to take place on a reasonable time scale, and where the thermal expansivity and other properties become that of a solid. In most systems the specific volume of the glass is greater than the crystal (density is lower). According to the theory of D. Turnbull and M.H. Cohen, upon cooling of a liquid the *free volume*, defined as the volume available for molecules or polyhedra to maneuver without encountering strong interactions with their neighbors, decreases continuously until at the glass transition all free volume has been removed, leaving each molecule trapped in a local energy minimum from which all other positions are inaccessible.

We notice in Fig. 1.45 that the volume changes at crystallization and vaporization are discontinuous. Since volume is a first-derivative function of the free energy $G$ (at constant composition $x$ and temperature $T$):

$$V = \left(\frac{\partial G}{\partial P}\right)_{x,T}$$

the discontinuities in $V$ at $T_m$ and $T_v$ define melting and vaporization as first-order phase transitions. In contrast, the change in $V$ at $T_g$ is continuous. The thermal expansivity $\alpha$ is a second-derivative function of $G$ (first derivative of $V$), and since changes in $\alpha$ at $T_g$ as well as other second-derivative functions such as heat capacity are fairly discontinuous, the glass transition has the appearance of a somewhat diffuse second-order phase transition. However, unlike equilibrium second-order phase transitions, the transition to a glass (which is not the ultimate equilibrium form but only metastable) occurs over a range of temperatures depending on the thermal history of the glass, as shown in Fig. 1.45*b*. A faster rate of cooling freezes structural rearrangement at a higher $T_g$ and specific volume, whereas slower cooling results in a denser glass with a lower $T_g$. Upon heating, hysteresis in the reverse glass-to-liquid transition can also occur if the heating and cooling rates are not the same. Some difficulty persists in defining the nature of the glass transition. It is perhaps sufficient for this discussion to say that the glass transition is a true phase transition (between a supercooled liquid and a glassy solid), but with characteristics determined primarily by kinetics rather than equilibrium thermodynamics.

Concurrent with the changes in volume shown in Fig. 1.45 are changes in the viscosity of the glass. Anyone who has watched a glassblower at work will recognize that glass viscosity is greatly temperature-dependent; we will see that it is also greatly composition-dependent. Glasses are often characterized by the temperature at which several viscosities of practical interest are achieved. The *working point*, where forming is possible, is defined as the temperature at which $\eta=10^4$ Poise; the *softening point* by $\eta = 10^{7.6}$. The *annealing point* is a viscosity at which internal stresses can be substantially relieved in 15 minutes or so, and is defined as $\eta = 10^{13.4}$ Poise. The viscosity at the glass transition is $10^{13}$-$10^{14.5}$ Poise for oxide glasses,and represents a limit above which structural rearrangements cannot take place at normal cooling rates.

## Continuous Random Networks

Amorphous $SiO_2$ (fused silica) is the prototypical oxide glass. As in the crystalline silicates, directional covalent bonding and ionic bonding in accordance with Pauling's rules promote the formation of tetrahedral $(SiO_4)^{4-}$ basic structural units. Therefore, short-range order is identical in crystalline and glassy $SiO_2$; the coordination of anions around cations is four, and the O-Si-O bond angle within each tetrahedral unit is 109.5°. The O/Si ratio of 2 indicates that all four corners of each tetrahedra are interconnected in glassy $SiO_2$, as is the case in the various crystalline phases of $SiO_2$. However, it is possible for complete connectivity to be maintained without crystalline order; and this is the basis of the *continuous random network* structure first proposed by Zachariesen in 1932 (*J. Am. Chem. Soc.*, 54, 3841). In two dimensions, the continuous random network structure of an $A_2B_3$ glass is shown in Fig. 1.46.

