

Pentacoordinate Silicon Intermediate States During Silicate Condensation and Decondensation. Crystallographic Support

F. LIEBAU

Mineralogisches Institut der Universität, 2300 Kiel, FRG

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In compounds $pM_m A_n \cdot qSiA_r$, the tendency of silicon to have coordination numbers higher than four increases with increasing pressure and with increasing electronegativity of A and M. A stereochemical analysis of 15 crystal structures reported to contain $[SiA_5]$ groups indicates that there is a continual change from an $[SiA_4]$ tetrahedron in a hexagonal close-packed array of A atoms to an $[SiO_5]$ trigonal bipyramid.

Following Dunitz' reaction-path concept it is suggested that this observation reflects an atomistic mechanism taking place during reactions of silicates. Mechanisms are proposed for condensation and decondensation reactions of silicates in aqueous solutions and in melts that involve $[SiO_5]$ groups as intermediates. Since the average lifetime of $[SiO_5]$ intermediates should increase with pressure, reaction rates of silicates in water and melts should pass a maximum when the lifetimes of $[SiO_4]$ and $[SiO_5]$ become comparable. Provided that the lifetime of $[SiO_6]$ reaches appreciable values only at pressures for which the lifetime of $[SiO_4]$ approaches zero, a second reaction rate maximum may exist at even higher pressures when lifetimes of $[SiO_5]$ and $[SiO_6]$ become comparable.

Introduction

In the overwhelming majority of silicates silicon is tetrahedrally coordinated by four oxygen atoms. In addition, a small number of phases is known in which silicon is octahedrally surrounded by six oxygen atoms. No phase has been found so far in which silicon is pentacoordinated by five oxygen atoms. This sometimes misleads silicate scientists—in chemistry as well as in materials science and geoscience—to assume that the mechanical properties as well as reaction kinetics of silicates can be interpreted on the basis of $[SiO_4]$ and $[SiO_6]$ as the only silicon-oxygen polyhedra existing. For example, geoscientists assume that in the earth's interior below a certain depth silica and silicates contain silicon in octahedral coordination whereas the coordi-

nation of silicon is tetrahedral above this zone (e.g. [1]). It has been suggested that condensation of low-molecular silicic acids to polymeric ones and decondensation of polymeric silicic acids in aqueous solution takes place by a temporary change of the coordination number of silicon from four to six [2].

On the other hand, a number of silicon organic compounds are known which contain $[SiA_5]$ groups with one or several of the ligands A other than oxygen, such as C, N, F or Cl. Considering $[SiO_n]$ polyhedra as special cases within the group of $[SiA_n]$ polyhedra should give further indications as to the stability of $[SiO_5]$ polyhedra.

Influence of the Electronegativity of Ligands and of Pressure on the Coordination Number of Silicon

The coordination number of silicon, CN(Si), is strongly dependent on the electronegativity of its ligands. This is clearly visible for instance from the data (Table I) on addition compounds of methylhalogenosilanes and pyridine reported by Hensen and Busch [3]. Within the series of systems $(CH_3)_{4-n}Si-Br_n$ -pyridine the coordination number of silicon

TABLE I. Melting Points in Degrees Kelvin of Addition Compounds of Methylhalogenosilanes and Pyridine. Values in brackets are incongruent melting points. +, phase exists, no melting point available. -, no addition compound exists.

| M | M CN(Si) = 4 | M·Py CN(Si) = 5 | M·2Py CN(Si) = 6 |
|------------------|-----------------|--------------------|---------------------|
| $(CH_3)_4Si$ | 174.3 | — | — |
| $(CH_3)_3SiBr$ | + | 300.6 | — |
| $(CH_3)_2SiBr_2$ | + | 274.6 | (259.6) |
| CH_3SiBr_3 | + | — | 289.0 |
| $SiBr_4$ | 278.7 | — | + |
| $(CH_3)_4Si$ | 174.3 | — | — |
| $(CH_3)_3SiCl$ | 216.3 | — | — |
| $(CH_3)_2SiCl_2$ | 197.3 | — | (213.3) |
| CH_3SiCl_3 | 195.3 | — | 252.9 |
| $SiCl_4$ | 205.3 | — | + |

