Polymerizations. The polymerizations were run in a one-necked 24/40 $\overline{\mathrm{T}}$ 250-cc flask equipped with a Teflon-coated magnet and a three-way stopcock attached to a side arm. All operations were carried out with dry equipment and under nitrogen. Toluene and alkylaluminum chloride solutions were added at room temperature. After cooling the flask in a Dry Ice bath, hexane solution of vanadium tetrachloride was slowly added. It made no difference if the vanadium solution was precooled to $-78°$ before reduction. If trialkylaluminum solution was used, it was added next. Ethylene was passed through molecular sieves and bubbled through a kerosene solution of trihexylaluminum before introducing it into the reaction flask. The ethylene was introduced through a needle placed about 1–2 cm above the stirred solution. It was not feasible to leave the needle below the surface because polymer collected rapidly on the open tip and soon plugged it. The polymer was recovered from the organic phase that was separated during the work-up of the mixture for the valence state determination.

Visible Spectra. Visible spectra were obtained using a Beckman DK28 spectrophotometer. The cell well was kept under a nitrogen blanket and cooled with a circulating acetone–Dry Ice bath.

All vanadium solutions were prepared so that [V] = 0.0078 *M* in ethanol–toluene (1:6 by volume), and all operations were performed under nitrogen. The solutions were either prepared at or cooled to $-78°$. We transferred the cold solutions using a dry syringe, jacketed with Dry Ice, to a 1-cm or 0.5-mm cell at about $-25°$.

V(II). This solution was prepared by reducing VCl_4 with i-Bu_2AlCl (Al/V = 5) in toluene at $-78°$. The solution was aged 1 hr at room temperature. Finally it was quenched with ethanol at $-78°$, and stored in a sealed vial at $-25°$.

V(III). Vanadium trichloride was added to an ethanol–toluene mixture by first mixing at $-78°$. A homogeneous solution was obtained by stirring the mixture overnight at room temperature. It was stored in a sealed vial at $-25°$. Prior to analysis, the solution was cooled to $-78°$ and treated with a toluene solution of i-Bu_2AlCl (Al/V = 5). About 30 min later the solution was transferred to the spectrophotometric cell.

V(IV). A 0.5 *M* hexane solution of VCl_4 was cooled to $-78°$. Ethanol and then toluene were added to give a 0.0078 *M* solution. This was stored in a flask at $-25°$.

V(V). Ethanol was added to toluene solution of $VOCl_3$ cooled to $-78°$. The cold solution was next transferred to a cell for analysis.

V(II) + V(IV). The standard V(II) and V(IV) solutions described above were cooled to $-78°$ and mixed in equal amounts. About 2 min after mixing the solution was analyzed with the spectrophotometer. About 45 sec passed in recording each spectrum, so we indicated in Figure 3 the starting time of each spectrum.

Acknowledgments. I wish to thank Drs. M. P. Dreyfuss and W. J. Kroenke for their helpful comments on the manuscript and Mrs. Lois Y. Farrand and Mr. K. E. Andrews for their laboratory assistance.

The Structon Theory Applied to Inorganic Crystals and Glasses Containing Macroions

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ABSTRACT: The over-all structures and many of the properties of matter in condensed systems can be related, often quantitatively, to the types, relative numbers, and properties of the *structons* of which they are composed. (Each structon type is an atom of a specified element, having a specified set of close-neighbor atoms.) This theory is applied to the structures of polyanions in silicate and other related types of crystals and glasses. In many cases the types and relative numbers of the structons present in the crystal or glass can be determined from the over-all composition, using well-established principles. Two useful functions, the *charge density function* and the *reticulation function*, are introduced. Both are closely related to structure and macroscopic properties. Some general principles concerning the types of structons present in polyanions containing Si, B, P, and Al are briefly discussed. Differences between crystals and glasses, with respect to their structures and structon compositions, are also dealt with.

