Technical Papers

Species Density Analysis of Silicate Glass Structure[1]

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The dependence of certain physical properties of silicate glasses on the ratio of metal to oxygen atoms has been discussed by Huggins (*1*). Considering the variation in the volume per gram atom of oxygen with composition, the latter expressed as ratio of silicon to oxygen atoms, he was able to demonstrate that a series of linear relations exists. The volume varies as straight lines between the ratios .500 and .435, .435 and .400, .400 and .364, and .364 and .333. With the exception of that at .435, these ratios correspond to the compositions of well-known silicate structural types, listed in Table 1. Huggins explained the breaks in the curve of volume per gram atom of oxygen as indicating that the structure of the glass is influenced by the number of oxygen atoms shared, on the average,

TABLE 1

SILICON-OXYGEN RATIOS OF SILICATE STRUCTURAL TYPES

Ratio	Structural Type
.500	Quartz, tridymite, cristobalite
.435	None
.400	Mica
.364	Amphibole
.333	Pyroxene

by each silicon-oxygen tetrahedron just as are the structures of the crystalline silicates. At the ratio .400, for instance, each tetrahedron shares three of its oxygen atoms with adjacent tetrahedrons. Similarly, at .364, half of the tetrahedrons share three and half share two oxygens. Between these two specific compositions, the physical properties of silicate glasses are additive.

It is immediately apparent that any method of treating the data on specific volume can be applied to its reciprocally related function, specific gravity. As will appear later, there are a number of advantages, quite apart from ease of computation, in favor of doing so. In Fig. 1, the densities of a series of sodium silicate glasses (*2*) have been plotted against the ratio of silicon to oxygen atoms. It can be seen that variations in the density can, indeed, be represented by several straight lines, with changes in slope at the values previously listed. (In the example given in Fig. 1, the particular glass series chosen did not include compositions high enough in sodium oxide to reveal the break at .333.)

THE SPECIES DENSITY ANALYSIS

Curves such as that shown in Fig. 1 are of limited usefulness, since all atomic species are lumped together, and it is impossible to deduce the packing characteristics of the various species and the relations between the framework and the metallic atoms. If, however, one separates the total density into the contributions of each individual species, a great deal of information can be obtained. The separation can be accomplished merely by multiplying the total density by the weight per cent of each species. The resulting values, which may be called the "species densities," will, when plotted as a function of the silicon to oxygen ratio, illustrate how the packing of the various species is influenced by the changes in linkage of the tetrahedrons.

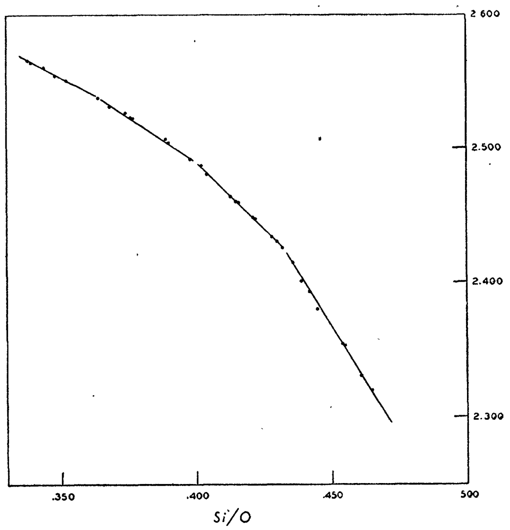

FIG. 1. The density in grams per cubic centimeter of sodium silicate glass as a function of the silicon to oxygen ratio.

The validity of the species-density concept can be shown quite simply. Obviously, the total mass in a unit volume is equal to the sum of the masses of the individual components. Assume a compound, AX, which has a specific gravity of 3.000 (or a density of 3.000 grams/cc.) and elements A and X having atomic weights of 60 and 40, respectively. In 100 cc. of this compound there are 300 grams. In each 100 grams of compound AX there are 60 grams of A

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and 40 grams of X. The density contribution of species A is equal to the weight fraction of A times the total density, or 60/100 of 3.000, which is equal to 1.800. Similarly, that of X will be 1.200. The sum, of course, is equal to the total density.

