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Polymerization of silicate and aluminate tetrahedra in glasses, melts and aqueous solutions—II. The network modifying effects of Mg^{2+}, K^+, Na^+, Li^+, H^+, OH^-, F^-, Cl^-, H_2O, CO_2 and H_3O^+ on silicate polymers

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Abstract—The effect of the group IA and VIIA ions, as well as Mg^{2+}, and the molecules H_2O, CO_2, H_3O^+ and OH^- on the energy of the Si–O bond in a $H_6Si_2O_7$ cluster has been calculated using semiempirical molecular orbital calculations (CNDO/2). Three types of elementary processes, i.e. substitution, addition, and polymerization reactions have been used to interpret data on the dynamic viscosity, surface tension and surface charge, hydrolytic weakening, diffusivity, conductivity, freezing point depression, and degree of polymerization of silicates in melts, glasses, and aqueous solutions. As a test of our calculational procedure, observed X-ray emission spectra of binary alkali silicate glasses were compared with calculated electronic spectra. The well known bondlength variations between the bridging bond [Si–O(br)] and the non-bridging bond [Si–O(nbr)] in alkali silicates are shown to be due to the propagation of oscillating bond-energy patterns through the silica framework. A kinetic interpretation of some results of our calculations is given in terms of the Bell–Evans–Polanyi reaction principle.

INTRODUCTION

CHEMICAL REACTIONS involving the polymerization or depolymerization of silicate and aluminate tetrahedra are important in many geochemical processes. Such reactions are of significance due to the effect they have on the rheological properties of aluminosilicate melts as well as on the rates of nucleation and growth of minerals from such melts. These reactions are equally important in the precipitation of silicates from geothermal brines, in the dissolution of minerals in the course of chemical weathering, and in the leaching of rocks by seawater at ocean floor spreading centers. The study of such processes and the delineation of aluminosilicate chemistry which is an essential ingredient for the understanding of these processes, dates back to the profound work of LEMBERG (1876, 1883) on the formation of zeolites from igneous silicates under hydrothermal conditions. Though there have been since that time numerous experiments, few have provided quantitative insight into the reaction mechanisms of aluminosilicate polymerization and depolymerization, and how these mechanisms are affected by the presence of network modifying cations (e.g. Na^+) or volatile components (e.g. H_2O and CO_2).

In the previous paper of this series (DE JONG and BROWN, 1980) we established the groundwork for modelling such reactions using molecular orbital calculations and discussed the chemical properties of ^{IV}Si–O–Si^{IV}, ^{IV}Si–O–Al^{IV}, and ^{IV}Al–O–Al^{IV}, linkages in the $H_6T_2O_7^{n-}$ (T = Si, Al) molecule which, we argued, simulates T–O–T-linkages in a three dimensional array of tetrahedra as present in a silicate melt, a glass, or silica-rich aqueous solution. More specifically, we modelled the effects of various geometric changes in the above molecule on the electron donating capacity of the bridging oxygen, the implicit assumption being that a change in the donor capacity of this anion affects the affinity for various electron acceptors.

In this paper we shall concentrate on the $H_6Si_2O_7$ tetrahedral dimer with a fixed geometry [$\angle$T–O–T = 140°, d(Si–O) = 1.62 Å]. Our goal is to use the calculated chemical interaction of a selected group of geologically common network modifying cations, anions, or molecules designated adions or admolecules respectively, with the bridging, O(br), and non-bridging, O(nbr), oxygens in the $H_6Si_2O_7$ molecule as a quantitative model (in the context of the CNDO/2 formalism) for general admolecule–silicate interactions in a melt or aqueous solution environment. In these calculations we have followed the same formalism (CNDO/2) and procedures discussed in DE JONG and BROWN (1980). The physical and chemical properties of aluminosilicates we seek to rationalize in terms of the aforementioned primitive interactions are the dynamic viscosity, surface tension, and freezing point depression of binary alkali–silicate melts, the alkali–hydrogen exchange in silicates and its effect on the Si–O bond, the attachment of water on a silica surface and the effect of various adions on the point of zero charge on this surface, and the polymerization reactions of silicic acid in aqueous solutions.

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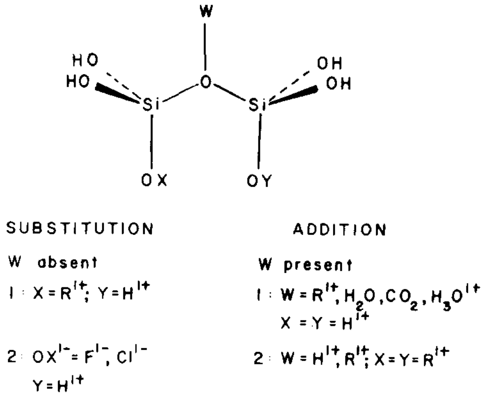

Fig. 1. The geometry of the $H_6Si_2O_7$ molecule [conformation e_1, $\angle T\text{–}O\text{–}T = 140°$, d(Si–O) = 1.62 Å, d(O–H) = 0.96 Å] used in the substitution and addition reactions considered in this study.

Modelling the interaction of the adions and admolecules with the dimers presupposes a knowledge of the molecular geometry of the interacting reactants. We have chosen for our calculations the simplest plausible geometry possible and have considered only a S_N1 (substitution nucleophilic unimolecular) reaction mechanism, i.e. a mechanism in which the elementary step is the rupture of a single bond. The reactions studied fall into three categories: substitution reactions, addition reactions, and polymerization reactions. The various substitution and addition reactions considered in this paper are illustrated in Fig. 1.

The adions and admolecules studied are the IA group cations (H^+, Li^+, Na^+, K^+), the VIIA group anions (F^-, Cl^-), Mg^{2+}, and the molecules CO_2, H_2O, OH^- and H_3O^+. We have considered the adions to be bare ions and hence have not taken into account their molecular environment. The calculations model gas phase reactions, occurring adiabatically at 0 K. We have not included screening parameters to account for the dielectric constant of the medium in which the reactions occur and have assumed that the trends in affinities of the various adatoms, adions, and admolecules for O(br) and O(nbr) remain the same in different chemical environments.*

Because our primary goal is to understand the relative effects of geologically common network modifiers on tetrahedral polymerization and the mechanisms by which these modifiers react with the tetrahedral frameworks as present in siliceous melts, we have studied the relative affinities of the various adions and admolecules with the $H_6Si_2O_7$ molecule. These calculated affinities can be related to the reactivities of the reactants if it is assumed that the Bell–Evans–Polanyi reaction principle is valid for these systems. This principle qualitatively predicts, as illustrated in Fig. 2, that the more exothermic reactions go faster (see BOUDART, 1968; DEWAR and DOUGHERTY, 1975). The reactions considered are of the donor–acceptor type. In most cases the donor is the O(br) or O(nbr) atom in the $H_6Si_2O_7$ molecule. The acceptor adion or admolecule is either a positively charged ion or an acceptor site on the H_2O, CO_2, or H_3O^+ molecule.

Three measures of relative affinity were used. The first one is the change in total energy, E_T, when the reactants are brought together from infinity to form either the precursor to a transition state complex (addition reactions) or the products (substitution reactions). In practice the total energy of the tetrahedral dimer and the adion before reaction was calculated by placing the adion at such a distance from the dimer that further separation did not cause a change in E_T. In the case of the alkali adions-$H_6Si_2O_7$ reactions, the limiting total energy is that of the $H_6Si_2O_7$ molecule. For the halogens, F^- and Cl^-, the maximum halogen-$H_6Si_2O_7$ distance for which the calculations converge is 8 Å, and the total energy calculated at that distance was taken as the limiting E_T. The total energy of the products was calculated with the adions or admolecules at the equilibrium internuclear separation (as calculated by CNDO/2) from the tetrahedral dimer. The difference in E_T between reactants and products for the various reactions is equal to ΔG at 0K ($=\Delta H$).

The second affinity criterion is based upon second order perturbation theory (FUKUI, 1954; KLOPMAN, 1967; KLOPMAN, 1974; HUDSON, 1974). This theory states that the interaction between two molecular fragments depends upon the relative position of the energy levels of the acceptor and donor atoms as well as on the overlap of the orbitals used in the charge transfer. According to this index, the strength of the interaction between reactants is measured by the fraction of the atomic orbitals of the acceptor adion which can mix with the occupied MO's of the $H_6Si_2O_7$ molecule. We refer to this criterion as the percentage mixing of the acceptor adatom.†

The third affinity criterion is based upon pairwise interaction between reacting atoms as estimated using the two center energy terms, E_{A-B}, which are proportional to the bond energies of the molecule (GORDON, 1969). This interaction includes the electron–electron, electron–nuclear, and nuclear–nuclear effects between the A and B atoms. The more negative the E_{A-B} value for the bond formed during the process, the higher the affinity of the reactants for one another.

Because we are particularly interested in changes in the silica polymerization, we have used the change in Si–O(br) bond energy as a reactivity criterion. As we shall show in the next section, trends in $E_{Si-O(br)}$ can either parallel or oppose the trends shown by the

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* A number of examples from organic chemistry where this assumption does not hold has been given by OLMSTEADT and BRAUMAN (1977).

† Though the % mixing is a useful criterion in assessing the interactions between molecules, its use in second order perturbation theory in predicting relative barrier heights between reactants and products from the curvature of the adiabatic potential energy surface is controversial (METIU *et al.*, 1974).