changes from $CN(Si) = 4$ for $n = 0$ via $CN(Si) = 4$ and 5 for $n = 1$ and via $CN(Si) = 4, 5$ and 6 for $n = 2$ to $CN(Si) = 4$ and 6 for $n = 3$ and 4. In the corresponding systems $(CH_3)_{4-n}SiCl_n$ -pyridine silicon has either $CN(Si) = 4$ only ($n = 0$ and 1) or $CN(Si) = 4$ and 6 ($n = 2, 3$ and 4) showing the same trend. In both series the melting points of the adducts show that, with the exception of $(CH_3)_3SiBr$, the stability of the phases having higher values of $CN(Si)$ increases as the number of electronegative ligands Br or Cl increases.

Taking into account only normal-pressure compounds of silicon which have just one kind of ligand A, only the most electronegative ligand F is readily able to form $[SiA_6]$ octahedra (Table II).

The influence of the second-nearest neighbour atoms M of silicon on $CN(Si)$ is clearly visible from the data given in Table III. As the electronegativity χ_M increases for oxocompounds of silicon the tendency of silicon to be coordinated by more than four oxygen atoms also increases. In particular, for compounds with oxygen as the only next-nearest neighbours A of silicon, $CN(Si)$ increases from four to six.

TABLE II. Correlation between the Coordination Number of Silicon, $CN(Si)$, and the Electronegativity of the Ligands, χ_A , in Phases Containing $[SiA_n]$ Groups with Only One Kind of Ligand A.

| Si-A | χ_A^a | $CN(Si)$ | Compounds |
|------|------------|-------------------|---------------------------|
| Si-H | 2.1 | 4 | SiH_4 |
| Si-C | 2.50 | 4 | SiC, SiR_4 |
| Si-N | 3.07 | 4 | Si_3N_4 |
| Si-O | 3.50 | 4, 6 ^b | $SiO_2, \text{silicates}$ |
| Si-F | 4.10 | 6, 4 | M_2SiF_6, SiF_4 |

^aElectronegativity values from Allred and Rochow [4].

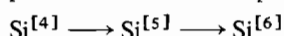
^bIn general $CN(Si) = 6$ only in high-pressure phases.

Coordination number five for silicon has only been observed in compounds in which at least part of the A ligands are not oxygen atoms.

For a given silicate the coordination number of silicon can also be increased from four to six with increasing pressure.

Since these parameters—increasing χ_A , increasing χ_M and increasing pressure—all increase the tendency of silicon to higher coordination, they complement each other. The higher the sum $\chi_A + \chi_M$, the less pressure has to be applied to obtain a phase transformation from $Si^{[4]}$ to $Si^{[6]}$ [5].

At first sight it may be surprising that no phases containing $[SiO_5]$ polyhedra have been found in high-pressure mineral assemblages nor recovered after exposing silicates to high static or shock pressures. Knowing that pentacoordinate silicon is quite stable in silicon organic compounds one would expect that the increase of coordination number of silicon with pressure follows the sequence



rather than changing from four to six in one step.

The apparent lack of silica polymorphs and silicates with $[SiO_5]$ groups is probably caused by their ionic character due to the relatively high electronegativity difference $|\Delta\chi| = |\chi_{Si} - \chi_A|$, which is 1.76 for the Si-O bond in comparison with $|\Delta\chi| = 1.33$ and 0.76 for the Si-N and Si-C bond respectively. In ionic oxygen compounds the oxygen ions have a strong tendency to close packing, and in fact many if not most silicates are distorted derivatives of simple hexagonal or cubic close-packed layer structures. Within such close-packed oxygen arrays there are only tetrahedral and octahedral interstices which can be occupied by the cations without severe distortions. Consequently, in silica and silicates silicon is either tetrahedrally or octahedrally coordinated.

