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A discussion of formulae of finite silicates

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Abstract

This article derives exact formulae for the structures of finite inosilicates [1], and clears a few misconceptions that students commonly have about formulae of polymeric silicates [1]. This article also discusses a few salient points regarding silicates and why the misconceptions arise at the first place, and how pedagogy can be modified to ensure such incorrect notions don't arise in students minds.

1 Introduction

Silicates are around us everywhere.From our ceramic utensils to our detergents, silicates are a very versatile group of chemical polymers that can be fashioned into many things of our daily usage.Thus, a study of silicates is commonly included in high school syllabi across the world.Despite this fact,many students have misleading notions about various fundamental aspects of this science, such as how there can be a fractional number of shared oxygens per silicon atom in double sheet silicates(a type of inosilicate[1]), or how the actual formula of a finite inosilicate differs slightly from that expected from the formula of its monomer.

This paper originated when the author tried to solve a doubt posed by a student, which went as follows:

If we manually evaluate the actual formula of a finite linear chain silicate of length, say 4, we notice that it comes out to be $Si_4O_{13}{}^{-10}$, not the expected $Si_4O_{12}{}^{-8}$ from the formula of its monomer.Then what is it that went wrong?

During the solution process the author realized that the solution of the problem could be generalized very naturally. The generalization method also clarifies many prevalent conceptual flaws in the minds of new chemistry learners.This motivated the authors to present and explain a few salient points about this issue to bring out more clarity in the mind of learners.[2]

2 Theory

We observe that Si being a Group 14 element has a valency of 4, and thus generally forms compounds with a tetrahedral coordination, such as, its polymeric compounds with oxygen, also known as silicates.To easily represent silicon's 3-dimensional compounds with oxygen, thus, a system of drawing these structures was established, which we shall briefly explain below:

In any silicate, the silicon atom itself is represented as a dot, while the oxygen atom(s) it's bonded to are represented as small circles.The whole tetrahedral structure is then viewed along a Si-O bond, and the paper on which we have
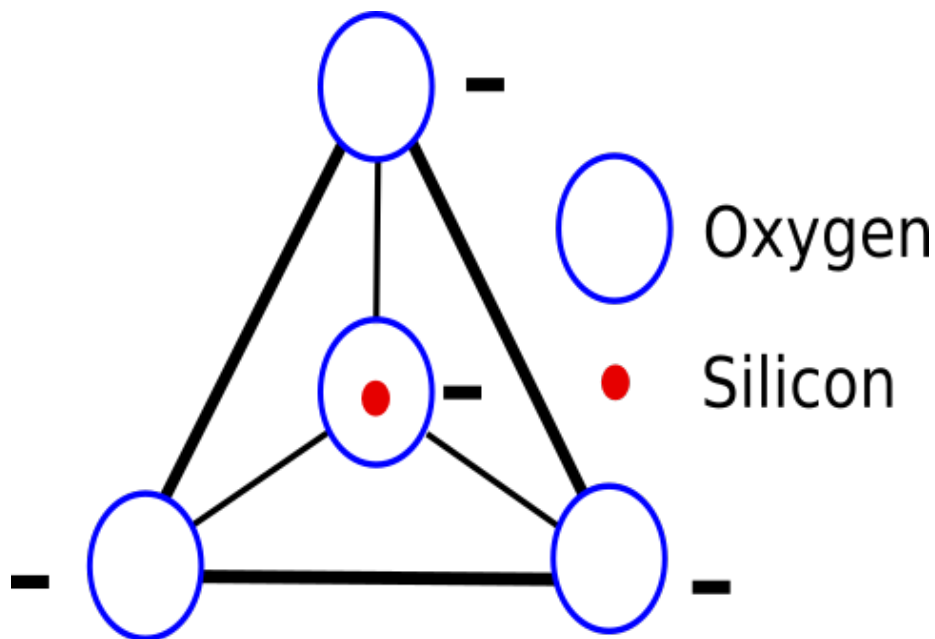
Figure 1: Orthosilicate diagram as pretext of explanation of silicate structure drawing

to represent the tetrahedron is in the plane on which the other 3 oxygen atoms are situated.We can then view the structure as a triangle with vertices as small circles, and at the centre of the triangle, we have another small circle with a dot at its centre (such a projection is known as an orthographic projection).
The representation so, of the anionic part of the simplest silicate there is, ie:- nesosilicate ($SiO_4{}^{4-}$) [1], is given in Figure 1:

Also note the fact that since oxygen has a valency of 2, if ever it is only singly bonded to some atom, then it must also bear a negative charge to complete its octet.Hence the negative charge on all the oxygen atoms in the orthosilicate, because all of them are bonded to a single atom only,ie:- silicon.This observation is of great importance in determining the total charge on a large silicate structure.