Table 1. Calculated charges (Q), percent mixing, and E_{A-B} values for the molecule $RH_5Si_2O_7$[1] and ΔG for reaction (1)

R atom	K[2]	Na	Li	H
Q(R)	0.894	0.753	0.490	0.153
Q(O(br))	-0.723	-0.729	-0.737	-0.744
Q(O(nbr))	-0.720	-0.713	-0.671	-0.614
Q(Si)[3]	1.348	1.441	1.563	1.730
% mixing R[4]	1.3	3.1	6.4	42.3
E_{R-O}[5]	-1.295	-5.111	-14.027	-21.678
$E_{Si-O(br)}$	-12.072	-13.137	-14.747	-17.121
$E_{Si-O(nbr)}$	-17.763	-17.233	-17.251	-15.024
ΔG[6]	+463	+431	+307	0

[1] Point group C_1, d(Si-O)=1.62 A, d(H-O)=0.96 A, d(Li-O)= 2.10 A, d(Na-O)=2.38 A, d(K-O)=2.78 A, ∠T-O-T=140°.

[2] Parameters for K : ξ=0.59459, $1/2(I_s+A_s)$=2.900 eV, $1/2(I_p+A_p)$=1.750 eV, β=6.67 eV

[3] The charge is calculated for the Si atom adjacent to the R-O(nbr) bond.

[4] The percent mixing per atomic orbital for an alkali atom is given by (1-Q(R))x100/(4)(2).

[5] The E_{A-B} values are expressed in eV(1 eV=23.061 Kcal). The total energy values reported in Table 5 in the first paper in this series have to be multiplied by 1.00048 to be consistent with the values in Kcal reported here.

[6] ΔG(=ΔH at 0°K) is calculated from E_T(products)-E_T(reactants) for the reaction $H_6Si_2O_7 + R^+ = RH_5Si_2O_7 + H^+$ in Kcal at the following calculated equilibrium distances : d(Li-O(nbr))= 2.10 A, d(Na-O(nbr))=3.30 A, d(K-O(nbr))=4.40 A. E_T for $H_6Si_2O_7$ at ∠T-O-T=140°=3.7582 KeV.

three affinity criteria. The two center energy, $E_{Si-O(br)}$ of the Si–O(br) bond in $H_6Si_2O_7$: −17.121 eV at ∠T–O–T = 140°, has been taken as the base level. The weaker this bond becomes during a process, the easier it will break. This weakening of the Si–O(br) bond reflects the perturbing influence of the various adions and admolecules on the tetrahedral framework of a silicate melt or glass, or on the polymeric unit in silica-rich aqueous solutions.

RESULTS

Substitution reactions

Although substitution reactions are often very complex in terms of actual mechanisms, they are conceptually the easiest ones to understand because their initial and final states are well defined. Therefore we shall discuss this reaction type before considering addition and polymerization reactions. The first substitution reaction we shall consider involves the replacement of a hydroxyl proton by R^+ adions:

$$H_6Si_2O_7 + R^+ = (RH_5Si_2O_7) + H^+ \qquad (1)$$

The R^+ ions in this reaction are the alkali adions, Li^+, Na^+, and K^+. The geometry considered is illustrated in Fig. 1, and the calculated charges (Q), E_{A-B}'s, and % mixing of the R^+ adions for this reaction are collected in Table 1 together with the ΔG's.

The affinity of the R^+ adion for O(nbr) increases from K^+ to H^+, as indicated by the % mixing sequence of the adions: $K^+ < Na^+ < Li^+ < H^+$. This sequence is parallel to that of the R–O(nbr) two center energies: $E_{K-O(nbr)} < E_{Na-O(nbr)} < E_{Li-O(nbr)} < E_{H-O(nbr)}$ and is the same as that inferred from empirical bondstrength calculations using parameters such as those provided by Brown and Wu (1976). The two center energies in the $RH_5Si_2O_7$ molecules show an alternating pattern, i.e. the stronger the R–O(nbr) bond, the weaker the adjacent Si–O(nbr) bond. This latter bond is associated with the strongest Si–O(br) bond. These relationships between two center cation–oxygen energies in the $RH_5Si_2O_7$ molecule are illustrated in Fig. 3 as a function of the % mixing of the R^+ adion.* The free energies for reaction (1), shown in Table 1, indicate that, due to the high energy of the H–O(nbr) bond, replacement of the H^+ by the other R^+ adions is always a strong endothermic process.

The second substitution reaction (see Fig. 1) is the replacement of OH^- by fluorine or chlorine adions:

$$H_6Si_2O_7 + (F, Cl)^- = (F, Cl)H_5Si_2O_6 + OH^- \qquad (2)$$

The results of these calculations are listed in Table 2. The interaction of the halogens with silicon is again of the hard donor (F^-, Cl^-), hard acceptor (Si^{4+}) type. The larger effect of the alkali adions relative to the halogen adions on the energy of the Si–O(br) bond is due to the larger radial extension of the atomic orbitals of the former which enhances charge transfer. This charge transfer dominates, according to our calculations, over the enhanced orbital mixing of the atomic orbitals of the halogens with those of silicon.

The Si–F bond at the conventional d(Si–F) (1.56 Å) is considerably weaker than the Si–OH bond. The

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* A number of variables, including experimentally determined electron affinities (Hotrop and Lineberger, 1975) of the R adatoms, average ionization potential of an sp^3 hybridized R adatom, or cationic field strength of the adatom, give essentially the same functional relationship with the E_{A-B}'s, indicating the linear dependence of these variables. The % mixing encompasses all of them.

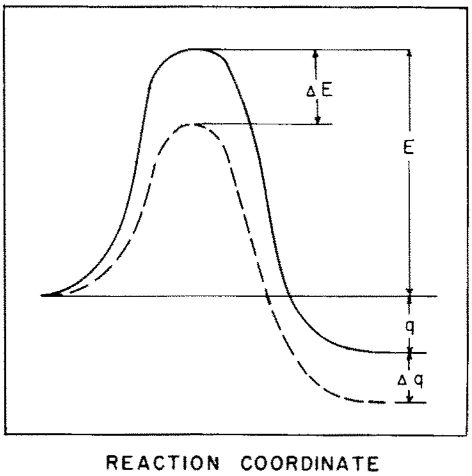

Fig. 2. Schematic illustration of the Bell–Evans–Polanyi principle which states that, for a family of elementary reaction processes, from the difference in the heat of reaction (Δq) the difference in the barrier height (ΔE) can be deduced.

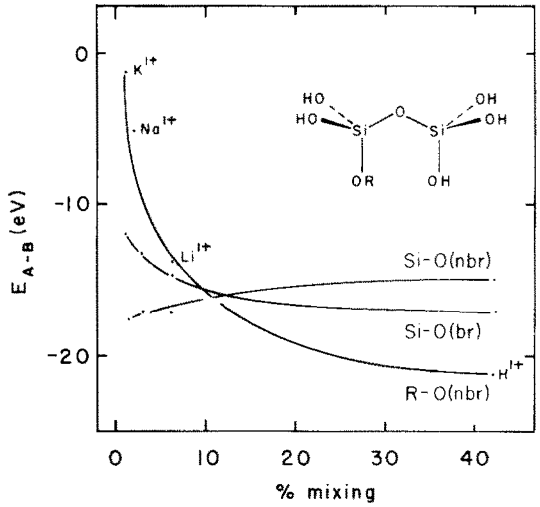

Fig. 3. Two center energy variation of the Si–O(br), Si–O(nbr), and R–O(nbr) in substitution reaction (1) as a function of the % mixing of the adion.

maximum Si–F two center energy (−13.221 eV) which occurs at d(Si–F) of 1.95 Å is about 2 eV less negative than the Si–OH two center energy. The Si–O(br) bond adjacent to the Si–F bond is higher in energy than the second Si–O(br) bond in the molecule, thus showing the alternating bond energy pattern previously associated with an adion which has a weak affinity for O(nbr). It follows from this result that F^- induces a slightly larger Si–O(br) bond energy increase than OH^-. The calculated charges on the fluorine atom remain almost constant over the d(Si–F) range considered (1.16–2.26 Å), reflecting the large difference between atomic energy levels of fluorine and silicon, the small overlap of the orbital on the two centers, and hence the limited amount of electron transfer.

The results of our calculations with Cl^- in reaction (2) (see Table 2) show that the Si–Cl two center energy at the calculated Si–Cl equilibrium distance (2.07 Å) is more negative than that of the Si–F bond, and that substitution of Cl^- for OH^- decreases the energy of the Si–O(br) bonds more than the F^- anion. The affinity of the halogen adions and OH^- for silicon is based upon our E_{A-B} values:

$$Cl^- > OH^- > F^-$$

The free energy for reaction (2) indicates that replacement of OH^- by F^- and Cl^- is an exothermic process, and that OH^- replacement by Cl^- rather than OH^- replacement by F^- is thermodynamically favored.

Addition reactions

The second type of reactions considered in this study are the addition reactions shown in Fig. 1. The first addition reaction models the effect of the group IA adions, H^+, Li^+, Na^+, K^+, and the admolecules H_2O, CO_2, and H_3O^+ on the $H_6Si_2O_7$ molecule according to the following reactions:

$$H_6Si_2O_7 + R^+ = (RH_6Si_2O_7)^+ \qquad (3a)$$

and

$$H_6Si_2O_7 + (H_2O,CO_2,H_3O^+) = [(H_2O,CO_2,H_3O^+) - H_6Si_2O_7] \qquad (3b)$$

The geometries used in reactions (3a) and (3b) are illustrated in Figs 4 and 5, and the results of these calculations are collected in Table 3a and 3b.

