drous Rochelle salt, and the third we tentatively suggest corresponds to solid complex.   At all events, the tie-lines show no indication of running to the sodium hydroxide corner.   For the reason previously given, it cannot be expected that the tie-lines should intersect in a point.   The appearance of the solid phase at this stage is remarkable.   It swells in bulk so as to occupy almost the total volume and resembles a stiff gel.   The numerical results are contained in Table III.

The triangular diagram is interesting and has therefore been reproduced.

It is hoped shortly to communicate similar work which has been done on camphoric acid and substituted tartaric acid.   Work is now proceeding on the acid and alkaline racemization of mandelic acid.

Summary

The process of inactivation of Rochelle salt when heated with sodium hydroxide has been investigated mathematically.   Measurements of the velocity of inactivation have been made in a special apparatus.   The drift of the constants is interpreted in the light of the equations deduced. The interpretation is rendered difficult by the fact that a levorotatory complex is formed, but the matter is discussed at length.   Experimental evidence for the existence of the complex, depending on (1) sign of rotation, (2) hydroxyl-ion concentration and (3) a phase rule study of the system Rochelle salt–H_2O–NaOH, is also adduced.

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THE ATOMIC ARRANGEMENT IN GLASS

BY W. H. ZACHARIASEN

1.   Introduction

It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses.   Glasses are described as supercooled liquids or as solids.   The former term is justifiable from the point of view of physical chemistry, the latter from the theory of elasticity.   It seems rather futile, however, to try to decide which of the two descriptions is the proper one to use, when we are ignorant about the characteristic properties of the atomic arrangement.

It has been said that the x-ray diffraction patterns obtained from glasses indicate that glasses consist of crystalline material.[1]   It is claimed, for example, that the main features of the diffraction pattern of vitreous silica can be accounted for on the following basis: (1) vitreous silica consists of cristobalite crystallites;   (2) the average linear dimension of the crystallites

[1] J. T. Randall, H. P. Rooksby and B. S. Cooper, Z. Krist., 75, 196 (1930).

is of the order of 15 Å.; (3) the lattice constants of the crystallites are 6.6% greater than those of large cristobalite crystals. These assumptions lead, however, to discrepancy between observed and calculated density. The diffraction patterns obtained from heat-treated specimens of vitreous silica cannot be satisfactorily accounted for, and above all the characteristic thermal properties can hardly be said to be in accordance with the assumptions. A generalization of this "crystallite hypothesis" to glasses of the general type would lead to even more serious difficulties. For these reasons it seems necessary to rule out the possibility that glasses are built up of crystalline material.

2. The Atomic Arrangement in Glass

Over large ranges of temperature the mechanical properties of glasses are directly comparable with those of crystals. As a matter of fact there is experimental evidence which indicates that the strength of glass may excel that of the corresponding crystalline form. It seems necessary therefore to assume that the atoms in glass are linked together by forces essentially the same as in crystals and that the atoms are oscillating about definite equilibrium positions. As in crystals, the atoms in glasses must form extended three dimensional networks. From the results of the x-ray diffraction experiments it follows, however, that this network is not periodic and symmetrical as in crystals. Yet it is not entirely random due to the fact that the internuclear distances do not sink below a given minimum value. All interatomic distances are for this reason not equally probable and x-ray diffraction patterns of the type observed will be a direct consequence.

If we make use of crystal structure terminology, we may say that the network in glass is characterized by an infinitely large unit cell containing an infinite number of atoms. Because of the lack of periodicity no two atoms are structurally equivalent, while in a crystal lattice like that of sodium chloride all the sodium atoms are equivalent and all the chlorine atoms (disregarding surface conditions arising in a lattice of finite extension).

The presence or absence of periodicity and symmetry in the network distinguishes a crystal from a glass.

The characteristic properties of glasses seem to be in accordance with our ideas of the atomic arrangement.

The isotropic character of glass is, of course, a natural consequence of the absence of symmetry in the network. The atomic arrangement will be statistically the same in all directions, unless external fields of sufficient intensity are present.

Since all atoms in glass are structurally unequivalent, the energy required to detach an atom from the network will be different for each individual atom. With increasing temperature we would therefore expect

to get an increasing number of detached atoms, so that the breakdown of the network would be a continuous rather than an abrupt phenomenon. Migration of the detached atoms at a given temperature naturally would occur too.   In a crystal lattice on the other hand the atoms are structurally equivalent.   As soon as the thermal energy reaches a definite value, all the equivalent atoms will be simultaneously detached; the crystal network breaks down abruptly.   With the migration of the detached atoms in a glass network it is impossible to say at which temperature a given glass passes from the solid to the liquid state.

It is a well-known fact that the chemical composition of a glass in general cannot be expressed by a simple formula, or rather a glass is not a chemical compound in the ordinary sense of the word.   Crystals on the other hand are compounds.   This principal difference between crystal and glass again follows from the presence of periodicity in the network of the former and from the absence of periodicity in the latter.   Each unit cell in a crystal necessarily must contain an integral number of stoichiometric molecules since all unit cells are alike.   It follows that the chemical composition can be expressed by a simple formula.   (It is to be remembered that certain modifications have to be introduced as a consequence of the phenomenon of isomorphous replacements.)   In glass the unit cell is infinitely large and consequently there will be no restrictions with regard to the relative numbers of chemically different atoms (except, of course, that the valences must be balanced).