A convenient form for computing species densities in silicate glasses is shown in Table 2. For simplicity, all computations are based on 100 grams of glass. The mass of each species in grams/100 grams of the glass (third, fourth, and fifth columns of Table 2) is, therefore, also the weight per cent of that species, which is the figure by which the total density must be multiplied to obtain the species density. The example chosen is a glass in the two-component sodium silicate system. Additional columns may be added for systems containing more than two components.

TABLE 2

SPECIES DENSITY COMPUTATION

Mass					Gram Atoms			Density			Ratio Si/O
Na_2O	SiO_2	Na	Si	O	Na	Si	O	Total	Na	Si,O	
27.85	72.15	20.66	33.71	45.63	.898	1.204	2.852	2.4488	.5060	1.9428	.421

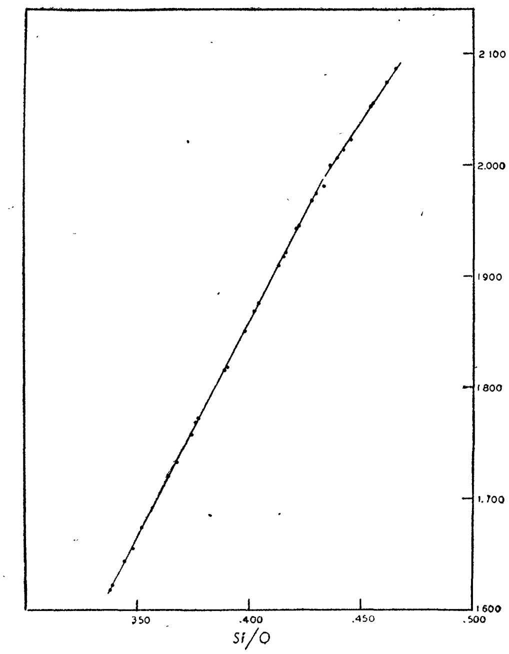

FIG. 2. The density in grams per cubic centimeter of the silicon-oxygen framework in sodium silicate glass as a function of the silicon to oxygen ratio.

THE SODIUM SILICATE SYSTEM

When the total densities plotted in Fig. 1 are broken down into species densities, and the contributions of sodium and of the silicon-oxygen framework are plotted against the ratio of silicon to oxygen, a rather striking picture results. Fig. 2 shows that fraction of the total density which is attributable to the silicon-oxygen framework, and Fig. 3, that which is due to the sodium atoms. It is of particular importance to note that the data concerning the framework (Fig. 2) can be represented by only two straight lines. The one break which appears is at the ratio for which no crystalline silicate type is known. (Actually, this break appears to be closer to .433 than .435, as reported by Huggins.) The contributions of sodium

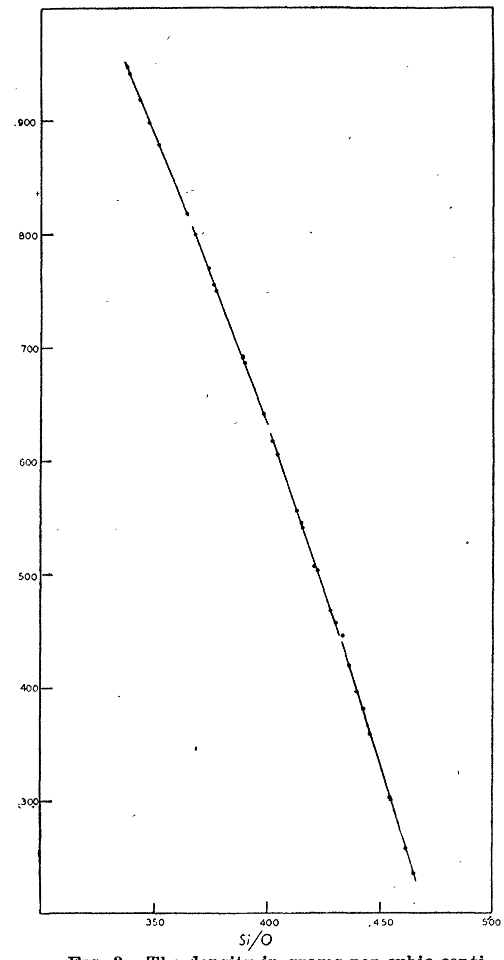

FIG. 3. The density in grams per cubic centimeter of sodium in sodium silicate glass as a function of the silicon to oxygen ratio.