Both of the above reactions describe to a first approximation, the initial perturbation of the Si–O(br) bond by a network modifier in a three dimensional array of silica tetrahedra. The products formed can be considered to resemble the transition state complex in

Table 2. Calculated charges(Q), % mixing, E_{A-B} values for the molecules $FH_5Si_2O_6$ and $ClH_5Si_2O_6$[1], and ΔG for reaction (2)

	F	Cl
Q(halogen)	-0.511	-0.351
Q(Si) [2]	1.752	1.551
Q(O(br))	-0.744	-0.729
% mixing halogen	93.9	91.2
$E_{Si-O(br)}$ halogen [3]	-17.459	-16.104
OH	-16.993	-16.778
$E_{Si-halogen}$	-8.120	-15.052
E_{Si-OH} [4]	-12.914	-12.914
ΔG [5]	-126	-152

[1] Point group C_1, d(Si-O)=1.62 A, d(O-H)=0.96A, d(Si-F)=1.56 A, d(Si-Cl)=2.07 A, ∠T-O-T=140°.

[2] The charge is calculated for the Si atom adjacent to the halogen atom.

[3] The energy of the Si-O(br) bond is calculated for both the Si-O(br) bond adjacent to the Si-halogen bond and the one adjacent to the OH bond. The energy values are given in eV.

[4] $E_{Si-OH}=E_{Si-O}+E_{Si-H}$

[5] ΔG for the reaction $(H_6Si_2O_7)+(F,Cl)^-=(F,Cl)H_5Si_2O_6+OH^-$ in Kcal at the calculated equilibrium distances: d(Si-F)=2.10A, d(Si-Cl)=2.30A.

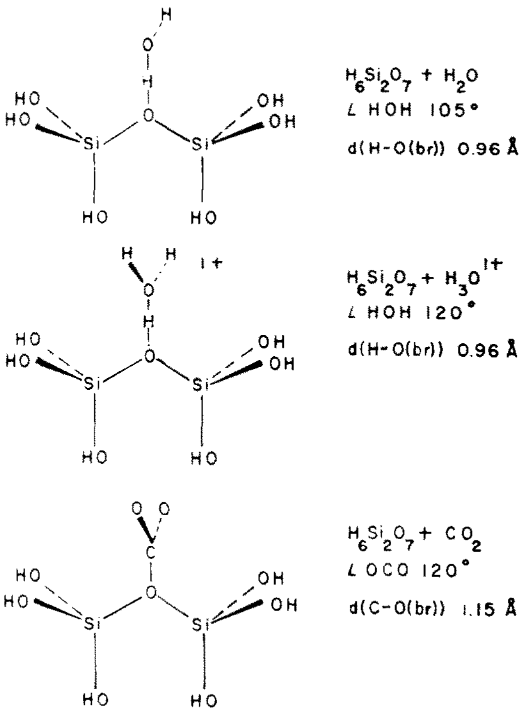

Fig. 4. Geometries considered in addition reaction (3b). Both the CO_2 and H_2O–$H_6Si_2O_7$ reactions are drawn in configuration II (see Table 3b).

the breakdown reaction of the $H_6Si_2O_7$ molecule. We have studied reaction (3a) in some detail to demonstrate the general features of the effects induced by the R^+ adions on the Si–O(br) bonds.*

In Figs 5a and 5b the calculated two center energies, E_{A-B}, of the R–O(br) and Si–O(br) bonds are shown as a function of d[R–O(br)] for reaction (3a). According to our calculations, the sequence of R–O(br) two center energies, and hence the affinity sequence of the group IA cations for O(br) is H–O(br) > Li–O(br) > Na–O(br) > K–O(br). The narrow and deep energy well for the H–O(br) interaction vs the broad and shallow well for the K–O(br) interaction illustrates the strong, short range character of the former and the weak, long range character of the latter. The energy of the Si–O(br) bond bears an inverse relationship to the energy of the R–O(br) bond, i.e. the stronger the R–O(br) bond, the weaker the adjacent Si–O(br) bond. This relationship is illustrated in Fig. 5a and 5b as a function of d[R–O(br)] and in Fig. 5c as a function of the % mixing of the atomic orbitals of the adion.

Inspection of the free energies for reaction (3a) in Table 3a shows that the most exothermic reaction is the one involving the H^+ adion, followed by Li^+, Na^+ and K^+. Thus the most stable complex formed in reaction (3a) is the $(H–H_6Si_2O_7)^+$ molecule. This sequence of stabilities for the $(R–H_6Si_2O_7)^+$ clusters is parallel to the affinity sequence for O(br) shown by the R–O(br) two center energies and the % mixing criterion. It is of importance to note that the hydrogen complex, which is the most stable one of the complexes considered in reaction (3a), and therefore the most readily formed according to the Bell–Evans–Polanyi reaction principle, has the weakest Si–O(br) bond.†

Addition reaction (3b) models the interaction of the admolecules H_2O, H_3O^+, OH^-, and CO_2 with O(br) in the $H_6Si_2O_7$ molecule. Our results indicate that the carbon atom in the bent CO_2 molecule forms the strongest bond with O(br) of all the admolecules considered in reaction (3b) at the calculated equilibrium distance d[C–O(br)] = 1.45 Å. The formation of the $H_6Si_2O_7$–CO_2 complex is exothermic for the linear as well as the bent CO_2 molecule. The ΔG for the reaction involving the bent molecule is about 12 Kcal more negative than that for the straight molecule. In the former reaction however a positive activation energy for bending is required [E_T (CO_2, straight) − E_T (CO_2, bent) + 78 Kcal]. The attachment of a water molecule to O(br) is also an exothermic process according to our calculations. As inspection of Table 3b shows, the calculated free energy for this reaction is considerably smaller (−5 kcal for configuration 1 and −9 kcal for configuration 2). It is therefore expected that, if reaction (3b) occurs as written, the attachment of the CO_2 molecule to O(br) in the $H_6Si_2O_7$ molecule occurs considerably faster than the H_2O attachment to O(br).

The degree of weakening of the Si–O(br) bond as a function of the adions and admolecules considered in reaction (3a) and (3b) follows the sequence:

$$H^+ > CO_2(\text{bent}) > OH^- > CO_2(\text{linear})$$
$$> Li^+ > H_3O^+ > Na^+ > H_2O > K^+ \ ‡$$

Thus the K^+ adion perturbs the Si–O(br) bond in the $H_6Si_2O_7$ molecule the least whereas the H^+ adion perturbs this bond the most.

Because of its importance in elucidating the dissolution of silica, we have calculated the free energy of

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* J. A. Tossell (personal communication, 1979) has pointed out that ΔG for the reaction $Li^+ + H_2O = (Li–OH_2)^+$ [d(Li–O) = 2.40 Å] is about −45 Kcal according to his CNDO/2 calculations [in comparison, the *ab initio* Hartree-Fock values for this reaction are about 10 kcal less negative (Saluja, 1976)]. Our calculations give the same value for this reaction. Because the calculated ΔG for the reaction $H_6Si_2O_7 + Li^+ = (LiH_6Si_2O_7)^+$ is −111 kcal (Table 3a), the nucleophilic character of O(br) in $H_6Si_2O_7$ is predicted to be about 2.5 times stronger than that of the oxygen atom in H_2O.

† The inverse relation between the affinity of the reactants and the strength of an individual bond in the product is not uncommon. For instance the hydrogenation reaction of benzene to form hexane is highly exothermic (−49.8 kcal). However d(C–C) increases from 1.39 to 1.54 Å in this process, reflecting a weakening of the C–C bond.

‡ The reactivity sequence of the adions and admolecules with respect to the Si–O(br) bond in the $H_6Si_2O_7$ does not coincide with the free energy of formation sequence of the various clusters which is according to Table 3a and 3b: $H^+ > Li^+ > H_3O^+ > CO_2(\text{bent}) > CO_2(\text{straight}) > Na^+ > OH^- > H_2O(II) > H_2O(I) > K^+$. Thus, the free energy of formation of the $(H–H_6Si_2O_7)^+$ cluster is most negative and that of the $(K–H_6Li_2O_7)^+$ cluster the least.

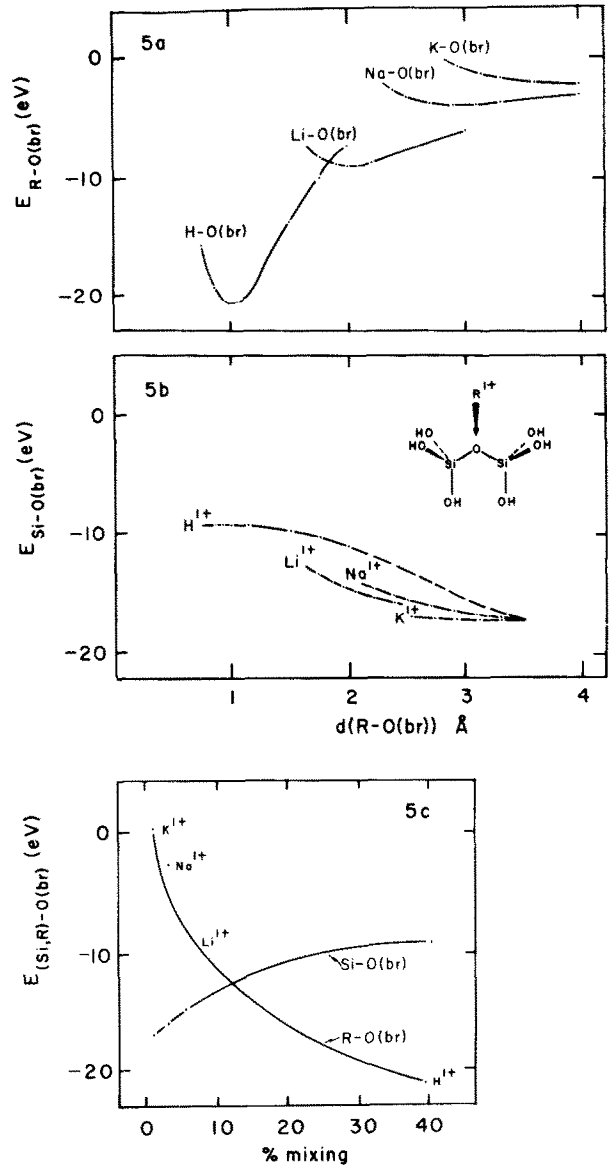

Fig. 5a. The two center energy for the R–O(br) bond as a function of R–O(br) distance in addition reaction (3a). Fig. 5b. The two center energy for the Si–O(br) bond as a function of R–O(br) distance. Fig. 5c. The two center energy variations of the R–O(br) and Si–O(br) bonds as a function of the % mixing of the R^+ adion.