Examining Fig. 1.46, and imagining the three-dimensional counterpart that is $SiO_2$, we can identify three structural parameters at a medium range of order that allow us to distinguish between the crystalline and continuous random network amorphous structures. These are: (1) the angle of the Si-O-Si bond between tetra-

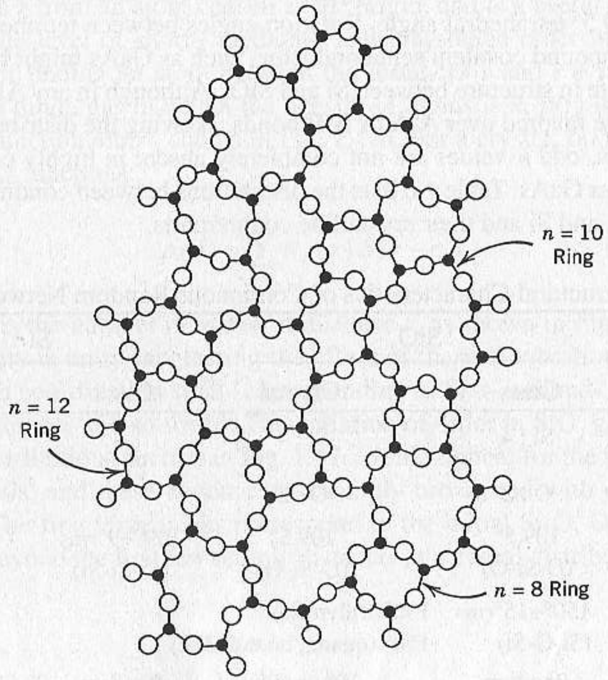

**Fig. 1.46** Continuous random network model of an $A_2B_3$ glass. [From W. H. Zachariesen, *J. Am. Chem. Soc.*, 54, 3841 (1932).]

hedra; (2) the rotational angle between tetrahedra; and (3) the number of Si-O bonds that complete each of the "rings" seen in Fig. 1.46. Each of these three parameters has firmly fixed values in crystalline $SiO_2$, but varies over a wider range in the corresponding glass (see Table 1.6.) The intertetrahedral Si-O-Si angle $\theta$ in amorphous $SiO_2$ takes on a broad range of values with an rms $\Delta\theta$ of about 15° centered at a mean of 150°. The rotational angle between tetrahedra is random, whereas in crystalline $SiO_2$ it is either 0° or 60°. And, if we examine the number of Si-O bonds $n$ that form an interconnected ring (ring statistics), we find well-defined distributions in the crystalline silicates with a minimum of $n = 12$ ($n$ must be an even number to avoid the occurrence of energetically unfavorable Si-Si or O-O bonds). In amorphous $SiO_2$ on the other hand, some $n = 8$ and 10 rings appear to exist (R. J. Bell and P. Dean, *Phil. Mag.*, 25, 1381, 1972).

Similar features are found in other $AB_2$ compounds with an anion coordination of 4 and cation coordination of 2. In covalent semiconductors such as Si and Ge that take on tetrahedral coordination in their crystalline form (diamond cubic structure), the amorphous form can also be described as a continuous random network of tetrahedra. In contrast to $SiO_2$, the coordination of every atom is 4, and odd-numbered rings are allowed, although $n < 5$ is not found due to the strain necessary to accommodate it (the minimum in the diamond cubic structure is $n = 6$). There is only one characteristic angle, Si-Si-Si, and it varies by a rms value of 9° about the 109.5° tetrahedral angle. Rotation angles between tetrahedra are again random. Compound covalent semiconductors such as GaAs might be considered as intermediate in structure between Si and $SiO_2$. Although in any $AB_2$ compound A-B bonds are favored over A-A or B-B bonds, skewing the distribution of rings toward even $n$, odd $n$ values are not completely absent in highly covalent compounds such as GaAs. Table 1.6 lists the distinctions between continuous random network $SiO_2$ and Si and their crystalline counterparts.