The fundamental principles of atomic structure and interatomic bonding have been shown to hold in crystals,[1–4] as well as in small molecules and ions. Quite properly, they are also generally assumed to hold in glasses. These principles lead directly to the often verified conclusion that many silicate (and borate, phosphate, aluminate, borosilicate, phosphosilicate, aluminosilicate, etc.) crystals and glasses contain macroanions.[4,5] In crystalline substances in these classes, polyanions of the chain, ribbon, sheet, and network types have been found. Many glasses certainly contain macroanions with irregular branched chain, cross-linked chain, and network structures. Between the macroanions (or within them, if they have network structures), in both crystals and glasses, small cations are located in such a manner as to satisfy, as well as possible, their coulombic and other attractions and re-

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(1) M. L. Huggins, *J. Amer. Chem. Soc.*, **44**, 1841 (1922).
(2) M. L. Huggins, *Phys. Rev.*, **19**, 346 (1922).
(3) M. L. Huggins, *J. Phys. Chem.*, **35**, 1270 (1931).
(4) M. L. Huggins, *Chem. Rev.*, **10**, 427 (1932).
(5) W. L. Bragg and G. F. Claringbull, "Crystal Structure of Minerals," G. Bell and Sons Ltd., London, 1965.

pulsions to atoms in the anions and to each other. For many crystals the precise arrangements of the atoms in the structures have been determined, usually using X-ray diffraction techniques, aided by established molecular structure principles.[5]

With regard to glass structures, much less information can be obtained directly by using X-ray diffraction or other available techniques. Because of the inherent randomness of the arrangements, the best that can be hoped for is to learn something about (a) local structures, such as the kinds of *structons*[6–8] (defined below), their relative numbers, and the existence of rings or other special structures involving more atoms than those specified in any single structon type; and (b) some average characteristics, such as the average charge density and the average degree of branching or netting in the anions. To obtain this knowledge one must rely largely on structural principles that have been developed and tested in other fields and on detailed information with regard to related crystal structures. In some instances, predictions of glass structures, based on principles and analogies, can be tested by X-ray, nuclear magnetic resonance, infrared, or other techniques, or by comparing calculated macroscopic properties of the additive type with observed properties.

Knowledge of structon compositions and their dependence on over-all composition makes possible the calculation of a variety of macroscopic properties of materials (crystals, glasses, pure liquids, solutions, etc.) from the contributions of the individual structons to these properties. Volumes (hence, densities), various optical properties, and heats of vaporization (hence, heats of formation, heats of reaction, etc.) are examples.

Some General Principles and Useful Parameters. This paper is concerned specifically with crystals and glasses containing macroions composed only of the elements Si, B, Al, P, and O. On the basis of both experimental and theoretical evidence, it will be assumed that each silicon or phosphorus atom in these anions is tetrahedrally surrounded by four oxygen atoms. This is also known to be often, but not always, true with regard to boron and aluminum atoms. Only compositions in which these atoms are known to be (or can reasonably be assumed to be) so surrounded will be dealt with here, except incidentally.

The symbol G will be used to designate any of the elements Si, B, Al, P, or (in later papers) other relatively electropositive elements of which (with oxygen) the anions are composed. The same principles as those dealt with here and the same or similar formulas apply to compositions containing these other electropositive elements, to those containing fluorine or organic groups replacing some of the oxygen, to those containing hydrogen (as hydroxyl groups or water molecules), and to those in which boron or aluminum atoms have less or more than four oxygen neighbors. Consideration of these more complex cases is reserved for other papers.

It is convenient for our purposes to represent the composition of a crystal or glass containing macroanions by a *normalized formula*, giving the (often nonintegral) numbers of the atoms of the component elements per G atom. For example, the normalized formula for a sodium calcium phosphosilicate would have the form $\mathrm{Na_{na}Ca_{ca}Si_{si}P_{1-si}O_{\sigma}}$ with the subscripts representing the appropriate numbers, integral or fractional. The subscript σ is used here, rather than lower case "o," to avoid confusion with zero. The numerical values of the subscripts must of course conform to the neutrality requirement, as in any proper formula for a neutral chemical substance or material. Thus

$$\mathrm{na} + 2\mathrm{ca} + 4\mathrm{si} + 5(1 - \mathrm{si}) - 2\sigma = 0 \qquad (1)$$