(Fig. 3), on the other hand, show all of the breaks seen in the total density curve.

A full explanation of the meaning of the difference in the two curves and of the structural relations that can be deduced from them will be deferred until a later date when the several alkali silicate systems can be covered. It is sufficient for the purposes of this discussion to point out that the break at .433 is most probably related to saturation of the cristobalite-like structure of silicate glass with sodium atoms. Above this ratio, the introduction of sodium does not cause much expansion of the framework, since there is sufficient void space to accommodate the additional atoms. Most of the lowering of framework density can be accounted for by the removal of silicon atoms. Below the critical ratio, however, it is necessary for the whole structure to expand as additional sodiums are added, because the voids in the framework are full. Changes in the numbers of oxygen atoms shared by each tetrahedron apparently produce no changes in the rate of change of the framework density. Changes in linkage do, on the other hand, influence the packing of sodium; hence the breaks in the species density curve of sodium.

Structure-Phase Diagrams

The curves illustrated in Figs. 1–3 are essentially phase diagrams in that they reveal compositional regions where certain structural characteristics are predominant. The word "phase" is not used in the restricted sense that it has in physical chemistry. To avoid confusion, it is proposed to refer to the compositional regions as "structure-phases." From Fig. 2 one may deduce that the framework of sodium silicate glasses has two structure-phases, one above and one below the ratio .433. The latter is further subdivided into four subphases which are characterized by different packing laws of the sodium atoms. Similarly, it has been found in the potassium silicate system that the framework has only one structure-phase and that this is divided into a number of subphases.

The concept of structure-phases can be extended to three component systems, such as sodium potassium silicate, as well as two component ones. In this case it is not possible to plot the species density as a function of the silicon to oxygen ratio, since two abscissa are required, each of which is a measure of the effect of one metallic atom species. The ratios used for such three-dimensional diagrams are the ratios of each metal to oxygen. Actually, Figs. 1–3 might well have been plotted against the sodium to oxygen ratio. The resulting curves would have had the same appearance as when plotted against the silicon to oxygen ratio, since the two ratios are linearly related by the equation $Na/O = 2 - 4Si/O$.

The construction of species density diagrams can be accomplished with a minimum of experimental data, a fact which is of considerable value in the study of glass systems. For the two component systems, each phase is represented by a straight line, and it is only necessary to determine the slope of the line. Given some background of knowledge of the system, two points may suffice for each phase. For three component systems, the phases are represented by planes, and in many cases three points may be sufficient.

Applications of the Species Density Analysis

Although the potential uses of structure-phase diagrams have not, as yet, been explored fully, it can be anticipated that applications will be found not only in the study of glass systems but also in such fields as mineralogy. Solid solutions in which one metallic species is progressively replaced by another might be analyzed for information as to the effect of size and charge of various species on structure. An interesting application is in systems containing atoms which take the silicon position at the center of the oxygen tetrahedron, as does aluminum. The structure in such cases is dependent, not on the silicon to oxygen ratio, but rather, on the silicon plus aluminum to oxygen ratio.

References

1. Huggins, M. L. *J. opt. Soc. Amer.*, 1940, **30**, 420.
2. Morey, G. W. *The properties of glass.* New York: Reinhold, 1938. P. 237.

Mechanism of Spontaneous Cure in Puberty of Ringworm of the Scalp[1]

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Since 1943 ringworm of the scalp hair caused by the fungus *Microsporon audouini* has been endemic among school children in numerous large cities of the United States (*1*). It has been known for more than 50 years (*3*) that although this infection is distressingly persistent during early childhood, it clears up spontaneously with oncoming adolescence. The scalp hair of adults is immune throughout life. For therapeutic purposes sex hormones have been administered to children with this disease in order to simulate pubertal conditions, but practicable doses have not been effective. From the therapeutic point of view it therefore seemed more promising to investigate the local changes on the scalp following puberty and to find out what makes the scalps of adults nonsusceptible to *M. audouini* infections. Such investigations were started a year and a half ago in the Division of

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