TABLE III. Correlation between the Coordination Number of Silicon, $CN(Si)$, and the Electronegativities of Nearest and Next-nearest Neighbours of Silicon in Normal Pressure Silicon Compounds (electronegativity values from Allred and Rochow [4]).

| Si-A-M | χ_A | χ_M | $ \chi_{Si} - \chi_A $ | $ \chi_A - \chi_M $ | $CN(Si)$ | Compounds |
|---------------------|----------|----------|------------------------|---------------------|----------|-------------------------------------|
| Si-O-Ca | 3.50 | 1.00 | 1.76 | 2.50 | 4 | Ca silicates |
| Si-O-Mg | 3.50 | 1.23 | 1.76 | 2.27 | 4 | Mg silicates |
| Si-O-Fe | 3.50 | 1.64 | 1.76 | 1.86 | 4 | Fe silicates |
| Si-O-Si | 3.50 | 1.74 | 1.76 | 1.76 | 4 | silica |
| Si-O-P | 3.50 | 2.06 | 1.76 | 1.44 | 4, 6 | silicon phosphates, e.g. SiP_2O_7 |
| Si-O-H | 3.50 | 2.1 | 1.76 | 1.4 | 4, 6 | $Si(OH)_4$, thaumasite |
| Si-O-C | 3.50 | 2.50 | 1.76 | 1.00 | 4, 6 | esters, chelates |
| Si-O-C ^a | 3.50 | 2.50 | 1.76 | 1.00 | 4, 5 | organosilicon compounds |
| Si-N-Si | 3.07 | 1.74 | 1.33 | 1.33 | 4 | Si_3N_4 |
| Si-N-C ^a | 3.07 | 2.50 | 1.33 | 0.57 | 4, 5 | organosilicon compounds |
| Si-C-C ^a | 2.50 | 2.50 | 0.76 | 0 | 4, 5 | organosilicon compounds |
| Si-C-N ^a | 2.50 | 3.07 | 0.76 | 0.57 | 4, 5 | organosilicon compounds |

^aCompounds with $[SiA_n]$ having more than one kind of ligands A.

As the electronegativity difference $|\chi_{\text{Si}} - \chi_{\text{A}}|$ decreases and with it the ionicity of the Si–A bond, the tendency to form close-packed structures lessens. As a consequence, silicon is no longer restricted to tetrahedral and octahedral interstices but can also form $[\text{SiA}_5]$ polyhedra. This is clearly visible from the data listed in Table III. In fact, organosilicon compounds have $\text{CN}(\text{Si}) = 4$ or 5 in contrast to the compounds with $[\text{SiO}_n]$ polyhedra where $n = 4$ or 6.

Stereochemistry of Pentacoordinate Silicon

Within recent years the crystal structures of a number of compounds with pentacoordinate silicon have been determined with sufficient accuracy in order to compare their silicon coordination spheres. In all these structures the $[\text{SiA}_5]$ groups are more or less distorted trigonal bipyramids.

Visual inspection of molecular diagrams projected in parallel corresponding directions of various $[\text{SiA}_5]$ groups already suggests that the geometries of these groups are intermediate between the geometry of an ideal $[\text{SiA}_4]$ tetrahedron and that of an ideal $[\text{SiA}_5]$ trigonal bipyramid (Fig. 1). This suggestion is confirmed if the mean values of the three X–Si–X angles of the various structures are plotted *versus* the mean values of the three angles X–Si–Y and of the three angles X–Si–Y'. Here X indicates the three equatorial ligands whereas Y and Y' are the apical ligands with the shorter and longer bond lengths respectively (Fig. 1e). In the plot (Fig. 2) the data points fall onto two lines connecting the points for the trigonal bipyramid (No. 17) with the points for an undistorted tetrahedron in a hexagonal close-packed array of oxygen atoms (No. 2). The two lines extrapolate to the data points for forsterite, Mg_2SiO_4 , (No. 1), an olivine having a distorted version of this atomic arrangement.