attachment of the H_2O, H^+, OH^- and H_3O^+ species to O(br) of the $H_6Si_2O_7$ molecule. The calculated sequence of attachment energies is:

$$\begin{array}{ccccccccc} H^+ & > & H_3O^+ & > & OH^- & > & H_2O(II) & > & H_2O(I) \\ (-317\,\text{kcal}) & & (-54\,\text{kcal}) & & (-17\,\text{kcal}) & & (-9\,\text{kcal}) & & (-5\,\text{kcal}) \end{array}$$

These results indicate that the affinity of O(br) for H^+ is largest and for H_2O smallest.

The second type of addition reaction involves the replacement of two H^+ ions by two R^+ ions (see Fig. 1) according to the following reactions:

$$Li_2H_4Si_2O_7 + R^+ = (R-Li_2H_4Si_2O_7)^+ \quad (4a)$$

and

$$R_2H_4Si_2O_7 + H^+ = (H - R_2H_4Si_2O_7)^+ \quad (4b)$$

These calculations model a silicate fragment with both bridging and non-bridging oxygens and as such can be used to simulate exchange reactions between R^+ adions in the 'W' or 'exchange' site in sheet or chain silicates.

The geometries used are illustrated in Fig. 1 and the results for reaction (4a) are collected in Table 4. The % mixing of the R^+ adions and the R–O(br) two center energies follow the trends discussed earlier. The calculated free energies indicate that the most stable complex by far is the $(H\text{–}Li_2H_4Si_2O_7)^+$ molecule. This also implies that exchange of H^+ by any of the

Table 3a. Calculated charges(Q), % mixing, E_{A-B} values (eV) for the molecule $(RH_6Si_2O_7)^{1+}$ [1], and ΔG for reaction (3a)

R atom	K	Na	Li	H
Q(R)	0.936	0.741	0.571	0.218
Q(O(br))	-0.780	-0.767	-0.734	-0.561
Q(Si)	1.728	1.737	1.767	1.773
% mixing R	0.8	3.2	5.4	39.1
$E_{R-O(br)}$	0.089	-2.780	-9.139	-20.629
$E_{Si-O(br)}$	-17.158	-16.225	-14.982	-9.308
ΔG [2]	-0.5	-23	-111	-317

[1] Point group C_{2v}, d(Si-O)=1.62 A, d(H-O)=0.96 A, d(Li-O)=2.10 A, d(Na-O)=2.38 A, d(K-O)=2.74 A, ∠T-O-T=140°.

[2] ΔG for reaction $H_6Si_2O_7 + R^+ = RH_6Si_2O_7^+$ in Kcal at the calculated equilibrium distances : d(H-O(br))=1.10 A, d(Li-O(br))=2.20 A, d(Na-O(br))=3.30 A, d(K-O(br))=5.80 A.

Table 3b. Calculated charges(Q), % mixing, E_{A-B} values (eV), E_T as well as ΔG for reaction (3b) [1]

	$H_2O(I)$ [2]	$H_2O(II)$ [3]	H_3O^+ [4]	OH^- [5]	$CO_2(I)$ [6]	$CO_2(II)$ [7]
Q(O(br))	-0.752	-0.751	-0.776	-0.620	-0.699	-0.650
Q(Si)	1.729	1.735	1.752	1.650	1.752	1.792
$E_{Si-O(br)}$	-16.964	-16.796	-15.175	-12.946	-14.256	-12.480
$E_{H-O(br)}$	-1.002	-2.528	-11.868	-0.839	-	-
$E_{C-O(br)}$	-	-	-	-	-13.177	-22.184
E_T	-4.29903	-4.29920	-4.31133	-4.27337	-4.94562	-4.94611
ΔG	-5	-9	-54	-17	-35	-46

[1] The equilibrium distances between O(br) and the oxygen atom on the admolecules are: 2.469 A d(O(br)-O(H_2O(I))), 2.560 A d(O(br)-O(H_2O(II))), 2.220 A d(O(br)-O$(H_3O)^+$), 2.460 A d(O(br)-O$(OH)^-$), 2.011 A d(O(br)-C(CO_2(I)), 2.260 A d(O(br)-C(CO_2(II))). The distances in the admolecules are : d(O-H)=0.96 A, d(C-O)=1.15 A, d(Si-O)= 1.62 A, ∠Si-O-Si=140°.

[2] Configuration(I) consists of two H atoms on the water molecule equidistant from O(br). ∠H-O-H=105°, $E_T(H_2O)$=0.5406 KeV.

[3] Configuration(II) consists of one H atom approaching O(br) along the z axis.

[4] $E_T(H_3O)^+$=0.5508 KeV.

[5] $E_T(OH^-)$=0.5144 KeV

[6] Configuration(I) corresponds to the straight CO_2 molecule. $E_T(CO_2)$=1.1859 KeV.

[7] Configuration(II) corresponds to a bent CO_2 molecule, ∠O-C-O=120°. $E_T(CO_2(bent))$= 1.1825 KeV.

[8] ΔG for the reaction $(H_6Si_2O_7+(H_2O, H_3O^+, OH^-))=(H_2O, H_3O^+, OH^--H_6Si_2O_7)$ in Kcal. The reactions with CO_2 were calculated according to : $(H_6Si_2O_7+ CO_2(straight))=(H_6Si_2O_7-CO_2(straight))$ and $(H_6Si_2O_7+ CO_2(straight))=(H_6Si_2O_7-CO_2(bent))$.

alkali adions is energetically an unfavorable process and not likely to occur. As in the case of reaction (3a), the most stable molecule, $(H\text{–}Li_2H_4Si_2O_7)^+$, has the weakest Si–O(br) bond. The tolerance of the Li silicate fragment for the R^+ adions decreases in the order $K^+ > Na^+ > Li^+ > H^+$. It should be noted that E_{Li-Li} in the $Li_2H_4Si_2O_7$ cluster is negative, reflecting a bonding interaction between the two alkali atoms in this molecule. For the higher atomic number alkali atoms the E_{R-R} interaction becomes repulsive.

Table 4. Calculated charges(Q), % mixing, E_{A-B} values for the molecule $(Li_2RH_4Si_2O_7)^+$ [1], and ΔG for reaction (4a)

R atom	-	K	Na	Li	H
Q(R)	-	0.936	0.727	0.551	0.200
Q(O(br))	-0.726	-0.764	-0.752	-0.720	-0.547
Q(Si)	1.621	1.595	1.595	1.620	1.611
Q(Li)	0.174	0.278	0.324	0.352	0.414
% mixing R	-	0.8	3.4	5.6	40.0
$E_{R-O(br)}$	-	-0.0997	-2.819	-9.251	-20.426
$E_{Si-O(br)}$	-16.199	-16.053	-15.015	-13.651	-8.127
$E_{Si-O(nbr)}$	-13.251	-14.301	-14.796	-15.249	-15.825
$E_{Li-O(nbr)}$	-10.942	-11.323	-11.504	-11.580	-11.641
E_{Li-Li}	-8.926	-6.993	-6.124	-5.583	-4.432
ΔG [2]	-	-5	-32	-139	-350

[1] Point group C_{2v}, d(Si-O)=1.62 A, d(O-H)=0.96 A, d(Li-O)=2.10 A, d(Na-O)=2.38A, d(K-O)=2.78 A, ∠T-O-T=140°.

[2] ΔG for reaction $Li_2H_4Si_2O_7+R^+=(R\text{-}Li_2H_4Si_2O_7)^+$ in Kcal at the calculated equilibrium distances : d(H-O(br))=1.06 A, d(Li-O(br))=2.10 A, d(Na-O(br))=3.00 A, d(K-O(br))=5.20A.

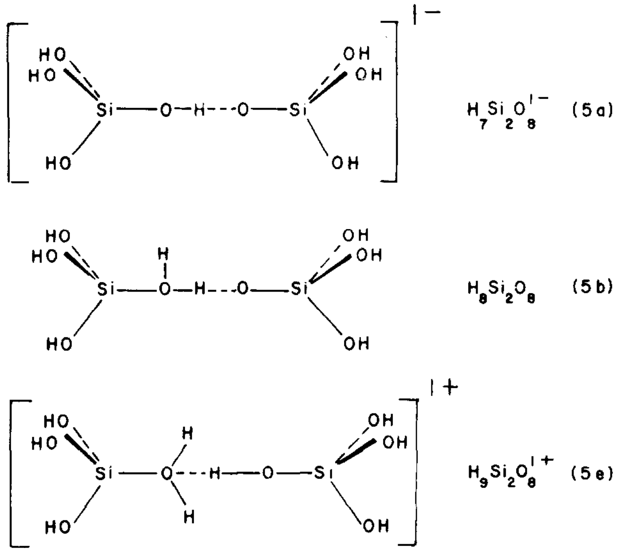

Fig. 6. Geometries used in the calculation of the polymerization reactions of silicic acid in aqueous solutions (reactions 5a, 5b, 5c, 5d and 5e).