**Table 1.6** Structural Characteristics of Continuous Random Network Glasses

| | $SiO_2$ | | Si | |
|---|---|---|---|---|
| | Glass | Crystal | Glass | Crystal |
| Number of nearest neighbors | Si : 4<br>O : 2 | Si : 4<br>O : 2 | 4 | 4 |
| Bond angles | 109.5° (O-Si-O)<br>150°+15°rms (Si-O-Si) | 109.5° (O-Si-O)<br>180°(tridymite)<br>150° (quartz, cristobalite) | 109°+9°rms (Si-Si-Si) | 109.5° (Si-Si-Si) |
| Rotation angle between tetrahedra | Random | 0° or 60° | Random | 0° (diamond cubic) |
| Ring counts | 8, 10, 12... | 12 | 5, 6, 7, 8,... | 6, 8, 10.... |

## Random Close-Packing

The nondirectional nature of metallic bonding combined with the absence of charge-neutrality requirements results in a very different structure for metallic glasses. They form in a random close-packed (rcp) structure of somewhat lower density (63.7% for a monatomic solid) than the close-packed FCC and HCP lattices (74.1%). Each atom occupies a local energy minimum position, and while this structure is metastable, reconstruction rather than a continuous change of atom positions is necessary to transform to the FCC and HCP structures. There is less order in the first coordination shell than in continuous random network structures. Common foamed polystyrene (Styrofoam™) is a reasonably good simulation of the rcp topology, being composed of deformable spheres of roughly constant size each of which represents the volume available to an atom. Close examination of compacts of deformable spheres (J. L. Finney, *Proc. Roy. Soc. (London)* A, 319, 479, 1970) shows that the polyhedra have on average 14.3 faces, in which the average number of edges per face is 5.16.[6]

## Radial Distribution Function

The radial distribution function $\rho(r)$ characterizes the variation in atom density with distance $r$ from an atom chosen as the origin, and is a useful parameter for illustrating the level of short-, medium-, and long-range order in glasses. The probability of finding an atom between the distances $r$ and $r + dr$ is given by $\rho(r)dr$. For a dilute gas in which the density of atoms is $n$, $\rho(r)$ is given by the continuous function $4\pi nr^2$, shown in Fig. 1.47*a*. For a crystal, $\rho(r)$ is given by a series of delta functions:

$$\rho(r) = \sum N_i(r)\,\delta(r - r_i)$$

where $N_i(r)$ is the number of atoms at distance $r$, as shown in Fig. 1.47*b*. Here the probability is unity (neglecting the effect of thermal vibrations) at the distance of each coordination shell (corresponding to first-, second-, third-nearest neighbor distances and so forth). The variation of order in $SiO_2$ glass is seen in the radial distribution function in Fig. 1.47*c*. Peaks appear for the first few coordination shells, and these become increasingly broadened with distance from the origin. The first three peaks correspond to the initial Si-O, O-O, and Si-Si distances. Beyond the first few atomic distances, the radial distribution function

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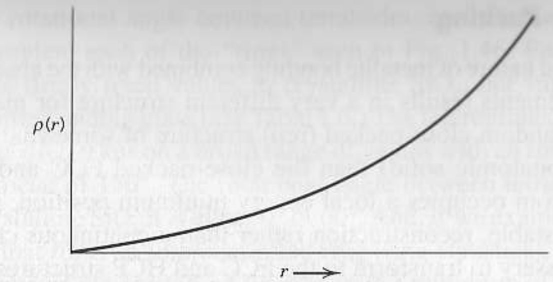
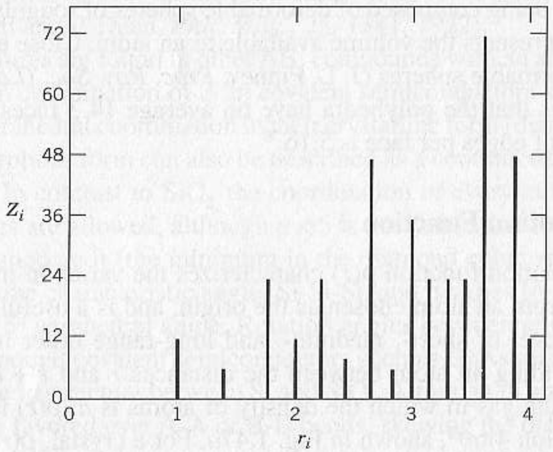
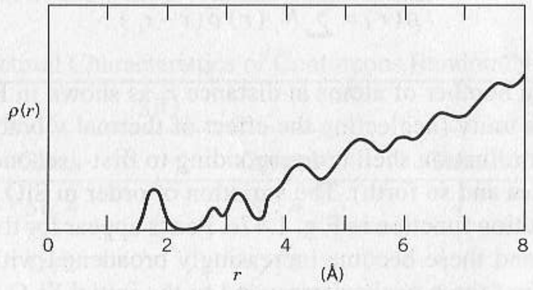
[6] These are therefore approximately tetrakaidecahedra (14 faces), which we may compare with the Kelvin tetrakaidecahedra (truncated octahedron) that is the ideal space-filling regular polyhedron representing polycrystalline microstructures obtained by enforcing angles of 120° between all grain boundaries, and 109.5° between the lines that are three-grain junctions. See Chapter 5.



