements silicon and sulfur.

**1. (30 points) Polyatomic ions of silicon and oxygen.** Silicon and oxygen are the dominant elements in forming minerals on the earth. Many such compounds contain polyatomic ions with discrete $Si_yO_z^{x-}$ units, with the variables *x*, *y* and *z* determining the way the silicon-oxygen framework supports different minerals. For our purposes, these all have a silicon with four oxygens bound to it—though some oxygens can bridge between silicon atoms

(a-5 points) What is the expected three-dimensional structure of the simple silicate ion ($SiO_4^{4-}$)?

(b-5 points) Zircon is a ternary compound formed from zirconium and the simple silicate ion. Why would zirconium be expected to form such a compound so readily (hint—think oxidation states)?

(c-10 points) The simplest oligomer of silicate has two silicon atoms ($y$ = 2) and seven oxygen atoms ($z$ = 7). What will the structure of this be? What do you expect the *charge* to be?

(d-10 points) Silicon and oxygen can also form circular structures, for example, a trimer with the basic formula $Si_3O_9^{x-}$. What structure do you expect for this? What charge?

**2. (30 points). Silicon and oxygen in extended structures.** Silicon and oxygen, building off the basic framework of the simple polyatomic ions, form a huge variety of extended structures.

(a-10 points) Silicon-oxygen extended chains are found in minerals like asbestos. These cleave (break up) in needle like structures that can be very hazardous. They have a basic repeat unit that has a formula of $SiO_3^{x-}$ (with a negative charge). Draw a structure of a linear chain with this repeat unit. What do you expect will be the charge on a linear $SiO_3$ structure?

(b-20 points). The ultimate silicon oxygen structure has just silicon and oxygen.
i. What will be the formula of such a substance?
ii. What will be the three dimensional structure of the substance with this formula (answer with words, a drawing, or both)?
iii. What is an example of a commonly found silicon-oxygen binary mineral?

**3. (40 points)**. **The earth chemistry of sulfur.**

The following points relate to sulfur in the earth system, including biotic and human factors. Construct a diagram showing this information. You may label the steps with the letters given. Also, clearly indicate which of the steps represent biotic, abiotic, and human factors.

A. Sulfate in minerals dissolves to form sulfate in water

B. Sulfate in water is reduced to sulfide by bacteria

C. Sulfide in water is oxidized to sulfate by bacteria

D. Sulfate in water is absorbed by plants and becomes organic sulfur

E. Organic sulfur is eaten by herbivores and higher trophic levels

F. Animals and plants die and their organic sulfur is oxidized to sulfate in water

G. Animals and plants die and their organic sulfur is captured in fossil fuels

H. Fossil fuels are burned by humans and sulfur oxides enter the atmosphere

I. Sulfur oxides in the atmosphere become acid rain and become sulfate in water (a-10 points) An important pollution problem is caused by acid rain, such as with sulfuric acid. Describe how rain can come to have sulfuric acid in it.

(b-10 points) When we think of naturally occurring energy cycles involving chemical substances we naturally consider the carbon system, based, for example on $CH_4$ / $CO_2$. But, especially at hydrothermal vents in the deep ocean, there is a rich chemistry driven by the oxidation-reduction cycles of sulfur. Critical to this is the reduction of sulfate minerals by metals

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For each of the following example minerals, present a structure that shows how the Si-O bonding works to create the mineral's extended structure. In each case a specific property is listed. Point out how that property is explained by the structure.

(a) Quartz, with the empirical formula $SiO_2$. Refer to your structure and explain why quartz is very hard.

(b) Mica,

(c) Asbestos

(b) A ternary compound

(b)

The terms "oxidation" and "reduction" are, in their origin, derived from particular kinds of chemical transformation. Why is oxidation called oxidation? Why is reduction called reduction? Your answer should include a *specific experimental situation* that justifies the terms, with at least two chemical reactions that justify the observation and your answer should *not* use the term or concept of oxidation number or oxidation state.

**2. (10 points)** Define the term "oxidation state." Your definition should include two examples of specific chemical substances.

**3. (10 points)** Calculate the oxidation state for carbon  in the compound glucose ($C_6H_{12}O_6$). Compare it to the oxidation number of carbon in graphite (C). (HINT: You should find that these are the same). Does glucose contain the same kind of carbon as graphite? Explain your answer.

**4. (10 points)**. The Pauling Electroneutrality Principle stands as a powerful argument against the over-application of oxidation state as a concept. What is the Principle, and how does it differ from oxidation state? Give specific chemical examples.

**5. (15 points).** Assigning the oxidation state—and therefore the *d*-electron count—of transition metal ions in complexes is an important skill in inorganic chemistry. Determine the oxidation state and the *d*-electron count of the transition metal atom in the following complexes or substances.

(a) $CpFe(CO)_2$ (b) $Li_3Fe(CN)_6$

(c) Fe(TPP)Cl (TPP = tetraphenylporphyrin)

**6. (15 points)**. Strong debates can arise around oxidation states. For each of the following complexes, indicate how particular issues with the *ligands* can affect a calculation of the transition metal oxidation state. Which oxidation state would *you* prefer, and why?

(a) $Co(CO)_3NO$ (b) $CpCo(\eta^4\text{-}C_4Ph_4)$

**7. (15 points)** $\pi$-acceptor ligands are most commonly found with metals in low oxidation states. Why is this so?

**8. (15 points)**. One of the remarkable features of the lanthanides is the preponderance of the +3 oxidation state. Yet, some lanthanides also have significant chemistry with other oxidation states. Examples include cerium (atomic number 58, oxidation state +3 or +4), samarium (atomic number 62, atomic number oxidation state +2 or +3) and ytterbium (atomic number 70, oxidation state +2 or +3). Explain the preponderance of the +3 oxidation state with the lanthanide elements and also why these three lanthanides can vary from the +3 state. (NOTE: you do not need a periodic table for this. If you need to think about the electron configuration of the element, work it out from the atomic number).