The normalized formula for the corresponding macroanion is

$$(\mathrm{Si_{si}P_{1-si}O_{\sigma}})^{-\rho}$$

where ρ, the *charge density function*, is the average negative charge per G atom in the anion. It is therefore also the sum of the positive charges on the cations, per G atom. For the compositions here considered

$$\rho = 2\sigma - \bar{v}_{\mathrm{G}} \qquad (2)$$

where $\bar{v}_{\mathrm{G}}$ designated the average valence (kernel charge) of the G atoms.

The charge density function is important in theoretical considerations concerning such properties as hardness, heat of formation, heats of reaction, and the relative stabilities of different structures for the macroanions. The numbers, sizes, and distributions of the cations and partial covalent character of the bonding between the macroanions and some types of cations also affect these properties, but these factors are here neglected, since the primary interest is in the macroanions.

In the *structon theory*[6–10] attention is concentrated on the compositions, numbers, and properties of the *structons* present. A structon is defined as an atom of a specified element, surrounded by close-neighbor atoms of specified numbers and kinds. The structons can be represented by formulas, structural or otherwise, as exemplified, for the silicon structons occurring in the anions of simple silicates, in Tables I and II. In a condensed structon formula representing neighbor atoms around a central atom, dots are inserted to avoid confusion with the numbers 20, 30, and 40.

In these formulas nonbridging oxygens (O′) and bridging oxygens (O′′) are differentiated, because these two types contribute very differently to the anion structure and to the properties of the structons. In the compositions here dealt with, it is believed that there are no oxide ions ($\mathrm{O^{2-}}$, not bonded to any G atoms) and no oxygens (O′′′, O′′′′) bonded directly to more than two G atoms. These types of oxygens are known to occur elsewhere.

The simple formula associated with each silicon structon type is readily deduced from its composition, considering each nonbridging oxygen and half of each bridging oxygen as "belonging to" the structon.

Calculations of the energies required, for comparable silicate systems, to separate completely all the component ions have led to the energy values (ϵ) for the

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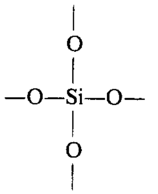
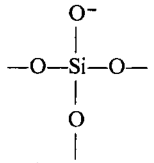
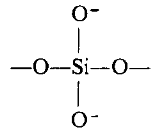
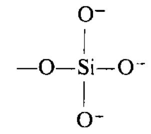
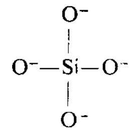
(6) M. L. Huggins, *J. Phys. Chem.*, **58**, 1141 (1954).
(7) M. L. Huggins, *J. Amer. Ceram. Soc.*, **38**, 172 (1955).
(8) M. L. Huggins, *Bull. Chem. Soc. Jap.*, **28**, 606 (1955).
(9) M. L. Huggins, *J. Amer. Chem. Soc.*, **77**, 3928 (1955).
(10) M. L. Huggins and T. Abe, *J. Amer. Ceram. Soc.*, **40**, 287 (1957).

TABLE I

SILICON STRUCTONS IN SIMPLE SILICATES

	 $\text{—O—}\overset{\overset{\vert}{\text{O}}}{\underset{\underset{\vert}{\text{O}}}{\text{Si}}}\text{—O—}$	 $\text{—O—}\overset{\text{O}^-}{\underset{\underset{\vert}{\text{O}}}{\text{Si}}}\text{—O—}$	 $\text{—O—}\overset{\text{O}^-}{\underset{\text{O}^-}{\text{Si}}}\text{—O—}$	 $\text{—O—}\overset{\text{O}^-}{\underset{\text{O}^-}{\text{Si}}}\text{—O}^-$	 $\text{O}^-\text{—}\overset{\text{O}^-}{\underset{\text{O}^-}{\text{Si}}}\text{—O}^-$
	Si(4O'')	Si(O', 3O'')	Si(2O', 2O'')	Si(3O', O'')	Si(4O')
σ	2.00	2.50	3.00	3.50	4.00
ϵ[a]	3110	3123	3131	3137	3142

[a] The dissociation energies, ϵ, are in kilocalories per mole.