Reaction (4b) models the interaction of the H^+ adion with different alkali atoms and magnesium in the 'octahedral' site in a silicate fragment. The trends in Si–O(br) two center energies show that the tendency for this silicate fragment to maintain its polymeric structure with respect to H^+ decreases in the sequence: $H > Li > Mg > Na > K$. Thus an H^+ adion affects the silicate frame more in the $K_2H_4Si_2O_7$ cluster than in the $H_6Si_2O_7$ cluster. This trend can easily be understood in light of substitution reaction (1), where it was shown that the Si–O(br) bond is weakest in the potassium silicate cluster and strongest in the hydrogen silicate cluster. Thus when H^+ adions are attached to O(br) of $R_2H_4Si_2O_7$ molecules according to reaction (4b), the changes in Si–O(br) two center energies reflect the fact that the weakest Si–O(br) bond is most affected by H^+ addition and that the strongest Si–O(br) bond is affected the least. As noted previously the calculated Li–Li interaction has a negative value. The value of E_{Na-Na} is slightly positive and that of E_{K-K} rather large and positive. These results suggest that, in going down the IA column of the periodic table, the character of the alkali–alkali interaction changes from atractive to repulsive.

Polymerization reactions

The third and last S_N1 reaction type considered in this study is the polymerization reaction. The molecular geometries common to the five reaction mechanisms studied are illustrated in Fig. 6 (see also Table 5). The first four reaction mechanisms have been proposed by BISHOP and BEAR (1972) to account for the difference in activation energy of the dimerization of silicic acid in dilute, slightly basic (pH = 8.5) aqueous solutions. The first two mechanisms are proposed in order to explain the negative activation energy in the temperature range between 25 and 35°C. The third and fourth mechanism are suggested by these authors to account for the positive energy of activation found in the temperature range between 35 and 45°C. The fifth mechanism has been proposed by ENGELHARDT *et al.* (1977) for silica polymerization in highly acidic solutions (pH between 0 and 2). The results of our calculations for the five reactions have been collected in Table 5.

According to our calculations the first reaction (5a) is endothermic ($\Delta G = +65$ kcal) and the formation of the reaction intermediate is exothermic ($\Delta G = -31$ kcal). The second reaction (5b) is exothermic ($\Delta G = -16$ kcal) and the formation of the reaction

Table 5. Calculated reaction mechanisms and reaction intermediates in the proposed polymerization reactions of silicic acid [1]

(5a)	$H_4SiO_4 + H_3SiO_4^-$	$= (H_7Si_2O_8)^-$		$= H_6Si_2O_7 + OH^-$	ΔG= +65 Kcal
	-4.2754 KeV	-4.2767 KeV		-4.2726 KeV	
(5b)	$2H_4SiO_4$	$= (H_8Si_2O_8)$		$= H_6Si_2O_7 + H_2O$	ΔG= -16 Kcal
	-4.2981 KeV	-4.2970 KeV		-4.2988 KeV	
(5c)	$H_4SiO_4 + H_3SiO_4^-$	$= H_6Si_2O_7 + OH^-$			ΔG= +65 Kcal
(5d)	$2H_4SiO_4$	$= H_6Si_2O_7 + H_2O$			ΔG= -16 Kcal
(5e)	$H_4SiO_4 + H^+$	$= (H_5SiO_4)^+ + H_4SiO_4$	$= (H_9Si_2O_8)^+$	$= H_6Si_2O_7 + H_3O^+$	ΔG= +39 Kcal
	-2.1491 KeV	-4.3107 KeV	-4.3073 KeV	-4.3090 KeV	

[1] d(Si-O)=1.62 A, d(O-H)=0.96 A, d(O-H) in Si-O--H-O-Si=1.20 A, ∠T-O-T=140°.

[2] 1 KeV=23061 Kcal; $E_T(H_4SiO_4)$=2.14905 KeV, $E_T(OH^-)$=0.5144 KeV, $E_T(H_3O^+)$=0.5508 KeV, $E_T(H_2O)$=0.5406 KeV, $E_T(H_6Si_2O_7)$=3.7582 KeV.

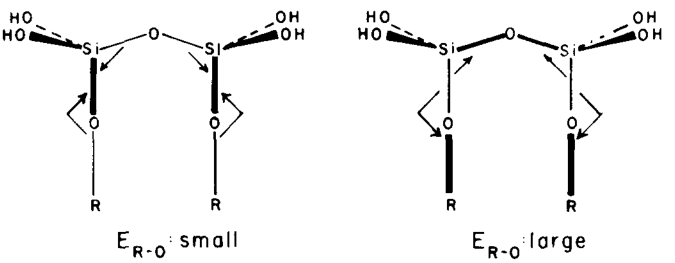

Fig. 7. The induced oscillatory two center energy pattern of the Si–O bond in the $RH_5Si_2O_7$ molecule.

intermediate is endothermic ($\Delta G = +26$ kcal). The third and fourth reaction mechanisms are single step mechanisms without the formation of intermediate complexes. The fifth reaction mechanism (5e) is endothermic with an endothermic reaction intermediate.

Bishop and Bear (1972) give the equilibrium constant for reaction (5d) at 25 and 45°C. From these data the free energy of reaction (5d) can be calculated; these values are −2.76 kcal (25°C) and −1.784 kcal (45°C). Linear extrapolation from these two points to 0 K gives a value of −17.4 kcal for the free energy of reaction (5d). The closeness of this value to the one calculated by us (−16 kcal) for the gas phase reaction is undoubtedly fortuitous. However the order of magnitude of the result suggests that solvent effects may not be very important in these polymerization reactions.

DISCUSSION

Substitution reactions

As mentioned previously, the inductive effects of the R^+ adions on the $H_2Si_2O_7$ cluster are manifested in an alternating pattern of bond energies. This oscillation pattern, represented schematically in Fig. 7 for the $R_2H_4Si_2O_7$ molecules with different R–O(nbr) two center energies, is one of the most important results of our calculations. A consequence of this oscillation is that the Si–O(br) bond in the $K_2H_4Si_2O_7$ cluster is weakened considerably more, and is therefore more susceptible to perturbing influences, than the Si–O(br) bond in the $H_6Si_2O_7$ cluster.* These relationships between the two center energies coincide with the bond energy relationships by Noll and others (see e.g. Brown and Gibbs, 1970) from bond length variations in alkali silicates and with similar relations in other metal oxide systems (see e.g. Gutmann, 1978).†

The extent to which the alkali silicate molecule in reaction (1) approximates a realistic description of the alkali–silica interaction can be tested by comparing the electronic energy levels with observed spectra for alkali silicate glasses. Differences between the projected densities of state (ρ_{ij}) of the two silicon atoms in the $RH_5Si_2O_7$ cluster correspond roughly to differences between the environment of a silicon atom in an alkali free silica framework vs one which has as second nearest neighbor an alkali adatom; similarly, differences between the projected densities of state of O(br) and O(nbr) correspond to the differences in environment between O(br) and O(nbr) adjacent to an alkali adatom. Calculated spectra illustrating the individual contributions of the two types of silicon and two types of oxygen are shown in Fig. 8. The calculated OKα spectrum shows that the difference in maxima corresponding to the two types of oxygen is about 1.6 eV. The difference in maxima corresponding to the two types of silicon in the calculated SiKβ and $SiL_{2,3}$ spectrum is about 1.6 eV. The calculated shift in the SiKβ spectrum is in good agreement with the observed shift of about 2 eV for binary alkali silicate glasses (Wiech *et al.*, 1976; de Jong *et al.*, 1980).

Variations in the physical properties of alkali silicate liquids can be rationalized in terms of specific bonds formed or broken during the particular process under consideration. Trends in these properties tend to follow the parallel trends in the two center energies of R–O(nbr) and Si–O(br) bonds, or that of the Si–O(nbr) two center energy (see Fig. 3). For example, the activation energy for viscous flow (Table 6) (Bockriss *et al.*, 1956) decreases with increasing R–O(nbr) two center energy for a fixed mole percentage of R_2O. We associate this trend with the increased ease of rupture of Si–O(nbr) bonds between flow units in a simple glide movement as a function of the type of alkali atom present (see Lacey, 1967). The activation energy for diffusion as well as that for electrical conductivity are associated with movement of alkali atoms in a three dimensional array of silicate

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* The alternating two center energy patterns which propagate through a silicate framework may interfere in or out of phase with one another. An example of the former is the change in the Si–O(br) two center energy in the mixed alkali silicate cluster, $LiNaH_4Si_2O_7$. In this molecule one of the Si–O(br) bonds has a higher two center energy, and the other a lower one than those of the Si–O(br) bonds in the end member cluster $Li_2H_4Si_2O_7$ and $Na_2H_4Si_2O_7$. This result suggests a rationalization for the commonly observed lowering of the melting point in mixed alkali compounds.