(a) Gas



(b) fcc crystal



(c) Amorphous $SiO_2$

**Fig. 1.47** Comparison of radial distribution functions for vapor, crystal, and glassy phases. For an fcc crystal, (*b*), the probablility of finding an atom is unity at each coordination shell, while the number of atoms $Z_{ii}$ varies. (after R. Zallen, *The Physics of Amorphous Solids*, J. Wiley and Sons, 1983.) (*c*) shows the experimental RDF for amorphous $S_1O_2$ [from R. J. Bell and P. Dean, *Phil. Mag.*, 25, 1381 (1972).]

quickly approaches that of a gas. The RDF's for different continuous random network glasses and for random close-packed glasses differ in their quantitative details. It is the careful experimental determination of RDF's, primarily by x-ray, electron, and neutron scattering experiments, that has confirmed the amorphous structures described above.

## Oxide Glasses

In his pioneering descriptions of glass structure, Zachariesen recognized that while cation/anion radius ratios in the correct range (<0.4) for tetrahedral coordination were often found in glass-forming oxides, this was a necessary but not sufficient condition for glass formation (i.e., many tetrahedrally coordinated crystalline oxides are not good glass formers). He enumerated the following structural rules, which are analogous to Pauling's rules for crystalline structures, for determining which compounds will form continuous random network oxide glasses. At the time, amorphous semiconductors and metallic glasses had yet to be discovered or characterized. Zachariesen's rules state:

1. Each oxygen atom is linked to no more than two cations.
2. The number of oxygen atoms surrounding the cation must be small, four or less.
3. The oxygen polyhedra share corners rather than edges or faces.
4. At least three corners of each oxygen polyhedra are shared.

These rules correctly predict ease of glass formation for the oxides $B_2O_3$, $SiO_2$, $GeO_2$, $P_2O_5$, and a few others. These oxides are known as *network formers*. Glasses made solely from network formers often have limited utility. For example, pure $B_2O_3$ glass ($T_g$ ~450°C) is not water resistant, and pure $SiO_2$ glass (fused silica) while valued for its chemical durability, high use temperatures (up to ~1200°C), and thermal shock resistance, must be processed above 1750°C. The great majority of useful glasses contain additives that serve to alter processing and properties. These are commonly termed *network modifiers* and *intermediates*, which we will now discuss. Table 1.7 classifies various cations with respect to their roles as network formers, modifiers, and intermediates in oxide glasses.

Network modifiers provide extra oxygen ions but do not participate in the network, thereby raising the O/Si ratio of the glass. The extra oxygen allows the *bridging* oxygen between two tetrahedra to be disrupted, and two *nonbridging* oxygen to terminate each tetrahedron. For example, in sodium silicates, each $Na_2O$ molecule results in the formation of two *nonbridging* oxygen in $SiO_2$, with the $Na^+$ ions providing local charge neutrality, as shown in Fig. 1.48. The fraction of nonbridging oxygen is readily determined from the composition (see Problem 24 at the end of the chapter). The effects of modifiers are directly analogous to the decreasing $SiO_4$ interconnectivity observed in crystalline silicates with increasing O/Si ratio described earlier. In glasses the loss of connectivity results in greatly decreased viscosities and $T_g$'s for modified silicates and reduces the processing temperatures of silicate glasses