Thus after having set these things in order, we now proceed to discuss the main issue of the article below.For reasons that will become clear to the reader after further perusal, we proceed to discuss inosilicates (single and double chain silicates) first, parting from the common pedagogical order.

2.1 Single Chain Silicates

Single chain silicates, also known as pyroxenes [1], are basically a polymeric form of silicates wherein the basic "repunits" (repeating units) are the tetrahedral units of orthosilicates connected to each other [2], in a linear fashion, as shown in Figure 2:
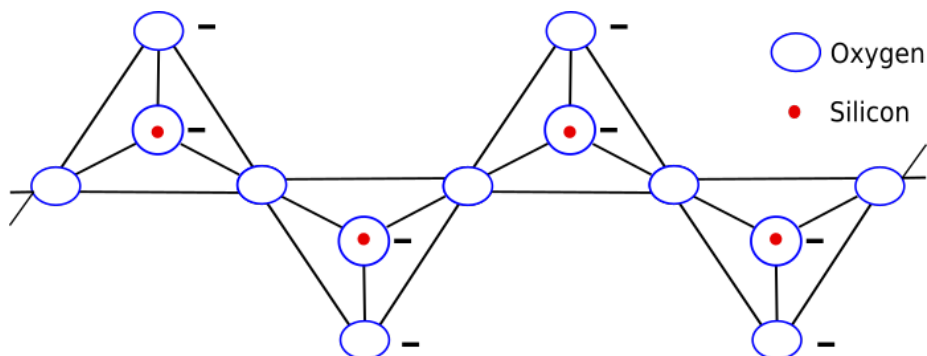
Figure 2: Single Chain Silicates, the simplest silicate polymers

Returning to the doubt posed by the student, we first have to understand first how the formula of the monomer is actually derived, as explained:

It's clear that there are 2 shared oxygens per tetrahedron.Thus, in a convention also used in many other parts of physical chemistry [2] (such as in the analysis of unit cells in crystalline compounds), it's assumed that **half of every shared oxygen belongs to a particular repunit**.Add to this the Si and two O^- already in the repunit, we get the monomer SiO_3^{2-}.

This also clarifies why the actual formula of a finite silicate won't tally with formula expected from the monomer: Because in the actual compound, the terminal tetrahedrons have only one oxygen shared, thus causing the mismatch of formulae.

If that is the case, then how do we derive the actual formula of a linear chain silicate with n silicon atoms?There are two methods by which one can do so, which are as follows:

2.1.1 Method 1

Take a linear chain silicate of length n. It contains $(n-2)$ SiO_3^{2-} repunits (the non-terminal tetrahedra), while the terminal tetrahedra have a formula of $SiO_{3.5}^{3-}$ (Why? Because the terminal tetrahedra have only one oxygen shared, that's why the other half (shared) oxygen which we used to deduct from SiO_4^{4-} to obtain our repunit must be added back again, and that erstwhile-shared-but-now-free oxygen will also add a negative charge to our repunit).

Hence the actual formula comes out to be $Si_nO_{3(n-2)+3.5(2)}^{2(n-2)+3(2)}$; which is $Si_nO_{3n+1}^{-2(n+1)}$.

Thus the desired formula is $\mathbf{Si_nO_{3n+1}^{-2(n+1)}}$.

2.1.2 Method 2

Observe that since we're talking of linear oligomers, the number of oxygen atoms and charge of the anionic compounds will be linear functions of the number of silicon atoms.Since any linear function can be uniquely determined by 2 data points, we can manually evaluate the formulae of linear chain silicates of length say, 2 and 4, and then evaluate the general formula for oligomers of length n.

Proceeding thus, let's assume our formula to be $Si_nO_{an+b}^{-(cn+d)}$, where a,b,c,d

are coefficients to be determined.We also manually determine the formulae to be $Si_2O_7{}^{-6}$ and $Si_4O_{13}{}^{-10}$ for n equaling 2 and 4 respectively (note how the $n = 2$ case yielded the formula for a **pyrosilicate**). Equating the coefficients yields:

$$2a + b = 7 \tag{1}$$
$$4a + b = 13 \tag{2}$$

$$2c + d = 6 \tag{3}$$
$$4c + d = 10 \tag{4}$$

Solving the equations yields $a = 3$; $b = 1$; $c = 2$; $d = 2$, and thus the desired formula is $\mathbf{Si_nO_{3n+1}{}^{-2(n+1)}}$.