TABLE II

STRUCTON COMPOSITIONS OF SOME SIMPLE SILICATES

Mineral	Normalized formula	Silicon structons	Oxygen structons O'' (2Si)	O' (Si)
Quartz[a,b]	SiO_2	1Si (4O'')	2	
Sodium disilicate[c,d]	$NaSiO_{5/2}$	1Si (O', 3O'')	3/2	1
Pyroxenes[5b]	$M(II)SiO_3$	1Si (2O', 2O''	1	3
Thortveitite[e]	$ScSiO_{7/2}$	1Si (3O', O''	1/2	3
Silicates[b]	$M(II)_2SiO_4$	1Si (4O')		4

[a] See ref 2. [b] See ref 5. [c] G. Donnay and J. D. H. Donnay, *Amer. Mineral*, **38**, 163 (1953). [d] A. Grund, *Bull. Soc. Fr. Minéral.*, **77**, 775 (1954). [e] D. W. J. Cruickshank, H. Lynton, and G. A. Barclay, *Acta Cryst.*, **15**, 491 (1962).

silicon structons given in Table I.[11,12] These measure relative stabilities. From the figures, it can be concluded that (neglecting possible specific effects of the neighboring cations) lowest energy (greatest stability) will be achieved if the only types of silicon structons present are the two having formulas bracketing the over-all normalized formula for the anion. Thus, the silicon structons in a simple silicate with an O/Si ratio (*i.e.*, a σ value) between 2 and 2.5 would be expected to be, for greatest stability, only those of the Si(4O'') and Si(O', 3O'') types. Their relative numbers are readily calculated. Designating by x the number of Si (O', 3O'') structons per Si in the glass or crystal, the number of Si (4O'') structons is $1 - x$ and the number of oxygens, σ, is $(1 + {}^3/_2)x + {}^4/_2(1 - x)$. This leads to $x = 2\sigma - 4$ and $1 - x = 5 - 2\sigma$. In a compound with a σ value of exactly 2.50, lowest energy is achieved if the only silicon structons are those of the Si(O', 3O'') type.

In all simple silicate crystals of known structure (to the best of the writer's knowledge), the structon types present conform to these criteria. In well-annealed glasses it seems likely that the actual structures approximate these lowest energy structures. One would expect other structon types in small relative amounts, depending on the energy differences, temperature-time relationships as the distribution of Si–O bonds becomes fixed during the cooling of the glass, and effects of unusual distributions of neighboring cations.

The oxygen structons in simple silicate crystals and glasses, of the nonbridging and bridging types, respectively, are those represented by the formulas O'(Si) and O''(2Si). Their numbers, per Si, can be computed from the numbers of the silicon structons and the requirement that the number of O' (or O'') neighbors around Si atoms must equal the number of Si neighbors around O' (or O'') atoms. Thus, for the above example, the number of O'(Si) structons per Si is $x = 2\sigma - 4$, and the number of O''(2Si) structons per Si is $[3x + 4(1 - x)]/2 = 4 - \sigma$. Alternatively, in this simple case, one can compute the latter relationship from the requirement that $O' + O'' = \sigma$.

The types and numbers of the cation structons can also be determined, in many cases, from known principles and relationships. In other instances one can, without further structural information, only limit the possibilities to two or a few, perhaps relying on analogy or judgment to determine which is most probably correct, or on future experimentation to determine which is actually correct. Since this paper is concerned primarily with macroanions in these materials, the subject of the distribution and local environments of the cations will not be dealt with further.

The assumption that in a well-annealed glass nearly all of the Si structons are those of lowest energy leads to the prediction that a graph of the specific volume, or other structon-additive property, of slowly annealed alkali silicate glasses, plotted against the weight fraction of SiO_2 in the glass, should show straight line segments, with quite sharp breaks between them, at the compositions where structon types change. This has been shown[6-8] to be true for sodium silicate glasses. It may confidently be predicted that many other examples of this type of behavior will be found.

