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The nature of silicon–oxygen bonds

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Abstract

Donnay and Donnay (1978) have stated that an electron-density determination carried out on low-quartz by R. F. Stewart (personal communication), which assigns charges −0.5 to the oxygen atoms and +1.0 to the silicon atoms, shows the silicon–oxygen bond to be only 25 percent ionic, and hence that "the 50/50 description of the past fifty years, which was based on the electronegativity difference between Si and O, is incorrect." This conclusion, however, ignores the evidence that each silicon–oxygen bond has about 55 percent double-bond character, the covalence of silicon being 6.2, with transfer of 2.2 valence electrons from oxygen to silicon. Stewart's value of charge +1.0 on silicon then leads to 52 percent ionic character of the bonds, in excellent agreement with the value 51 percent given by the electronegativity scale.

Donnay and Donnay (1978) have recently referred to an "absolute" electron-density determination carried out on low-quartz by R. F. Stewart, and have stated that "It shows the Si–O bond to be 75 percent covalent and only 25 percent ionic; the 50/50 description of the past fifty years, which was based on the electronegativity difference between Si and O, is incorrect."

I formulated the electronegativity scale in 1932, and in 1939, in the first edition of my book *The Nature of the Chemical Bond,* p. 74, I wrote that "The Si–O bond is of especial interest because of its importance in the silicates. It is seen to have 50 percent ionic character, the value of $x_O - x_{Si}$ being 1.7." Here x is the electronegativity, 1.8 for silicon and 3.5 for oxygen. The value 50 percent comes from a curve (p. 70) relating the amount of ionic character of a bond to the difference in electronegativity of the atoms, the principal experimental basis for the curve being the observed values of the electric dipole moment of molecules. The curve in fact gives 51 percent, which does not differ significantly from 50 percent.

Stewart (private communication) has shown by a careful determination of the electron density in low-quartz that a reasonable assignment of electrons to silicon and oxygen leads to the resultant charge +1.0 on each silicon atom and −0.5 on each oxygen atom. If we assume that there is a covalent bond with partial ionic character between each silicon atom and each of the four surrounding oxygen atoms, this observation leads to the conclusion that the amount of ionic character in the silicon–oxygen single bond is 25 percent. It is, however, not justified to make this assumption.

In the first edition of my book (1939) I pointed out that the observed Si–O bond length in silicates, given as 1.60A, is about 0.20A less than the sum of the single-bond radii of the two atoms (p. 222), and I wrote a valence-bond structure representing all four atoms as attached to the central atom by double bonds (p. 224). Some years later (1948) I formulated the electroneutrality rule. This rule is based on the argument that a large amount of energy is needed to remove a second electron from a singly-charged cation, and a singly-charged anion has zero or negative electron affinity. It states that in most stable molecules and crystals each atom is close to being electrically neutral, with its residual charge lying within the limits +1 and −1. If we accept the assignment of 50 percent partial ionic character to the Si–O bonds, the electroneutrality principle rules out a structure for tetrahedral silicate in which there are single bonds between the silicon atom and each of the four surrounding oxygen atoms, because this structure places a charge +2 on the silicon atom. In the third edition of my book (1960) a more thorough discussion of the structure of tetrahedral silicates is given, beginning on p. 320 and based upon an equation (p. 241) for bond length of bonds in which a single bond is in resonance with multi-bonded structures involving both the p_x and p_y orbitals. The observed Si–O bond length was taken as 1.61A, in agreement with the value 1.610(9)A given by Baur (1978) as the average for 64 compounds in which the silicate group shares oxygen atoms with other tetrahedral Al, B, Ga, P, or Si atoms. The result of this consideration of the observed bond length is that the bond number for each silicon–oxygen interaction is placed at 1.55, the covalence of silicon being 6.2, with transfer of 2.2 valence electrons from the oxygen atoms to each silicon atom. Stewart's value +1.0 for the resultant charge on the silicon atom then leads to 51.6 percent ionic character of the bonds [(1 + 2.2)/6.2], in excellent agreement with the value 51 percent expected from the electronegativity difference.