Even though the second method is mathematically perfectly sound, it's regarded by the authors to be less intuitive regarding its exposition of the chemical nature of the inosilicates under investigation, and thus they recommend the first method more strongly.

From this relatively simple case of linear chain silicates, we shall now proceed onto the more difficult case of double chain silicates, which are another category of inosilicates.

2.2 Double Chain Silicates

Double Chain Silicates, also known as **amphibole** silicates [1] have a structure as shown in Figure 3:
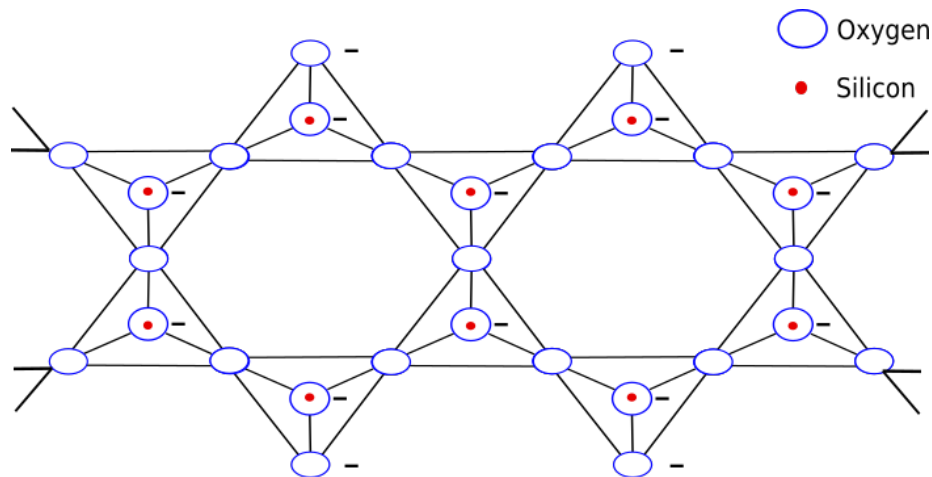

Figure 3: Double Chain Silicates

Even the repunit of an amphibole silicate has a complicated structure, as shown in Figure 4:
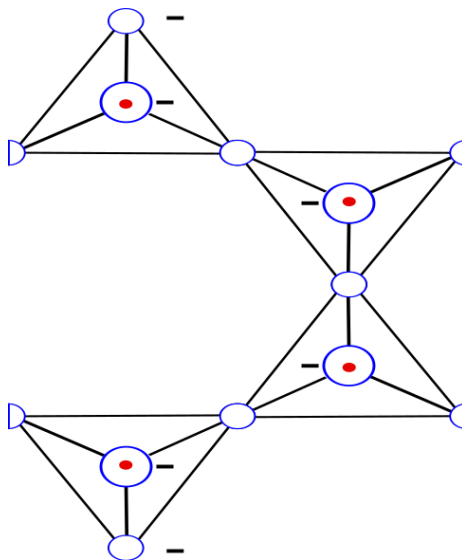
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Figure 4: Repunit of amphibole silicates, with the semi-circles highlighting half a shared oxygen

Let's explain the structure of this repunit: Two central tetrahedra are connected to the two terminal tetrahedra as well as to themselves, thus having 3 shared oxygen atoms per tetrahedron.Meanwhile, the two terminal tetrahedra are only connected to the central ones and to the tetrahedra in the next repunit, thus having only two shared oxygen atoms per tetrahedron.This brings us to our first conclusion, that, **on an average, the number of shared oxygens per tetrahedron in a double chain silicate is 2.5**.Following this, one can also quickly tally out the number of oxygens and the total charge on the repunit (with the convention of only half a shared oxygen being counted into our repunit) to get the formula of the monomer to be $Si_4O_{11}{}^{6-}$.As discussed previously, one can see even more clearly now why the formula expected from the monomer would differ from the actual formula in the finite case.
So we now commence the derivation of the actual formula as shown below:

2.2.1 Method 1

Unlike in the case of linear chain silicates, note that a double chain silicate of any arbitrary length is not possible: More precisely stated,if one extends the above repunit k times, then the total number of silicon atoms in the compound must be $4k + 6$, as is made clear by Figure 5:
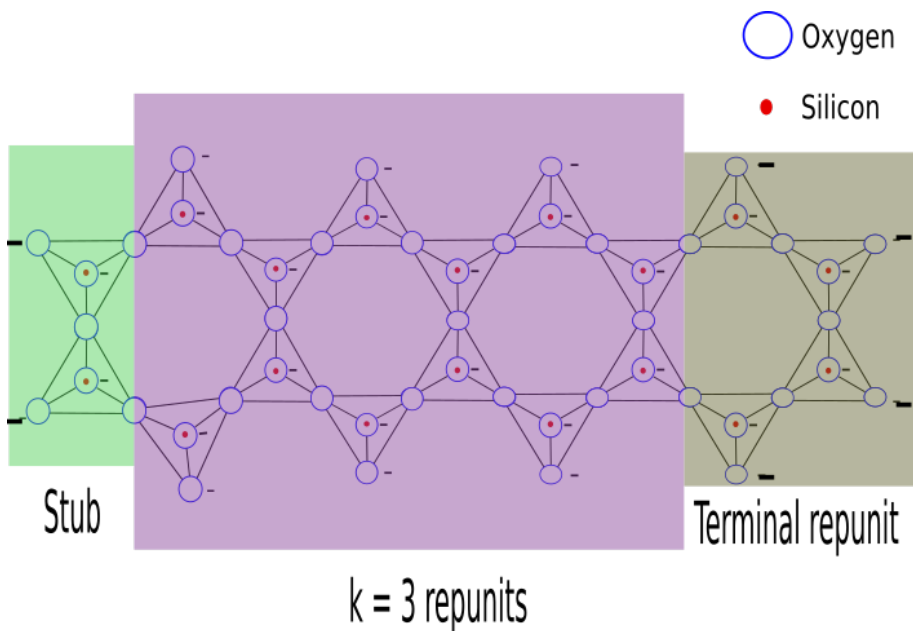
Figure 5: Diagram for the derivation, with different colours to highlight different phases of the derivation

In fact, a closer study of the diagram shows us the way : Note that for representing n ($= 4k + 6$) silicon atoms, one needed $(n - 6)/4$ "complete" repunits (of formula $Si_4O_{11}{}^{6-}$), one "terminal" repunit (of formula $Si_4O_{12}{}^{8-}$: Why? Because unlike the complete repunits, this unit was not connected in both sides to some other unit, thus "liberating" two half shared oxygens, increasing the tally of oxygens by one.Moreover, this oxygen atoms each also bring a negative charge of their own, thus adding to the charge count by 2) and a "stub" (of formula $Si_2O_6{}^{4-}$: Why? Note that this "stub" is a result of a "pyrosilicate" structure sharing two half oxygens.Thus we have to deduct a total of one oxygen but both of their charges from $Si_2O_7{}^{6-}$), thus making the net formula of the oligomer out to be $Si_nO_{11(n-6)/4+12+6}{}^{6(n-6)/4+8+4}$, ie:- $Si_nO_{(11n+6)/4}{}^{-(3n+6)/2}$. Thus the desired formula is $\mathbf{Si}_n\mathbf{O}_{(11n+6)/4}{}^{-(3n+6)/2}$.
One may note that the coefficient of oxygen and the charge of the compound are integers since n is of the form $4l + 2$, where l is an integer greater than or equal to 1.

2.2.2 Method 2

As in the previous section, we can conclude similarly here too that the number of oxygen atoms and the total charge of the oligomers will be linear functions of the number of silicon atoms, and proceed as we had done earlier.But since the case of double chain silicates is much more complex than its linear counterpart, manually counting the total number of oxygens and charge is more prone to mistakes here, further building up the case against acting upon this method (apart from the still valid criticism of being chemically unintuitive).
Hence the authors decided not to explicitly show the calculations under this

section, though readers may attempt it if they wish to.

2.3 A Few Salient Points

Readers may legitimately wonder why instead of covering the cases of phyllosilicates or tectosilicates, the authors moved on to a section of concluding nature.Thus, we shall explain the cases of phyllosilicates and tectosilicates and a few other things below.

- **Phyllosilicates** It's amply clear from the above discussion that phyllosilicates [1], also known as "2-D Sheet Silicates", of a finite size will not have the formula $(Si_2O_5)_n{}^{2n-}$.Then why is that we didn't derive the exact formula for a finite phyllosilicate? Because phyllosilicates have a two dimensional polymeric structure, **the exact shape of a finite phyllosilicate is ill-defined, unlike in the case of inosilicates which, owing to their linear structure have well defined shapes for all** n**.** Think of it this way: there will be multiple ways of packing, say 20 silicon atoms in a phyllosilicate framework.Each will have different numbers of terminal tetrahedra, thus having different formulae.
  Thus any attempt to find the "actual" formula of a finite phyllosilicate must be dealt on a case-to-case basis.