Another useful composition-dependent parameter is the *reticulation function*, φ, measuring the degree of branching or cross-linking in the macroanions. It may be defined by eq 3 for the compositions here con-

$$\varphi = 2(z_G - 1) - 2 = 6 - 2\sigma \qquad (3)$$

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[11] M. L. Huggins and K.-H. Sun, *Trans. Soc. Glass Technol.*, **28**, 463 (1944).

[12] M. L. Huggins and K.-H Sun., *J. Amer. Ceram. Soc.*, **28**, 149 (1945).

sidered. Here, z_G is the average coordination number of the G atoms. The reticulation function is zero when the anionic composition is that for rings or infinitely long chains, and unity for an average of one branch per G atom.

Neither ρ nor φ give any information as to the distribution of the branches, the distribution of bonds around the G atoms to bridging and nonbridging oxygens, or the distribution of orientations (*i.e.*, conformations) around the single bonds. It may be noted that rotation of one Si–O bond relative to the other, in a Si–O–Si bridge, is very easy, unless restricted by coulombic or other forces involving more distant atoms. The structures of macroions in glasses are very random, as regards both configurations around the G atoms and conformations around the oxygen bridges.

In crystals this randomness is absent. Whereas, in a glass many different local arrangements of nearly equal stability can coexist, in a crystal there are only those which permit a regularly repetitive structure and which (at the time of the formation of the crystal) are most stable, considering the summation of coulombic and van der Waals forces, in addition to the closest neighbor forces emphasized in the structon treatment. For many compositions, the requirements that the structure be repetitive in three dimensions and that like atoms, insofar as possible, be surrounded in a like manner (that giving greatest stability) lead directly to structures composed of small rings. Also, if a crystal is formed directly from a melt, in which small ring structures are greatly favored, it is especially likely to incorporate these rings in its structure. This likelihood does not exist, however, in a crystal produced from a glass which is no longer liquid and which has had time, after solidification but before reorganization of the Si–O bonds has ceased, for the transformation of many of the rings into other structures of approximately the same energy. Glasses produced without rapid quenching would likewise be expected to have relatively few small rings, especially when the reticulation function is not very large. One cannot logically reason that, if a crystal structure of a given composition is built up of rings of a given type, a glass of the same composition is likewise composed, exclusively or predominantly, of the same type of ring.

The discussion of rings in the preceding paragraph concerns interactions between atoms which are not closest neighbors. It is related to the structon theory only in this way: with or without rings, the over-all structure is expected to be composed of structons of the most stable types, in such relative proportions as to give the correct over-all composition. For greatest stability the distribution of these structons should be such as to give the true over-all composition within as small a volume as possible, with the distribution of excess charges close to that giving the lowest coulomb energy. (Usually, this will be as uniform a distribution of these charges as possible.) These requirements are often best achieved, especially in a three-dimensionally repetitive structure, by small ring formation. This does not imply, however, any greater stability for the ring structures than for other structures built up of the same structons in the same proportions. The detailed application of these ideas to crystal structures will be dealt with elsewhere.

The rigidity of a glass is greatly dependent on the values of ρ and φ. Other things being equal, increasing either of these parameters increases the rigidity. This theoretical conclusion has been confirmed experimentally.[13] Rigidity is also increased by replacing univalent cations by cations of higher charge.

Phosphorus, Boron, and Aluminum in Macroanions. Phosphorus atoms can replace silicon atoms in the macroions. The coordination number is the same (4) for P as for Si, hence, for the same ratio, σ, of oxygen atoms to G atoms, φ remains the same (see eq 2). Because of the change in valence (ν), however, the value of ρ is decreased (see eq 1).

