

## 7.9: Comparison Between Silicon and Carbon

An understanding of the differences between carbon and silicon is important in understanding the relative chemistry of these Group 14 elements.

### Size

As expected silicon is larger than carbon due to the presence of a second shell: i.e.,  $C = 1s^2 2s^2 2p^2$  while  $Si = 1s^2 2s^2 2p^6 3s^2 3p^2$ . A comparison of the relative sizes of carbon and silicon are given in Table 7.9.1.

Table 7.9.1: Atomic, covalent, and van der Waals radii of carbon and silicon.

Element	Atomic radius (Å)	Covalent radius $sp^3$ (Å)	van der Waal radius (Å)
C	0.70	0.75	1.70
Si	1.10	1.14	2.10

Covalent and van der Waal radii from [Royal Society of Chemistry Online Periodic Table](#). [Webelements](#) has a more detailed discussion of all three types of radii, the atomic radii quoted here are empirical.

### Coordination number

Carbon is known to have a coordination number of 2, 3, and 4 in its compounds depending on the hybridization. A coordination number of 1 can also be considered for CO and  $CN^-$ . Four-coordinate carbon may be considered to be coordinatively saturated. In contrast, in the absence of overwhelming steric bulk, silicon is observed to have coordination numbers of 3, 4, 5, and 6. Examples of five and six-coordinate silicon include  $Si(acac)_2Cl$  and  $SiF_6^{2-}$ , respectively. Coordination numbers of higher than 4 have been ascribed to the use of low-lying  $d$  orbitals; however, calculations show these are not significant. Instead, hypervalent silicon is better described by the formation of 3-center molecular orbitals, e.g., Figure 7.9.1.

#### Note

A hypervalent molecule is a molecule that contains one or more typical elements (Group 1, 2, 13-18) formally bearing more than eight electrons in their valence shells.

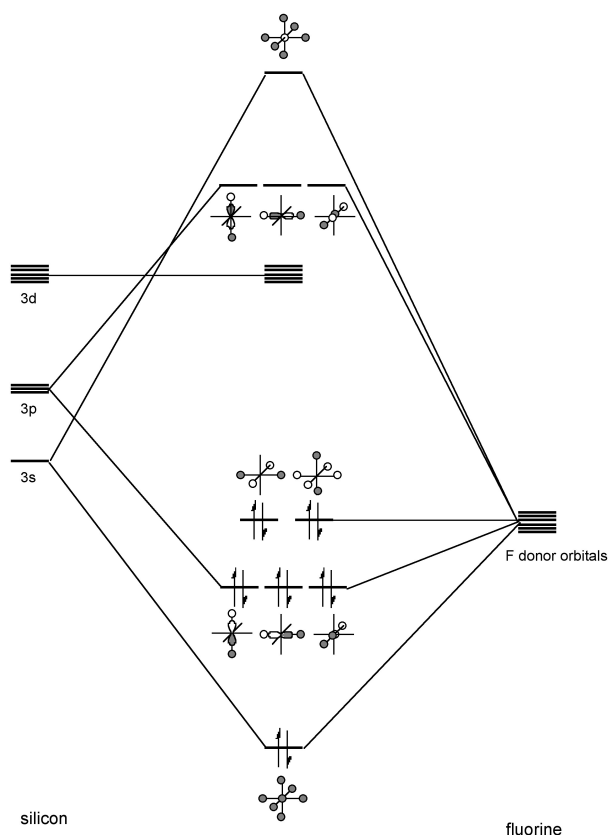


Figure 7.9.1: Molecular orbital diagram for  $\text{SiF}_6^{2-}$ .

## Electronegativity

The electronegativities of silicon and carbon are given in Table along with hydrogen. Since carbon is more electronegative than hydrogen the C-H bond is polarized towards carbon resulting in a more protic hydrogen (Figure 7.9.2a). In contrast, the lower electronegativity of silicon results in a more hydridic hydrogen (Figure 7.9.2b). This difference is reflected in the reaction chemistry of  $\text{SiH}_4$  versus  $\text{CH}_4$ .

Table 7.9.2: Selected Pauling electronegativity values. [Royal Society of Chemistry Online Periodic Table](#)

Element	Pauling scale
C	2.55
H	2.20
Si	1.90

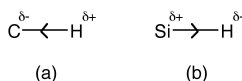


Figure 7.9.2: Relative polarization of C-H and Si-H bonds.

## Bond energies

The E-E and E-O bond energies for carbon and silicon are given in Table 7.9.3. The bond energy for a C-C bond is slightly greater than for a C-O bond, while the Si-O bond is significantly stronger than the Si-Si bond. This difference is reflected in the chemistry of silicon versus carbon compounds. The chemistry of carbon is dominated by catenation: the ability of a chemical element to form a long chain-like structure via a series of covalent bonds. Although silicon does form Si-Si bonds, they are far more reactive than their C-C analogs, and polymers of silicon are predominantly comprised of Si-O chains (as a result of the very strong bond).

Table 7.9.3: Selected bond energies for carbon and silicon. [Royal Society of Chemistry Online Periodic Table](#)

Element	E-E bond energy (kJ/mol)	E-O bond energy (kJ/mol)
C	345.6	357.7
Si	222	462

## Multiple bonds

While unsaturated compounds for carbon (i.e., alkenes and alkynes) are common, the analogous silicon compounds (disilenes) were only reported in 1981, and disilynes in 2004. The Si=Si double bond lengths are 2.14 - 2.29 Å which is 5 - 10% shorter than the Si-Si single bond lengths. This bond shortening is less than *ca.* 13% in carbon compounds.

### Note

The traditional lack of multiple bonds for the Period 3 elements and lower led to the formulation of the double bond rule which states that *chemical elements with a principal quantum number greater than 2 do not form multiple bonds (e.g., double bonds and triple bonds) with themselves or with other elements*. This rule was made obsolete starting from 1981 with the discovery of silicon and phosphorus double bonds. Double bonds that would ordinarily not form can be stabilized with proper functional groups through kinetic stabilization, i.e., either electronically or sterically.

## Bibliography

- R. West, M. J. Fink, and J. Michl, *Science*, 1981, **214**, 1343.
- A. Sekiguchi, R. Kinjo, and M. Ichinohe, *Science*, 2004, **305**, 1755.

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