- **Tectosilicates** The above given logic hold for tectosilicates [1] too, just that they are more complex due to their three -dimensional cross-linking.Not only that, but also since all oxygens are shared per tetrahedra in a tectosilicate, **the "monomer" of a tectosilicate is uncharged**.In fact, the source of charge in tectosilicates originates from charged non-tetravalent elements (mostly aluminium) substituting for silicon atoms in the 3-D framework.This just adds another dimension of complexity to any exact calculation of the formula for a tectosilicate.

- **Asymptotic Nature of the formulae of oligomers** Observe that the two formulae for the finite inosilicate oligomers which we found out asymptotically tend to the formulae of the integral multiples of monomers as n grows very large.This elucidates to us the true purpose behind expressing the formulae of polymeric silicates as multiples of their monomers: For unknown (presumed to be very large) n, the difference between the actual formulae and the empirical ones become negligible for practical purposes. One may observe that in sub subsection 2.1.2, using the above insight, one could have directly predicted the values of a and c to be 3 and 2, respectively, from the formula of the monomer, ie:-$SiO_3{}^{2-}$.

- **Misconceptions and pedagogy** The above nuances however, are not mentioned in famous textbooks of inorganic chemistry, which gives rise to wrong notions among students: In a very interesting misconception that one of the authors found among one of his students, when the student was asked what sort of silicate was the (hypothetical) compound $Na_{16}Si_7O_{22}$ (after solving the doubt stated in the introduction and presenting the $n = 7$ case), and after realising that the compound did not match any of

the expected formulae of silicates, she suggested that perhaps the compound was a **mixed salt of two or more silicates**. It is rather concerning to see that if not we had known that it was a linear chain silicates of length 7, that was a very real possibility.

One may note that in [2], in Fig.16.19 on page 181, Muller et. al. has captioned the diagrams for the (silicate part of the) structures of Wollastonite and Enstatite as $(SiO_3{}^{-2})_\infty$, recognising that the formula has boiled down to a multiple of the empirical one only due to the very large chain length (tending to infinity) of the silicate involved. However, this nuance is not elaborated upon and this may lead to some student missing the point behind that (infinity) subscript.

It's precisely to avoid such types of situations that mentioning such intricacies explicitly in textbooks and other pedagogical references is so necessary.

- **Similarity in formulae of various silicates** As pointed out earlier, the formula for a **pyrosilicate** is in fact the simplest case of the formulae for pyroxenes (the $n = 2$ case): Then why is it that these are classified separately? A reason not very different from the reason why disaccharides and oligosaccharides are classified separately in biochemistry: Because polymerisation can potentially destroy reactive sites of the monomer (in the case of saccharides, the anomeric hydroxy group), thus leading to different chemical properties.

- **How cyclic silicates are described exactly by their formulae** It's obvious why orthosilicates and pyrosilicates have exact formulae: Their sizes are uniquely defined. However, it turns out that even **the formula for a cyclic silicate of size** n **$((SiO_3)_n{}^{2n-})$ is exact**: Why? The reason for formulae of oligomers of inosilicates differing from being integral multiples of their repunits is due to the differing **topology** of a terminal repunit from a non-terminal one in a linear arrangement, while in the cyclic case (a "circular" arrangement), the topology of every repunit is identical.

  By this, it's meant that in a linear arrangement, the terminal monomer isn't bound to other groups on both sides (unlike non-terminal monomers), thus leading to differences in it's molecular formulae, while in a circular arrangement, one can't make the distinguishment between terminal and non-terminal monomers itself!

3   Conclusions

Throughout the article, we attempted to clear various misconceptions about silicates, such as how it's possible to have a fractional number of oxygen atoms shared per tetrahedron in a double chain silicate (due to the different numbers of oxygens shared per tetrahedron within the monomer itself) and derived exact formulae for finite length inosilicates ($Si_nO_{3n+1}{}^{-2(n+1)}$ and $Si_nO_{(11n+6)/4}{}^{-(3n+6)/2}$ for linear and double chain silicates respectively). Near the end we also elucidated various finer points about silicates and their formulae, such as why it's not possible to characterise exact formulae for phyllosilicates and tectosilicates, or why the formula for cyclic silicates was exact for any length. Finally, we also suggested

how pedagogy could be modified to better represent the nuances mentioned in this article to students.

References

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