Table 1.7 Coordination Number and Bond Strength of Oxides

| | M in $MO_x$ | Valence | Dissociation Energy per $MO_x$ (kcal/mole) | Coor-dination Number | Single-Bond Strength (kcal/mole) |
|---|---|---|---|---|---|
| Glass formers | B | 3 | 356 | 3 | 119 |
| | Si | 4 | 424 | 4 | 106 |
| | Ge | 4 | 431 | 4 | 108 |
| | Al | 3 | 402–317 | 4 | 108 |
| | B | 3 | 356 | 4 | 89 |
| | P | 5 | 442 | 4 | 111–88 |
| | V | 5 | 449 | 4 | 112–90 |
| | As | 5 | 349 | 4 | 87–70 |
| | Sb | 5 | 339 | 4 | 85–68 |
| | Zr | 4 | 485 | 6 | 81 |
| Intermediates | Ti | 4 | 435 | 6 | 73 |
| | Zn | 2 | 144 | 2 | 72 |
| | Pb | 2 | 145 | 2 | 73 |
| | Al | 3 | 317–402 | 6 | 53–67 |
| | Th | 4 | 516 | 8 | 64 |
| | Be | 2 | 250 | 4 | 63 |
| | Zr | 4 | 485 | 8 | 61 |
| | Cd | 2 | 119 | 2 | 60 |
| Modifiers | Sc | 3 | 362 | 6 | 60 |
| | La | 3 | 406 | 7 | 58 |
| | Y | 3 | 399 | 8 | 50 |
| | Sn | 4 | 278 | 6 | 46 |
| | Ga | 3 | 267 | 6 | 45 |
| | In | 3 | 259 | 6 | 43 |
| | Th | 4 | 516 | 12 | 43 |
| | Pb | 4 | 232 | 6 | 39 |
| | Mg | 2 | 222 | 6 | 37 |
| | Li | 1 | 144 | 4 | 36 |
| | Pb | 2 | 145 | 4 | 36 |
| | Zn | 2 | 144 | 4 | 36 |
| | Ba | 2 | 260 | 8 | 33 |
| | Ca | 2 | 257 | 8 | 32 |
| | Sr | 2 | 256 | 8 | 32 |
| | Cd | 2 | 119 | 4 | 30 |
| | Na | 1 | 120 | 6 | 20 |
| | Cd | 2 | 119 | 6 | 20 |
| | K | 1 | 115 | 9 | 13 |
| | Rb | 1 | 115 | 10 | 12 |
| | Hg | 2 | 68 | 6 | 11 |
| | Cs | 1 | 114 | 12 | 10 |

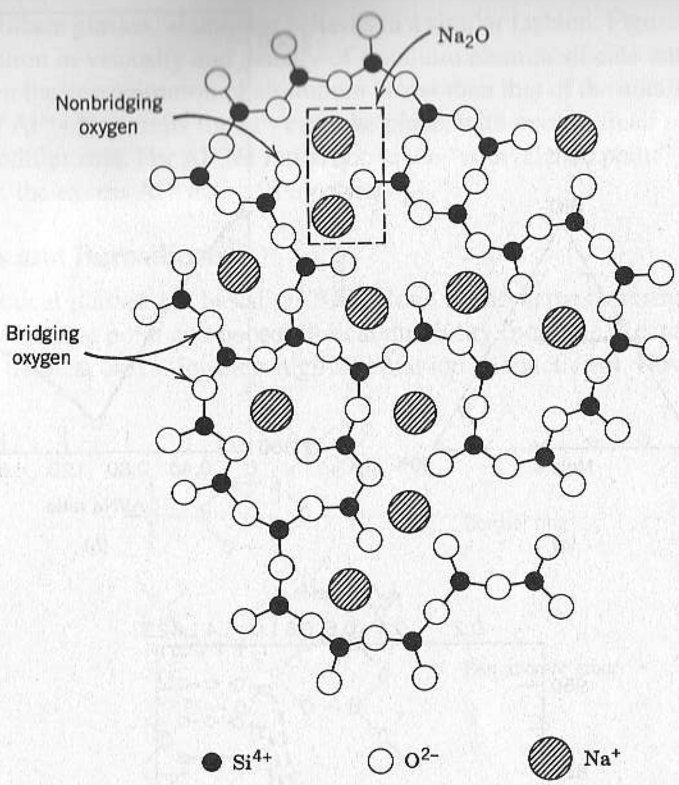


**Fig. 1.48** Schematic representation of the structure of a sodium silicate glass. Each $Na_2O$ addition results in the formation of two nonbridging oxygen terminating silica tetrahedra.