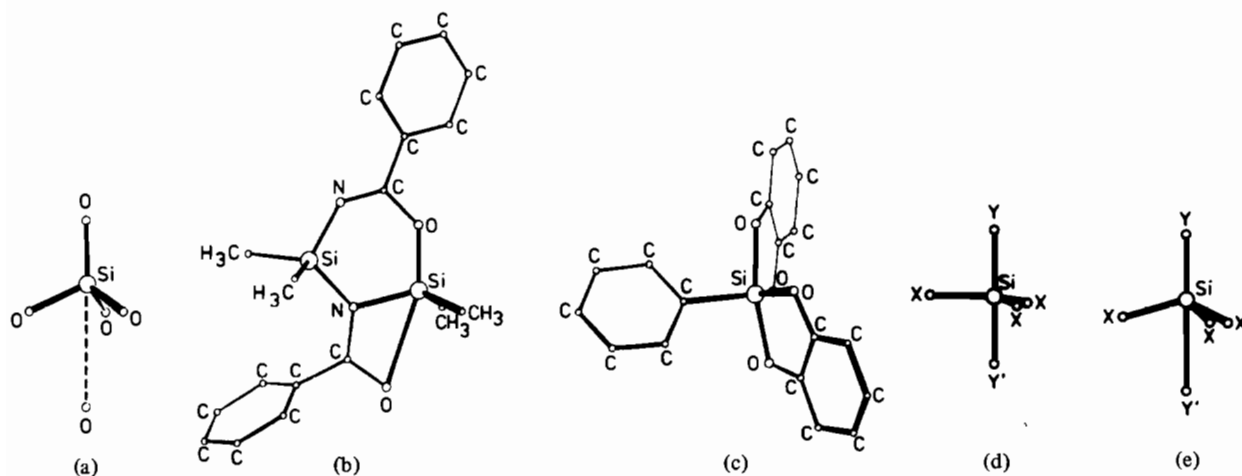


Fig. 1. Geometric arrangement of ligands around silicon in a) forsterite, Mg_2SiO_4 , b) cyclobis(benzamidodimethylsilane), $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2\text{Si}_2$, c) tetramethylammonium bis(*o*-phenylenedioxy)phenylsiliconate, $(\text{C}_6\text{H}_5)\text{Si}(\text{O}_2\text{C}_6\text{H}_4)_2[\text{N}(\text{CH}_3)_4]$, and d) ideal trigonal bipyramid, (for references see Fig. 2). e) Designation of ligands. Large circles indicate silicon.

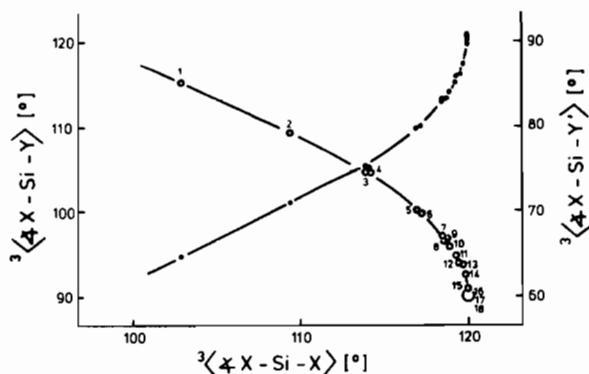


Fig. 2. Correlations between the mean values of bond angles X–Si–X and the mean values of bond angles X–Si–Y, (○), and X–Si–Y', (●), in crystalline compounds containing pentacoordinate silicon. The numbers refer to: 1, forsterite, Mg_2SiO_4 [6]; 2, ideal tetrahedron in hexagonal close-packed anion arrangement; 3, cyclobis(benzamidodimethylsilane), $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2\text{Si}_2$ [7]; 4, trimethyl-(1,2,3,4-tetrahydro-1,10-phenanthroline)silane, $\text{C}_{12}\text{H}_{11}\text{N}_2\text{Si}(\text{NH}_3)_3$ [8]; 5, phenyl-(2,2',2''-nitritotriphenoxy)silane, $(\text{C}_6\text{H}_5)\text{Si}(\text{OC}_6\text{H}_4)_3\text{N}$ [9]; 6, methyl-(2,2',3-nitridioethoxypropyl)silane, $\text{C}_8\text{H}_{17}\text{NO}_2\text{Si}$ [10]; 7, phenyl-(2,2',2''-nitritotriethoxy)silane, $(\text{C}_6\text{H}_5)\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ [11]; 8, *p*-fluorophenylsilatranone, $\text{C}_{12}\text{H}_{14}\text{FNO}_4\text{Si}$ [12]; 9, *m*-trifluoromethylphenylsilatranone, $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_4\text{Si}$ [12]; 10, *m*-nitrophenyl-(2,2',2''-nitritotriethoxy)silane, $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_5\text{Si}$ [13]; 11, (4-bromobenzoyloxy)methyl-trifluorosilane, $\text{BrC}_6\text{H}_4\text{COOCH}_2\text{SiF}_3$ [14]; 12, trifluoro-(1,2,3,4-tetrahydro-1,10-phenanthroline)silane, $\text{C}_{12}\text{H}_{11}\text{N}_2\text{SiF}_3$ [8]; 13, trichloro-(1,2,3,4-tetrahydro-1,10-phenanthroline)silane, $\text{C}_{12}\text{H}_{11}\text{N}_2\text{SiCl}_3$ [8]; 14, chlorodimethyl-(1,2,3,4-tetrahydro-1,10-phenanthroline)silane, $\text{C}_{12}\text{H}_{11}\text{N}_2\text{SiCl}(\text{CH}_3)_2$ [8]. 15, hexamethylenediammonium-bis(ethylenedioxy)methylsilane, $[\text{CH}_3\text{Si}(\text{OCH}_2\text{CH}_2\text{O})_2]_2\text{[H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]$ [15]; 16, tetramethylammonium-bis(*o*-phenylenedioxy)phenylsiliconate, $(\text{C}_6\text{H}_5)\text{Si}(\text{O}_2\text{C}_6\text{H}_4)_2[\text{N}(\text{CH}_3)_4]$ [16]; 17, ideal trigonal bipyramid; 18, tetrapropylammonium-phenyltetrafluorosilicate, $[\text{C}_6\text{H}_5\text{SiF}_4][\text{N}(\text{C}_3\text{H}_7)_4]$ [17].