In boric oxide each boron atom has only three close neighbors. Density,[14] optical refraction and dispersion,[14] X-ray diffraction,[15] nuclear magnetic resonance[16,17] and infrared,[18,19] data show that an alkali or alkaline earth oxide, added in not too large a proportion, changes the coordination number of some of the boron atoms to four. For every oxygen ion added, two boron atoms change their coordination numbers. The oxygen atoms added form bridges between pairs of boron atoms, as in the original boric oxide.

The addition of nonbridging oxygen atoms, from silicates or phosphates containing them, to boric oxide or to another composition containing 3-coordinate boron atoms, also, I propose, has the effect of increasing the coordination numbers of some (at least) of the latter. At the same time, the nonbridging oxygens become bridging oxygens. Nuclear magnetic resonance data on sodium borosilicate glasses are in agreement with this hypothesis.[20]

Aluminum atoms in glasses and crystals, I propose, behave similarly. If there are nonbridging oxygens in a structure in which all the aluminum atoms have a coordination number of four, those nonbridging oxygens should tend to form bridges to aluminum atoms, increasing their coordination numbers to five or, if there is then still an excess of nonbridging oxygens, to six. Other factors are involved, especially if the resultant structure is crystalline, but I believe that the tendency of nonbridging oxygen atoms (attached to B, Si, or P atoms) to increase the coordination number of boron from three to four and that of aluminum from four to five or six is a very important one. Further study of the literature or new experiments will show whether or not this is so.

From coulomb energy considerations it can be concluded that, other factors being equal, nonbridging oxygens are preferentially attached to the G atoms with the highest kernel charge. For a crystal or glass

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(13) M. L. Huggins, H. J. Eding, J. G. Martner, and E. M. Carr, unpublished research at Stanford Research Institute.

(14) M. L. Huggins, *J. Amer. Chem. Soc.*, **62**, 2248 (1940).

(15) B. E. Warren, *J. Amer. Ceram. Soc.*, **24**, 256 (1941).

(16) A. H. Silver and P. J. Bray, *J. Chem. Phys.*, **29**, 984 (1958).

(17) P. J. Bray and J. G. O Keefe, *Phys. Chem. Glasses*, **4**, 37 (1963).

(18) J. Krogh-Moe, *ibid.*, **3**, 1 (1962).

(19) J. Krogh-Moe, *ibid.*, **6**, 46 (1965).

(20) Y. Masuda, S. Tsuchihashi, and M. L. Huggins, unpublished research.

containing P, Si, and (4-coordinated) B atoms, the expected preference is

$$\mathrm{P} > \mathrm{Si} > \mathrm{B} \tag{4}$$

I believe that, in general, reactions of the type

$$\mathrm{G{-}O{-}G} + \mathrm{G'{-}O{-}G'} \longrightarrow 2\mathrm{G{-}O{-}G'} \tag{5}$$

result in an increase in stability. Practically all of the crystal structure evidence, of which I am aware, is in agreement with this, but in one borosilicate crystal, danburite,[21,22] B–O–B and Si–O–Si bridges coexist. This exception is to be explained by considerations other than the general ones discussed here.

Extensions and Applications. The principles, equations, and procedures presented and discussed in this paper are readily extendable to other compositions. They should lead in a straightforward manner to the deduction of the types and numbers of close-neighbor arrangements as functions of over-all compositions in many chemical systems, in both crystalline and glassy states. They should also lead to the determination of the contributions of the different structon types to various additive properties, and thereby to the theoretical calculation of these properties for many substances and materials. One of the most important applications, in the writer's opinion, will be to the calculation of lattice energies, heats of formation, and related properties for many inorganic compounds and mixtures for which direct experimental data are not available. Research in this direction is in progress and will be reported in due course.

Acknowledgment. Some of the ideas and procedures reported here were developed while the writer was employed by the Eastman Kodak Co. and Stanford Research Institute.

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(21) G. Johansson, *Acta Cryst.*, **12**, 522 (1959).

(22) V. V. Bakakin, V. B., Kravchenko, and N. V. Belov, *Compt. Rend. Acad. Sci. USSR*, **129**, 420 (1959).