For the oxygen atom, as the resonance occurs between single and double bonds, the bond orbitals for the structures with two single bonds formed by the oxygen atom, and a single bond and a double bond have mostly *p* character, whereas those for the structure with two double bonds have sp^3 character. For the silicon atom the bonds may be considered to be essentially of the sp^3d^2 type, permitting each silicon atom to form two single bonds and two double bonds, which resonate among the four positions determined by the four surrounding oxygen atoms.

Support for this description of the bonds is given by a calculation of the value of the Si–O–Si bond angle. The angles corresponding to the greatest stability for the structures with two single bonds formed by the oxygen atom, a single bond and a double bond, a double bond and a single bond, and two double bonds are 108°, 114°, 114°, and 180°, respectively. If we allow the single and double bonds of the two adjacent silicon atom to resonate independently into the two positions and accept 55 percent of double-bond in each position, the four structures for the oxygen atom contribute 0.2025, 0.2475, 0.2475, and 0.3025, respectively. With the assumption of Hooke's law for the dependence of the strain energy on the deviation of the angle from the most stable values for the individual structures, and with the Hooke's-law constants in the ratios 1:2:3, the equilibrium angle is calculated to be 141.9°, in good agreement with the observed value, 143.68° (Le Page and Donnay, 1976). The calculated value is not very sensitive to the assumptions; thus for constants in the ratios 1:2:4 it is 146.6°.

The bond angle Si–O–X depends upon the values of the bond number *n* for both Si–O and O–X, the value 141.9° being that for $n = 1.55$ for each. When *n* is 1 for O–X, as in $Si(OCH_3)_4$, the calculated value of the bond angle is 111.3°, in good agreement with the experimental value, 113±2° (Pauling, 1960, p. 322).

The deviation of the bond number 1.55 from the value 3/2 may not be significant. Accordingly a simple approximate description of binding in low-quartz and similar silicate crystals may be given. Each of the two oxygen atoms donates an electron to a silicon atom, permitting it to form six covalent bonds (two double bonds and two single bonds) with its four oxygen neighbors. These bonds have about 50 percent ionic character, leading to acceptable values of the resultant charges, −0.5 for oxygen and +1.0 for silicon.

In order to avoid confusion, I point out that I here use the word bond to refer to a structure involving two shared electrons, with one atomic orbital on each of the two bonded atoms. A double bond involves two shared electron pairs, and a triple bond involves three. Thus the gas molecule PN can be ascribed the triple-bond structure $:\mathrm{P} \equiv \mathrm{N}:$. The amount of partial ionic character per bond is one third of the magnitude of the charge on each of the two atoms. With this definition, 100 percent of ionic character of all three bonds would correspond to the extreme ionic structure $:\mathrm{P}^{3+}\ :\underset{\cdot\cdot}{\ddot{\mathrm{N}}}:^{3-}$. Another possible way of discussing the matter is to define a bond as the whole complex of interactions between the two bonded atoms, with the amount of ionic character equal to the charge on either atom (or the fraction determined by the ligancy). For PN the amount of ionic character on this basis would be three times that per shared-electron-pair bond, and the extreme ionic structure would be described as having 300 percent of ionic character.

I have striven, following Gilbert Newton Lewis, to formulate a reasonably simple, logical, and consistent theory of the shared-electron-pair chemical bond, and I have tried to make it consistent with the fundamental principles of quantum mechanics. An advantage of the shared-electron-pair approach is that it takes the transfer of an electron from one atom into the otherwise unused atomic orbital of another atom into account. Thus I contend that in quartz each oxygen atom, on the average, transfers one electron to a silicon atom. The silicon atom then has six valence electrons, each in its sp^3d^2 orbital, and a corresponding formal charge −2. With 50 percent ionic character of each of the six bonds, the resultant charge is changed from −2 to +1. Thus the charge of the atom is the result of two kinds of electron transfer: transfer into a previously unoccupied orbital, increasing the number of electron-pair-bonds that can be formed, and transfer of charge within the bond, resulting from the difference in electronegativity of the two bonded atoms. In quartz the second effect transfers three electronic charges from the silicon atom to the adjacent oxygen atoms, which is 1/2 of a charge for each of the six electron-pair bonds that it forms; that is, these bonds have 50 percent ionic character.

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