† Some examples of d(Si–O) variations in crystalline alkali silicates are: Li_2SiO_3 (Hesse, 1977), d[Si–O(nbr)] = 1.592 Å, d[Si–O(br)] = 1.680 Å; coordination: O(br) = 3, O(nbr) = 4, Li = 4. Na_2SiO_3 (McDonald and Cruickshank, 1967), d[Si–O(nbr)] = 1.592 Å, d[Si–O(br)] = 1.673 Å; coordination: O(br) = 3, O(nbr) = 5, Na = 5. $K_4(Si_8O_{18})$ (Schweinsberg and Liebau, 1974), d[Si–O(nbr) = 1.543 Å, d[Si–O(br)] = 1.643 Å; coordination: O(br) = 3, O(nbr) = 3, K = 8–11. $Rb_6Si_{10}O_{23}$ (Schichl *et al.*, 1973), d[Si–O(nbr)] = 1.57 Å, d[Si–O(br)] = 1.63 Å; coordination: O(br) = 2–4, O(nbr) = 3–5, Rb = 7–8.

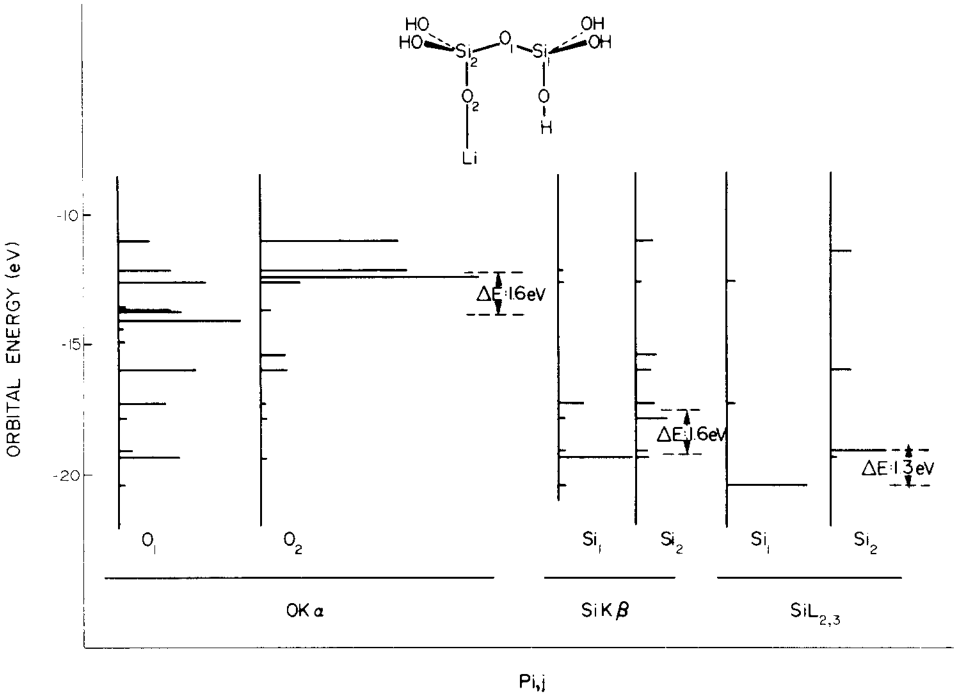

Fig. 8. Calculated OKα, SiKβ, and $SiL_{2,3}$ spectroscopic shifts due to a Li-O-Si bond in $LiH_5Si_2O_7$. It is assumed in this interpretation that the O ls and Si ls core levels are fixed.

tetrahedra.* The lack of a clear trend in these activation energies may be indicative of compensation between long range repulsions and weak R–O bonds (e.g. K) and short range attractions and strong R–O bonds (e.g. Li). The melting points for a fixed mole percentage R_2O of alkali silicate melts (KRACECK, 1930a,b; KRACECK *et al.*, 1929) indicate that the higher melting points of the glasses are correlated with higher R–O(nbr) two center energies. Especially in light of the very small thermal expansion of the Si–O bond (see HAZEN and PREWITT, 1977), it seems plausible that melting of a silicate is initially associated with the rupture of R–O(nbr) bonds. Finally surface tension data for alkali silicate melts (SHARTSIS and SPINNER, 1951) indicate that the surface tension of the melt increases with increasing Si–O(br) and R–O(nbr) two center energies. The fact that the surface tension of Li_2O–SiO_2 liquid is higher than that for SiO_2 suggests that the surface sheet which prevents the liquid from sinking in a capillary rise experiment is stronger in a Li_2O–SiO_2 melt than in a pure silica melt. If it is assumed that the coherence in this sheet is due to Si–O(br) bonds, the surface tension data suggest that the surface Si–O(br) bonds are stronger in a Li silicate melt than in a pure silica melt as a result of the oscillating two center energy pattern.

The role of chlorine and in particular of fluorine in silicate melts has been the subject of many studies and reviews among which are those of, FENN and SWANSON (1980), MASSON and CALEY (1978), MILLS (1977), BAILEY (1977), SWANSON and FENN (1977) and KEENE and MILLS (1976). The similarity between the calculated effects of these two halogens on the energy of

Table 6. Activation energy for viscous flow, E_η, for electrical conductivity, E_ω, and for self diffusion, E_σ, of R_2O-SiO_2 liquids, together with the freezing point depression, ΔT, and surface tension γ

	E_η(Kcal)[1]	E_ω(Kcal)[2]	E_σ(Kcal)[3]	ΔT(°K)[4]	γ(ergs/cm^2)[5]
R_2O	$33R_2O$-$67SiO_2$	$33R_2O$-$67SiO_2$	$33R_2O$-$67SiO_2$	$15R_2O$-$85SiO_2$	$20R_2O$-$80SiO_2$
Li_2O	33	15.6	12-16	243	307.6
Na_2O	38	15.2	13.2, 15.7, 16.3	345	273.1
K_2O	45	14.5	16.0	613	217.5

[1] Bockriss *et al.*(1956). [2] Ravaine *et al.*(1975), Göbel *et al.*(1979). [3] From Tables in Frischat (1974). [4] Kraceck(1930a,b). [5] Shartsis and Spinner(1951).

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* As the quality of conductivity data of silicate glasses seems superior to that of diffusion data, it may be advantageous to calculate the latter from the former by using the Einstein relation. According to CARRON (1969) this relationship properly relates electrical conductivity and diffusion in silicate liquids. However, from these data it is not possible to calculate the dynamic viscosity because of the fact that the Stokes Einstein relation, which couples the dynamic viscosity with diffusion does not seem to be valid for silicate liquids (MURASE, 1962; CARRON, 1969).

the Si–O(br) bond is substitution reaction (2) poses something of an enigma because it is well known that though fluorine lowers the viscosity and the freezing point of a silicate liquid, chlorine remains relatively inert (Fenn and Swanson, 1980, Hirayama and Camp, 1969). A poor parameterization of fluorine and chlorine in the CNDO/2 method may be the cause for the similarity in effect of these two anions on Si–O(br). A more attractive alternative is that the mechanism for reaction (2) as written, is improper, and that other, energetically more favourable reactions occur. This would agree with the general consensus in the geologic and glass literature that fluorine is partitioned preferentially in the liquid and that chlorine goes into the vapor phase. (For a review see Bailey, 1977.) Fluorine lowers the liquidus temperature as well as the viscosity and the surface tension of the liquid in accordance with the small decrease in Si–O(br) bond energy shown in Table 2. The alternative reaction explaining the relative inertness of chlorine in silicate liquids is thought to be the formation of a volatile alkali chloride in the liquid. This causes a decrease of network modifying atom activity in the liquid (Hirayama and Camp, 1969). Permissive geologic evidence for this volatilization of chlorides is the presence of halite and sylvite crystals in fluid inclusions in basaltic rocks (Roedder, 1972).

Addition reactions

The effect of R^+ adions on the adjacent Si–O bond in the $RH_5Si_2O_7$ cluster in substitution reaction (1) is similar to that for the adions in addition reaction (3a) (compare Fig. 3 and Fig. 5c). The difference between the two reaction types is that in the former reaction the R^+ adion is adjacent to the Si–O(nbr) bond whereas in the latter reaction this atom is adjacent to the Si–O(br) bond. Because of the fact that the Si–O(br) bond is associated with the structural coherence of a three dimensional silica framework, the addition reactions enable us to study the degree to which this coherence is perturbed.

Our calculations for reaction (3a) and (3b) suggest that a three dimensional array of silica tetrahedra is affected least by a K^+ adion and most by a H^+ adion. As evidence for the inertness of K^+ ions in a silicate framework, Kracek (1930a) pointed out that the most silica rich, thermodynamically stable potassium silicate known is a tetrasilicate. The most silica rich, thermodynamically stable lithium or sodium silicates on the other hand are disilicates (Kracek, 1930a). Some other evidence for the relative stability of a silica polymer in a solid as a function of the type of adion present is suggested by the ΔG^0 of silication of layer silicates (Tardy and Garrels, 1974). These ΔG^0 of silication values suggest that the silicate sheet in the potassium layer silicate is considerably more stable than that of any of the lower molecular weight alkali layer silicates.