into more practical ranges. While alkaline oxides ($Na_2O$, $Li_2O$, $K_2O$) are very effective modifiers, they result in glasses that are not chemically durable. (Sodium silicates are known as *water glasses* as they are water-soluble.). In the commercially important soda-lime-silicates most commonly seen as windows and containers, the chemical durability is greatly improved with the additional modifier CaO. One thus has the reduced processing temperatures of a modified glass without the drawbacks of an alkaline silicate. Container and window glasses have O/Si ratios of 2.3–2.4; in glazes and enamels it varies from 2.25 to 2.75. Other commonly used modifiers in silicate glasses include PbO, MgO, ZnO, and BaO.

*Intermediates* as the name implies are not clearly modifiers or network formers and may contribute in part to the network structure. They are generally cations with higher valence than the alkalis and alkaline earths, but which do not satisfy Zachariesen's rules for network formers. One of the most interesting intermediates is $Al^{3+}$, for its structural role depends on the presence and concentration of alkali ions. In discussing clay minerals, we pointed out that $Al^{3+}$ can often substitute for $Si^{4+}$ as long as charge neutrality is achieved by having an adjacent alkali

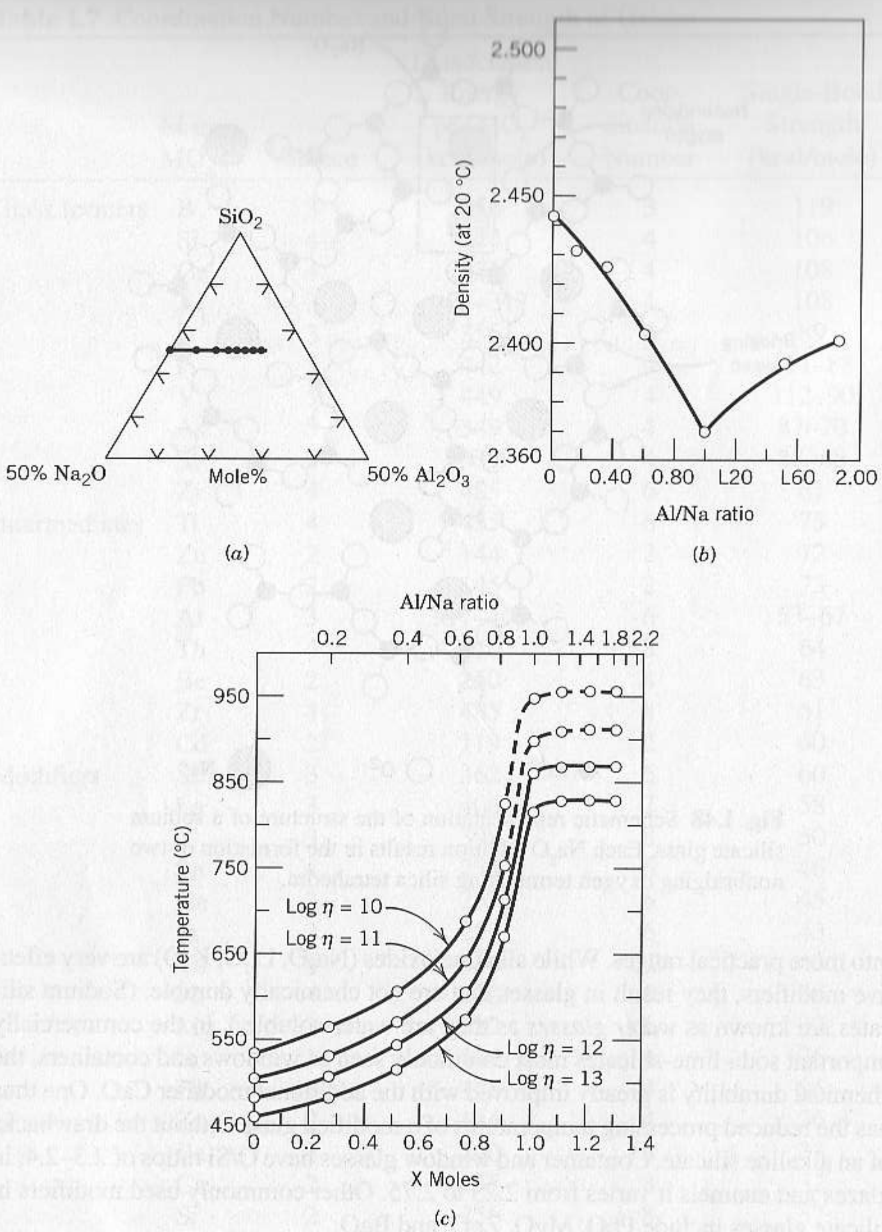