Since the bond angles, as a first approximation, are independent of the size of the ligands the angular data points of all the structures fall on the same two lines independent of the chemical nature of the ligand. In contrast, the bond lengths $d(\text{Si}-\text{X})$, $d(\text{Si}-\text{Y})$ and $d(\text{Si}-\text{Y}')$ depend strongly on the chemical nature and, in particular, on the size of the different ligands. Consequently, within each of these three groups of bond lengths, oxygen, carbon, nitrogen, fluorine *etc.* have to be treated separately.

If this is taken into consideration, then it becomes evident from plots of bond lengths *versus* mean angle ${}^3\langle\text{X}-\text{Si}-\text{X}\rangle$ (Fig. 3) that, for a given element (O, C or N), the bond lengths $d(\text{Si}-\text{Y}')$ decrease strongly as the mean bond angles ${}^3\langle\text{X}-\text{Si}-\text{X}\rangle$ increase whereas the mean bond lengths ${}^3\langle d(\text{Si}-\text{X})\rangle$ and the bond lengths $d(\text{Si}-\text{Y})$ show a slight increase.

Although sufficiently accurate structural data on pentacoordinate silicon compounds are still scarce the

correlations contained in Figs. 2 and 3 indicate that there is a more or less continuous series of $[\text{SiA}_n]$ polyhedra from the sp^3d_2 hybrid to the sp^3 hybrid and even beyond.

Following the reaction-path concept of Dunitz [18] and his school it is reasonable to assume that this series of 'static' crystalline structures reflects an atomistic mechanism taking place during reactions of silicates, provided the tendency to attain a close-packed structure is sufficiently reduced.

One possibility to reduce this tendency is to provide sufficient thermal energy to melt the silicate; another is to dissolve the silicate in water.

Reaction Mechanisms of Hydrolysis and Condensation of Silicic Acids and Silicates

For reactions to take place a certain mobility of the reactants is necessary. In aqueous solutions of