The effect of water on silicate melts has recently been reviewed by a number of authors including Scholze (1966), Boulos and Kreidl (1972) and Mysen (1977). The calculated effects on H_2O, H_3O^+, H^+ and OH^- on the Si–O(br) bond [reaction (3b)] all indicate the strong network modifying effect of the H^+ adion. Even water itself affects the Si–O(br) two center energy more than the K^+ adion. According to Scholze (1966) the aforementioned species, H_3O^+, is only present in melts with a water content larger than 0.5 mol%. The decrease in the viscosity of the melt as well as the lowering of the liquidus temperatures are in agreement with Eggler and Rosenhauer's (1978) suggestion concerning the marked affinity of the aqueous species for O(br) in a three dimensional array of silica tetrahedra. According to our calculations, the attachment of H_2O (configuration II) to O(br) is, exothermic, but the attachment of H_2O to O(nbr) with the subsequent expulsion of H^+ is endothermic, in agreement with Eggler and Rosenhauer's (1978) suggestion. A similar role for water has been inferred by Griggs (1967), Kirby (1977) and Kirby and McCormick (1979) for the hydrolytic weakening of quartz. The first step in their reaction mechanism is the hydrolysis of O(br) followed by diffusion of some species associated with water.* The effects of water on silicate liquids are similar to those of R_2O alkali oxides. Hence, as has been suggested by Shelby and McVay (1976), the interaction of water with alkali-oxides may give rise to a mixed alkali effect.

Following the H^+ adion, the bent CO_2 molecule is the strongest network modifier considered in this study. The effects of this molecule on silicate melts of geologic relevance, recently reviewed by Eggler and Rosenhauer (1978), are not in agreement with those from our calculations, which show that the reaction of CO_2 with O(br) is exothermic and the reaction with O(nbr) is endothermic.† CO_2 is reported to enhance the polymerization of silicate melts, and presumably to increase the dynamic viscosity of these melts. This discrepancy between observed and calculated effects leads us to the suggestion that CO_2, rather than reacting with the O atoms associated with silicon, reacts more readily with the alkali oxides (Eitel and Weyl, 1932). In this manner the activity of the alkali in the silicate liquid is reduced resulting in an increase in the dynamic viscosity of the liquid, enhanced even more by the submicroscopic unmixing of the carbonates which might lead to Bingham plastic behaviour of the liquid. The very large sensitivity to temperature of the

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* The activation energy for oxygen diffusion in silica with excess oxygen is, according to Hetherington and Jack (1964), 27 kcal/mol for type I silica glass. This value is close to the observed activation energy for creep of 25.8 ± 1.7 kcal/mol observed by Kirby and McCormick (1979), and of the same order of magnitude as the activation energy for H_2O diffusion ~30 kcal/mol found by van Damme *et al.* (1976).

† The affinity of H_2O and CO_2 for O(br) vs O(nbr) is calculated for the reactions $[H_6Si_2O_6–O(br)] + (H_2O,CO_2) = [H_5Si_2O_6–O(br)(Co_2, H_2O)] + H^+$ and $[H_6Si_2O_6–O(br)] + (H_2O, CO_2) = [H_6Si_2O_6–O(br)\text{-}(CO_2, H_2O)]$.

dynamic viscosity of sodium silicate melts (PEARCE, 1964) seems indicative of the CO_2 release from sodium carbonates in these melts and thus of the alkali–CO_2 affinity. The work of EITEL and WEYL (1932) shows convincingly the preferential CO_2–alkali interaction in silicate melts. A very important discovery by these authors is the fact that Li silicate melts take up only 1/30th the amount of CO_2 in comparison to comparable Na silicate melts. This is the more surprising as the ΔG of formation of $Li_2CO_3(T = 293\,K)$ is 20 Kcal more negative than that of Na_2CO_3(JANAF Tables, 1972). Hence according to the Bell–Evans–Polanyi principle the formation of Li_2CO_3 is favored kinetically as well as thermodynamically over that of Na_2CO_3. We shall discuss the possible implications of this phenomenon for the distribution of alkalis in silicate liquids elsewhere (DE JONG *et al.*, 1980).

Addition reaction (4a) models the effect of the R adions on a lithium sheet silicate fragment. The results of reaction (4a) are readily interpreted in the light of previous addition reactions. Thus the smaller the two center energy between the R^+ adion and O(br), the smaller the change in the two center energy of Si–O(br). It is therefore expected that the K^+ adion in the exchange site affects the coherence of the silicate polymer less than a H^+ adion in the same site.

The effect of an H^+ adion on a silicate fragment [reaction (4b)] can also be readily explained. The oscillatory pattern of bond energies [reaction (1)] shows, as mentioned previously, that the stronger the R–O(nbr) bond, the stronger the Si–O(br) bond, and hence the smaller the effect of the H^+ adion on this bond. If we associate the degree of weakening of the Si–O(br) bond, as the H^+ adion approaches O(br), with the solubility of these silicate fragments, we predict the following order of solubilities:

$$\begin{aligned}(H\text{–}K_2H_4Si_2O_7)^+ &> (H\text{–}Na_2H_4Si_2O_7)^+\\ &> (H\text{–}MgH_4Si_2O_7)^+\\ &> (H\text{–}Li_2H_4Si_2O_7)^+\end{aligned}$$

The equilibrium constants for the solubilities of the R_2SiO_3 metasilicates are collected in Table 7. This solubility sequence agrees with the calculated one except for the solubilities of the magnesium and lithium cluster. These results suggest that the rupture of a surface Si–O(br) bond, rather than the highly exothermic alkali–hydrogen exchange[*], is the rate determining step in the dissolution process (BURNHAM, 1975; PETROVIC *et al.*, 1976; DIBBLE and TILLER, 1980)[†]. However the two steps have to depend to a degree upon one another, as can be inferred from the decrease in the rate of leaching upon alkali–alkaline earth depletion in the surface layer of silicate glasses as observed by CARLSON *et al.* (1974).

Table 7. Equilibrium constants for the reactions $R_2SiO_3(R'SiO_3) + 2H^+ = 2R(R'^{2+}) + SiO_2 + H_2O(25^\circ C$, 1 atm) [1], and H_2O solubility in R_2O–SiO_2 melts($1700^\circ C, P_{H_2O} =$ 760 torr) [2] (mole %)

R(R')[3]	log K	solubility[4]
K	30.146	1.05
Na	22.247	0.65
Li	15.942	0.45
Mg	11.469	-

[1] Tardy and Garrels(1977). [2] Franz and Scholze(1963). [3] R' is an alkaline earth. [4] Measured for $33R_2O$–$67SiO_2$ melts .

Reaction (4b) can also be used to rationalize the solubility of water in silicate melts. This solubility depends upon the ease with which the Si–O(br) bond can be broken and hence the ease with which another reactive site can be created. The pattern previously shown for the solubility trends of silicate fragments in aqueous solution should be similar to that of the water solubility in silicate melts. It is therefore expected that a potassium silicate melt, for a fixed mole percentage R_2O, dissolves more water than a sodium or lithium silicate melt. Data (Table 7) on the solubility of water in various alkali silicate melts bear this out.

Polymerization reactions

The utility of molecular orbital calculations becomes most apparent in testing the validity of suggested reaction mechanisms such as those collected in Table 5. Rather than mapping out the complete potential surface for each of the reactions in this Table, we have calculated the proposed reaction intermediates at one point on the surface at the approximate equilibrium distance d(O–H) of 1.20 Å. The calculated exothermic pre-equilibrium step in reaction (5a) agrees with the suggestion of BISHOP and BEAR (1972) concerning this reaction. However our calculations suggest that the overall process is endothermic and hence is not in agreement with the observed spontaneous dimerization of silicic acid. The second mechanism [reaction (5b)] calculated suggests a positive activation energy barrier in disagreement with Bishop and Bear's suggestion. Our calculations also suggest that the proton catalyzed mechanism proposed by ENGLEHARDT *et al.* (1977) for the polymerization of silicic acid at low pH is not feasible [reaction (5e)]. A discussion of the activation energy for polymerization of silicic acid is given by ROTHBAUM and ROHDE (1979) who suggest that between 5 and 90°C the activation energy for polymerization is small

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[*] Even though the alkali–hydrogen exchange is not important in characterizing the leaching process, it is very important in catalyst synthesis. For instance NH_4^+ exchange for Na^+ followed by calcination at 300°C is the standard way of manufacturing zeolites with very acidic protons [see for example SCHUIT (1977)].

[†] The role of the surface Si–O(br) bonds in describing the leaching process suggest a proportionality between the surface tension and the rate of leaching, i.e. the higher the surface tension the smaller the rate of leaching.

and positive whereas it is negative between 90 and 180°C.*

From the reported equilibrium constants (BISHOP and BEAR, 1972), the ratio of monomers to dimers can be calculated. At quartz saturation at 25°C only one percent of the total silica concentration occurs as dimers in the solution. At amorphous silica saturation, 21% of the total silica occurs as dimers according to their data, which seems a bit high. It should be mentioned that Bishop and Bear, in contrast to other workers in this field, do not make mention of an induction period in their experiments. ENGELHARDT *et al.* (1977) find in acidic solutions (pH 2) only middle groups (connectivity = 2) but no endgroups (connectivity = 1). These results suggest that in this pH range the character of the silica polymerization reactions is quite different from that in the range considered by BISHOP and BEAR (1972). It is claimed by ENGELHARDT *et al.* (1977) that in these dilute aqueous solutions cyclotetra species, similar to those found by INGRI (1959) in alkaline solutions (pH = 10.5), predominate. According to their interpretation of the NMR spectra, cyclotri species occur commonly, especially in dilute aqueous solution, indicating the absence of steric hindrance of these small ring systems. However the spectral assignment of ENGELHARDT *et al.* (1977) is not consistent with the one given earlier by ENGELHARDT *et al.* (1975). According to the earlier assignments no ring species occur in dilute solution at pH = 2. Because of the fact that ring condensation decreases with smaller Na/Si ratio (ENGELHARDT *et al.*, 1975), it seems that the earlier spectral assignment is correct and that the more recent one is faulty.