**Fig. 1.49** Variation in properties of $SiO_2$-$Al_2O_3$-$Na_2O$ glass with Al/Na ratio. (*a*) Composition series in which Al/Na ratio is varied at constant $SiO_2$ content; (*b*) variation in density showing minimum at Al/Na = 1, the equivalence point, where all Al is believed to be tetrahedrally coordinated (D. E. Day and G. E. Rindone, *J. Am. Ceram. Soc.*, 45[10] 489 (1962).; (*c*) isoviscosity lines showing sharp decrease in viscosity for compositions with excess modifier, Al/Na < 1. [T.D. Taylor and G.E. Rindone, *J. Am. Ceram. Soc.*, 53[1] 692 (1976).]

ion. In silicate glasses, aluminum behaves in a similar fashion. Figure 1.49 shows the variation in viscosity and density of a sodium aluminosilicate with Al/Na ratio. When the concentration of aluminum is less than that of the alkali, the substitution of $Al^{3+}+Na^{1+}$ units for $Si^{4+}$ can take place, with excess alkali serving in its usual modifier role. For Al/ Na ratios above the "equivalence point" (Al/ Na =1) however, the excess $Al^{3+}$ acts as a modifier.

## Borates and Borosilicates

Few practical glasses are based on $B_2O_3$ alone as the network former due to its very low melting point and poor chemical durability (possible exceptions are the alkaline borates, useful for their high alkaline ion conductivity). However, when

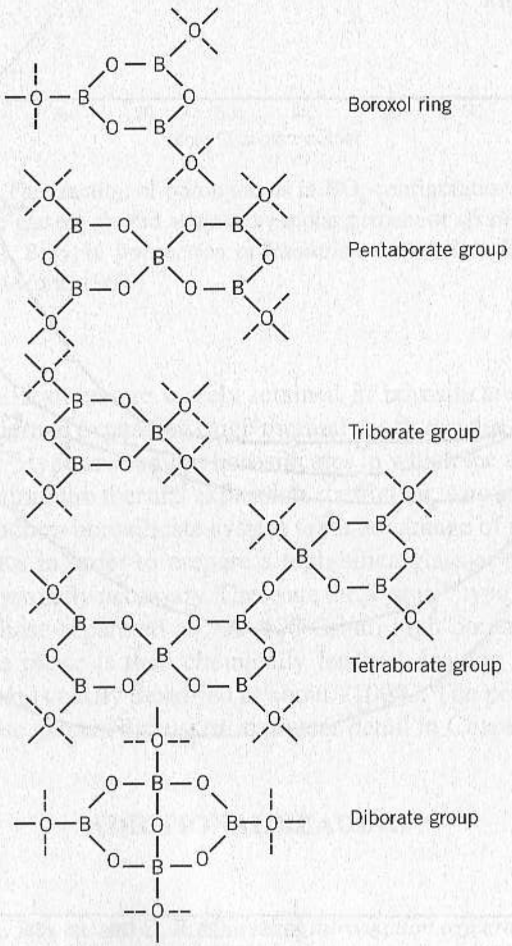


**Fig. 1.50** Possible structural elements of borate glass. (From W. Vogel, *Chemistry of Glass*, The American Ceramic Society, Columbus, OH, 1985.)