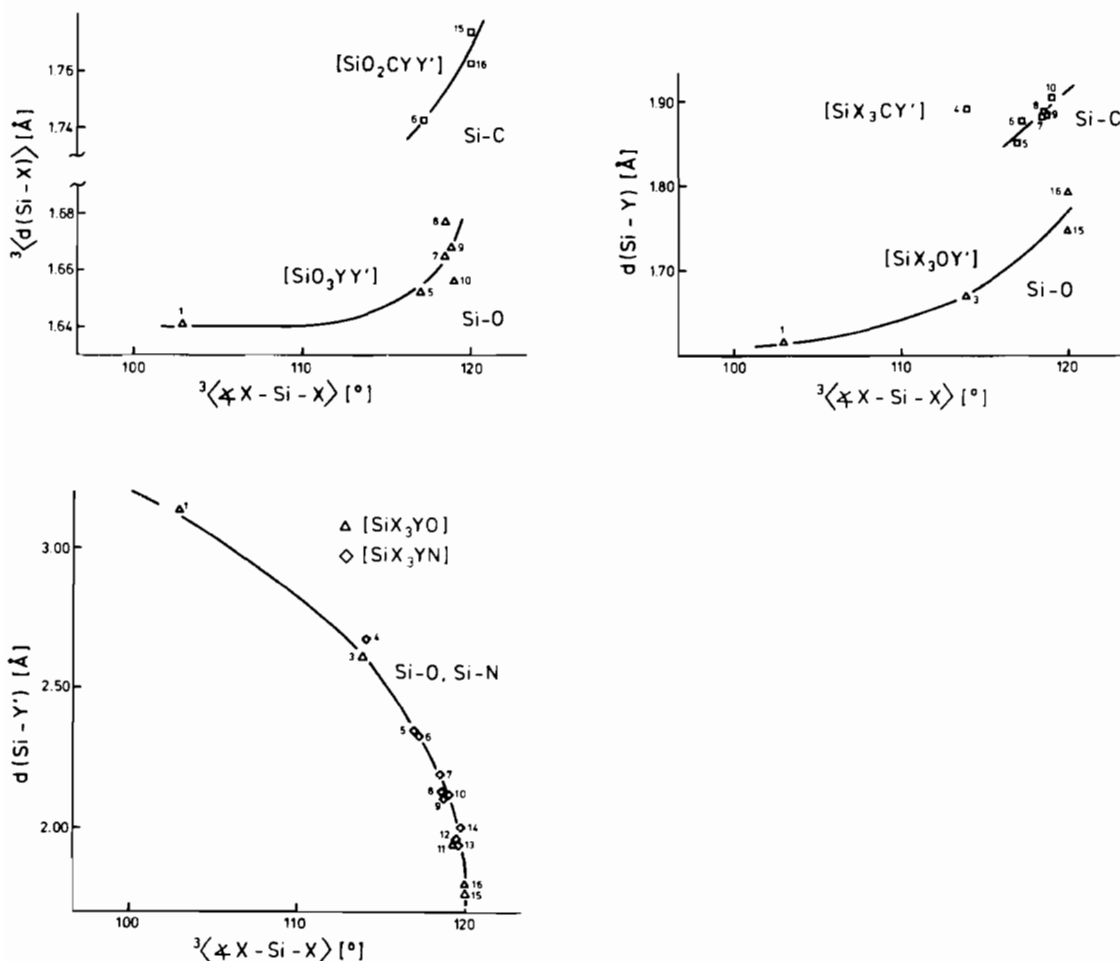


Fig. 3. Correlations between the mean values of bond angles $\text{X}-\text{Si}-\text{X}$ and the bond lengths a) $d(\text{Si}-\text{X})$, b) $d(\text{Si}-\text{Y})$, and c) $d(\text{Si}-\text{Y}')$ in crystalline compounds containing pentacoordinate silicon (for numbering of the data points see Fig. 2).

silicates the mobility of water molecules, hydroxyl ions, H_3O^+ ions, and low molecular silicic acid molecules or ions are high even at moderate temperatures. In contrast, the ion mobilities in solid silicates are low and reach considerable values only at relatively high temperatures, becoming high in general at the melting point. Consequently, silicate reactions will most readily take place in aqueous solutions and in silicate melts, *i.e.* under the same conditions under which the tendency to form close-packed structures is low.

Transferring the static picture of crystal structures depicted in Figs. 2 and 3 to the dynamic process of, for example, the hydrolysis of disilicic acid*, $\text{H}_6\text{Si}_2\text{O}_7$, in aqueous solution leads to the reaction scheme illustrated in Fig. 4. A water molecule approaches one tetrahedron of the disilicic acid to occupy what is to become the apical position of a trigonal bipyramid of an intermediate state. As the water molecule attacks the basal face of the tetrahedron formed by the three non-bridging oxygen atoms O_{nbr} , it attracts the silicon atom thus weakening and extending the $\text{Si}-\text{O}_{\text{br}}$ bond to the bridging oxygen atom and reducing the $\text{O}_{\text{br}}-\text{Si}-\text{O}_{\text{nbr}}$ angles of this tetrahedron to 90° . The reaction proceeds by further strengthening and shortening the new $\text{Si}-\text{OH}$ bond at the expense of the already reduced strength of the $\text{Si}-\text{O}_{\text{br}}$ bond until the $\text{Si}-\text{O}-\text{Si}$ bond is broken.