The polymerization reactions of silica in aqueous solutions do not seem to be essentially different from those in silicate melts with a high water content. We have previously discussed the role of water as a strong network modifier. However, some authors suggest a more complex role for water. According to SCHOLZE *et al.* (1975), a reaction may occur in which the formation of water starts to compete with the depolymerization reaction of silica and water. Thus according to these authors the reaction between a sodium silicate glass and water proceeds as follows:

$$\text{Si–O–Na}_{\text{glass}} + \text{H}^+_{\text{solution}} = \text{Si–O–H}_{\text{glass}} + \text{Na}^+_{\text{solution}}$$

However, according to SCHOLZE *et al.* (1975), Si–O–H groups, if present in sufficiently high concentration, may polymerize to form chains according to the reaction:

$$2\text{Si–O–H} = \text{Si–O–Si} + \text{H}_2\text{O}$$

This polymerization reaction is used by KIRBY and MCCORMICK (1979) to explain the work hardening of quartz in their experiment. Earlier, KURKJIAN and RUSSELL (1958) proposed a similar network linking reaction involving water:

$$\text{H}_2\text{O} + 2(\equiv\text{Si–O}) = 2\text{OH}^- + \equiv\text{Si–O–Si}\equiv$$

which UYS and KING (1963) used to explain their observation that the solubility of water increases in silicate melts with increasing mole percent R_2O or RO when R is a strong base (such as Li or Ca), whereas it decreases in the case of weak bases (such as Fe or Zn). The fact that the maximum growth rate in alkali feldspar occurs at water undersaturated conditions and decreases with increasing water content (FENN, 1977) may also be affected by these types of reactions. The dual role of water led NOLL (1963) to the statement that water in catalytic amounts functions as a network modifier, but in stoichiometric amounts as a network former in silicate melts.†

In order to stress the fact that to a first approximation the behaviour of silica does not seem to be solvent dependent, we have shown in Fig. 9 a comparison between a calculated polymeric distribution of a sodium silicate melt from a FLORY (1941) and HUGGINS (1941) type analysis by BALTA (1972), and the silica species distribution as inferred from ^{29}Si pulsed NMR measurements on highly alkaline aqueous solutions by ENGELHARDT *et al.* (1974). This similarity in polymer distribution between the two systems as a function of Na/Si ration is one example of the conclusion reached by SILVERMAN (1917) that the chemical behaviour of aqueous and vitreous solutions is often quite similar.

Charge effects on a quartz surface

Our molecular orbital calculations also enable us to reach some conclusion concerning the charge on a surface at the solid water interface as a function of the adion present.‡ Substitution reaction (1) and addition reaction (3a) and (3b) describe the surface attachment of various adions to an O(nbr) or O(br) atom respectively which are exposed to the surface. The point of zero charge for quartz occurs at a pH = 2. At this

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* At slightly higher silica concentrations MAKRIDES *et al.* (1980) find an activation energy of attachment of about +17 kcal between 75 and 105°C, i.e. about 5 times higher than that found by ROTHBAUM and ROHDE (1979). Our ^{29}Si NMR data (DE JONG *et al.*, 1979) indicate that, in agreement with the positive activation energy for attachment, the concentration of monomeric silica increases in the temperature range between 35 and 90°C.

† Extrapolation of the freezing point depression curves from the higher molecular weight alkali oxides–silica system to water suggests a rather large region of stable or metastable liquid immiscibility in the latter system.

‡ Recently some semiempirical calculations on silica have been published by DUNKEN and HOBERT (1979). Three objections have to be raised with respect to their results. Firstly the charge on O(br) and the Si atoms are very far removed from what should be the approximately correct values of about −0.7 for oxygen and +1.4 for silicon (see DE JONG and BROWN, 1980). Secondly the infrared frequencies for (Si = O) and (Si–O) bonds are assigned in accordance with BADGER's rule (1935) but the assignment has in fact to be inverted according to BELL *et al.* (1970). Thirdly it is incorrect to associate calculated bond orders with surface attachment energies. The former is an atomistic concept the latter a thermodynamic one. For example the free energy for surface attachment to O(br) of the H^+, HO^-,

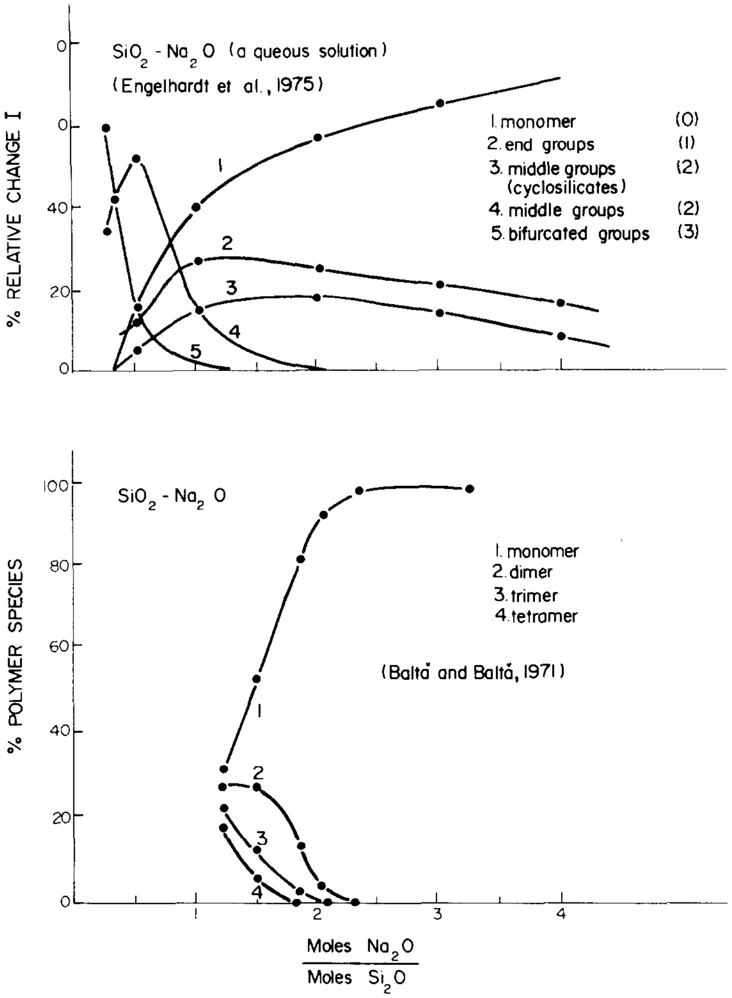

Fig. 9. Comparison between the experimentally determined silica species distribution in water (Engelhardt *et al.*, 1975) and the calculated silica species distribution in silicate melts (Balta, 1972).

point the quartz surface is saturated with H^+ adions. According to our calculations the charge on the O(br) and O(nbr) atoms in the presence of H^+ adions varies between -0.56 for O(br) and -0.61 for O(nbr). (See Table 1 and Table 3a.) Replacement of H^+ by other adions changes the charge on O(nbr) from -0.61 to -0.71 (H^+–Na^+ exchange; see Table 1) and O(br) from -0.56 to -0.77 (H^+–Na^+ exchange; see Table 3a).§ Thus at high pH and a small rate of alkali–hydrogen exchange, the SiO_2 surface is negatively charged, due to adsorbed alkali adions. Hence in order to reach the isoelectric point, the acidity of the solutions has to be increased. Inspection of Table 1 and Table 3a also show that the less negative the R–O two center energy, the larger the negative charge in the O(br) and O(nbr) atoms. As a consequence a quartz surface with adsorbed K^+ adions will be more negatively charged than a surface with an equimolar amount of Li^+ adions adsorbed on it.

SUMMARY AND CONCLUSIONS

The effect of network modifiers on the Si–O(br) bonds depends strongly on the type of modifier present as well as on the site, i.e. O(br) or O(nbr), on which the modifier is attached. Of all the modifiers considered H^+ has the most destructive effect on the properties of adjacent Si–O bonds and hence, in the case of a Si–O(br) bond, on the integrity of a three dimensional silica framework. The K^- adion on the other hand affects adjacent Si–O bonds the least, manifesting alkali silica relations similar to those

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H_3O^+ and H_2O species follow according to our calculations the sequence:

$$\underset{(-317\,\text{kcal})}{H^+} > \underset{(-54\,\text{kcal})}{H_3O^+} > \underset{(-17\,\text{kcal}}{(OH^-)} > \underset{(-9\,\text{kcal})}{H_2O(II)} > \underset{(-5\,\text{kcal})}{H_2O(I)}$$

but the sum of the two center energies between O(br) and the atoms in the admolecules follows the sequence:

$$\underset{(-475\,\text{kcal})}{H^+} \quad \underset{(-280\,\text{kcal})}{H_3O^+} \quad \underset{(-32\,\text{kcal})}{H_2O(I)} \quad \underset{(-3\,\text{kcal})}{H_2O(II)} \quad \underset{(+41\,\text{kcal})}{(OH^-)}$$

§ At higher pH the quartz surface has a negative charge.

inferred by Tardy and Garrels (1974) from their ΔG of silication.

Modifying atoms attached to non bridging oxygen atoms induce an oscillatory two center energy pattern in the adjacent Si–O bonds, in accordance with known bond-length variations in crystalline alkali silicates. The trends in calculated free energies for the gas phase addition, substitution, and polymerization reactions, can be used to rationalize a number of observations on silicate liquids including freezing point depressions, dynamic viscosities, diffusion and conductivity, surface tension and surface charge, as well as H_2O solubilities in melts and polymerization tendencies of silicic acid in aqueous solutions.

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