This process can equally well be described as the silicon atom passing through the basal face of its $[\text{SiO}_4]$ tetrahedron to form a new tetrahedron which includes the oxygen atom of the attacking H_2O molecule.

*Due to the low dissociation constants of silicic acids, water-soluble silicates exist as silicic acids in aqueous solutions:

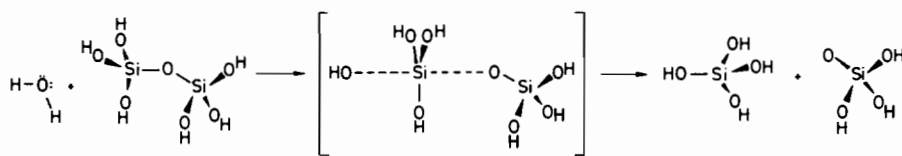
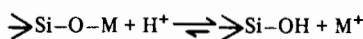


Fig. 4. Schematic representation of the mechanism suggested for the hydrolysis of silicic acid in aqueous solution and of hydrolytic attack of water on solid silicates.

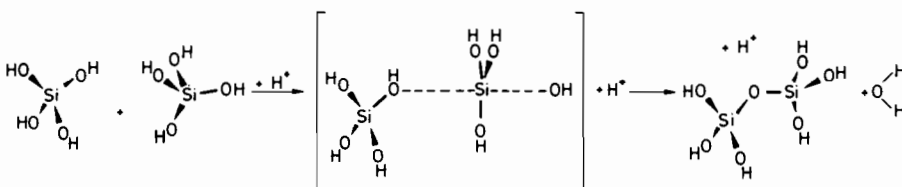


Fig. 5. Schematic representation of the mechanism suggested for the condensation of silicic acids in aqueous solution.

The process is very similar to the 'filled-empty tetrahedron migration' mechanism suggested by Taylor [19] and Dent Glasser & Glasser [20] to take place during some phase transformations and solid state reactions.

Such reaction mechanism would not be restricted to the hydrolysis of silicate species in solution, *i.e.* when the silicate species as well as the attacking groups (H_2O , OH^- , H_3O^+) are both mobile. It could work equally well in the hydrolytic attack of water and hydrous solutions on solid silicates and silica, in agreement with Iler's [21] assumption of involvement of a pentacoordinate state during the dissolution of silica in water. However, the latter reaction is expected to be slower because not only are the silicate species no longer available as mobile species on the left hand side of the reaction scheme in Fig. 4, but also the mobile species may be sterically hindered in their approach to $[\text{SiO}_4]$ tetrahedra in the surface of the solid particle.

Condensation of silicic acid probably also invokes a pentacoordinate silicon intermediate state. A likely mechanism is delineated in Fig. 5.

The lifetime of the intermediate state with pentacoordinate silicon in aqueous solutions of silicates and silicic acids is probably very short. It is therefore described as a transition state rather than as a true intermediate having a minimum in its potential energy *versus* reaction coordinate plot. However, from the data listed in Table III, with decreasing difference $|\chi_A - \chi_M|$ of electronegativities it is evident that in such solutions the tendency of silicon to adopt coordination numbers $\text{CN}(\text{Si}) > 4$ cannot be neglected. In silicon organic compounds with $|\chi_A - \chi_M|$ values lower than that for the $\text{Si}-\text{O}-\text{H}$ bond (*e.g.* $\text{Si}-\text{O}-\text{C}$ and $\text{Si}-\text{N}-\text{C}$) this tendency is even higher so that the pentacoordinate silicon complexes become stable. In agreement with this concept it is widely accepted by organic chemists that bimolecular nucleophilic replacements at silicon involve pen-

tacoordinate silicon intermediates [22]. In this sense it is proposed that decondensation and condensation of silicic acids in aqueous solutions follow the S_N2 reaction mechanism [23] and are special cases of bimolecular nucleophilic replacements with short-lived pentacoordinate transition states.

Influence of Pressure on the Stereochemistry of Silicon

Since the tendency θ of silicon for $CN > 4$ increases as pressure increases, the lifetime of the pentacoordinate intermediates should also increase with increasing pressure enhancing the reaction rate.

In melts of silica and polymer silicates the tendency θ of silicon for $CN > 4$ is probably lower than in aqueous solutions due to the high temperatures involved. However, as pressure increases this tendency also increases so that the dynamic processes of breaking and forming Si–O–Si bonds at high pressures and temperatures are also very likely to take place with formation of intermediate states having trigonal bipyramidal silicon. At very high pressures the stability of such intermediates, and consequently their lifetimes, should increase considerably. Due to the stereochemically-adverse effects of temperature and pressure, octahedral $[SiO_6]$ groups are to be expected to gain considerable stability only at very much higher pressures.

Consequences

In Fig. 6a the change of the tendency θ_n of the silicon atoms to be surrounded by four, five or six oxygen atoms as a function of pressure is presented schematically for two different temperatures. For a given temperature, the lifetime τ_n of the three coordination complexes $[SiO_4]$, $[SiO_5]$ and $[SiO_6]$ changes with pressure in the same way as the tendencies for the various coordination numbers, whereas changes with temperature of the two properties are inverse (Fig. 6b).

If at a certain temperature–pressure range only one structural state (for our discussion only one type of $[SiO_n]$ polyhedron, say $[SiO_4]$), has a lifetime considerably different from zero then the reactivity will be low. As soon as (with increasing pressure) a second structural state, $[SiO_5]$, reaches a certain minimum lifetime, it can serve as transition state and the reactivity will increase. With increasing lifetime τ_5 and, therefore, stability of the $[SiO_5]$ complex, the reactivity will increase until the stability of the $[SiO_4]$ complex is lower than that of the $[SiO_5]$ group and then the reactivity decreases giving rise to a maximum of reactivity. There will be a second reactivity maximum if the pressure is raised until

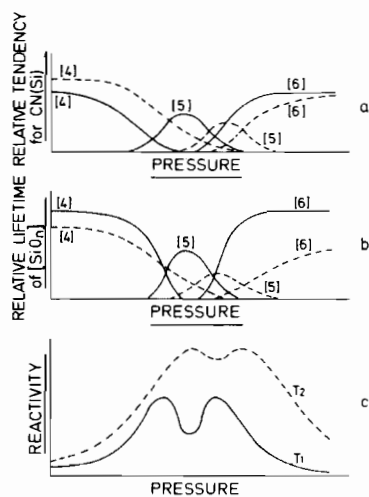


Fig. 6. Schematic diagrams of the influence of pressure on a) the tendency θ_n of silicon in silica and silicates to have coordination numbers 4, 5, and 6, b) on the lifetimes τ_n of the corresponding $[SiO_n]$ polyhedra and c) on the reactivity of silicates at two temperatures T_1 (solid lines) and T_2 (dashed lines) with $T_1 < T_2$.

$[SiO_5]$ and $[SiO_6]$ polyhedra are of comparable stability (Fig. 6c).

Provided that the lifetime τ_6 of hexacoordinated silicon reaches considerable values only at pressures for which τ_4 of tetracoordinated silicon approaches zero, the two reactivity maxima are expected to be separated. If instead with increasing pressure τ_6 reaches considerable values before τ_4 comes near to zero, the two maxima will merge to one broad maximum.

Provided that this very simplified picture is not changed too much by the influences exerted *e.g.* by different structural states with the same coordination number of silicon, one would expect that the change of reactivity with pressure described by the solid line for lower temperatures in Fig. 6c comes near to the situation in aqueous solutions, whereas the dashed line for higher temperatures better describes the situation in silica and silica-rich melts.

This concept is in agreement with the results published by Angell *et al.* [24, 25] who concluded from ion dynamics computer simulations that in melts of jadeite composition, $NaAlSi_2O_6$, at 6000 K the diffusivities of the network-forming constituents silicon, aluminium and oxygen show one maximum each between 20 and 30 GPa, and that these maxima are correlated with a prevalence of pentacoordinate silicon.

The broad diffusivity maximum obtained for silicon in the computer simulation seems to correspond to the two reactivity maxima of Fig. 6c which become superimposed due to the high temperature of 6000 K assumed in Angell's calculations.

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