The transparency of glasses is explained by the existence of extended networks in just the same manner as the transparency of crystals is accounted for.

From simple considerations of this kind one gets the impression that our picture of the atomic arrangement in glass is a very promising one. So far our discussions have been of a very general type; in the following sections, however, we will go into more detailed considerations.

3.   **The Vitreous Oxides.**—In the following only oxide glasses will be discussed, except for a few references to fluoride glasses.   At first we will consider the very simplest type of oxide glasses, namely, those formed by individual oxides, like SiO_2 and B_2O_3.

Of all the possible oxides only a very few are able to form glass.   While for example SiO_2 and B_2O_3 very readily may be prepared in the form of glass, all attempts to make a TiO_2 or an Al_2O_3 glass have been in vain.   An explanation of the glass-forming ability of the oxides has not yet been given. V. M. Goldschmidt[2] has tried to correlate the ability to form glass with the value of the radius ratio R_A/R_O for oxides A_mO_n.   His results are very interesting.   He finds that the radius ratio for all the oxides which have

    [2] Goldschmidt, "Geochemische Verteilungsgesetze der Elemente VIII," Vid. Akad. Skr. Oslo, No. 8, 137, 1926.

been prepared in the vitreous form is around 0.2–0.4. This range of the radius ratio in general corresponds to a tetrahedral arrangement of oxygen atoms around atom A, and Goldschmidt therefore believes that tetrahedral configurations are necessary for the formation of glass. However, we cannot reason the other way and say that any oxide with a radius ratio of about 0.3 can form a glass. The value of the radius ratio for BeO for example is very nearly the same as for SiO_2. Still BeO has never been prepared in the vitreous form.

The conditions for the formation of a glass apparently are more complicated.

We have stated that the atomic arrangement in glass is characterized by an extended three-dimensional network which lacks symmetry and periodicity. The interatomic forces we concluded had to be essentially the same as in crystals. In the glass network no two atoms could be structurally equivalent. For these reasons it may be concluded that the energy of a glass will tend to run higher than that of the corresponding crystal. The same result is borne out by the fact that glasses show a more or less pronounced tendency to devitrify. Glasses which do not devitrify very rapidly will have an energy only slightly greater than that of the crystal. The ultimate condition for the formation of a glass we may consequently express as follows: the substance can form extended three-dimensional networks lacking periodicity with an energy content comparable with that of the corresponding crystal network.

In the crystalline forms of the oxides it is invariably found that the oxygen atoms form polyhedra of one kind or another around atoms A, just as if we could treat the oxygen atoms as anions and the atoms A as cations. Whether the atoms are truly ionized or not is of little consequence as long as we can use the ionic interpretation as a convenient means of description. Because we have postulated that the interatomic forces in crystal and glass are essentially the same, it follows that also in glass networks we should have polyhedra of oxygen atoms around the atoms A. We can in this manner conveniently describe the whole crystal or glass as a network of such oxygen polyhedra. The three-dimensional linking is effected by the sharing of corners between different polyhedra. The energy of the network will in the first place depend upon the nature of the oxygen polyhedra, in the second place upon the way in which the polyhedra are linked together. From our experience with crystal lattices we have learned that there may be several ways of linking polyhedra of a given type together so as to give approximately the same energy. TiO_2 for example can occur in three different modifications, as rutile, anatase and brookite. In all the three crystals Ti is surrounded by octahedra of oxygen atoms and only the linking together of the octahedra is different. An analogous example is the polymorphous SiO_2.

If the energy of a glass is to be comparable with that of the crystal, we must require that oxygen polyhedra in glass and crystal are essentially the same.   In vitreous SiO_2 we must for example expect to find tetrahedra of oxygen atoms around silicon.   If silicon were surrounded by three or by five or any other number of oxygen atoms, the potential energy would be much greater.

The linking together of the oxygen polyhedra in crystal lattices is done in such a manner that no two atoms are brought into close contact.   From the point of view of ions this, of course, is obvious.   If the atoms are ionized we would expect a cation to be surrounded by as many anions as possible and *vice versa*.   The upper limit for the number of anions which could surround a given cation would be determined by the requirement that the anions should not be brought into contact with each other.   Ions carrying charges of the same sign will tend to be as far apart as possible.   We have to apply just the same principles on the network in glass.   Our object is to find under which conditions we can form a network of polyhedra satisfying these requirements.

The network in vitreous silica according to our argument is built up of oxygen tetrahedra which surround the silicon atoms.   The oxygen tetrahedra share corners with each other in such a manner that an oxygen atom is linked to two silicon atoms. In the crystalline forms of silica the relative orientation of two tetrahedra with a common corner will be the same throughout the entire lattice. That is not the case in vitreous silica, where the relative orientation may vary within rather wide limits.   In low quartz for example the angle between the bonds from an oxygen atom to the two neighboring silicon atoms is the same for all oxygen atoms. In vitreous silica on the other hand we must expect that this bond angle varies from oxygen to oxygen atom as we pass through the network.
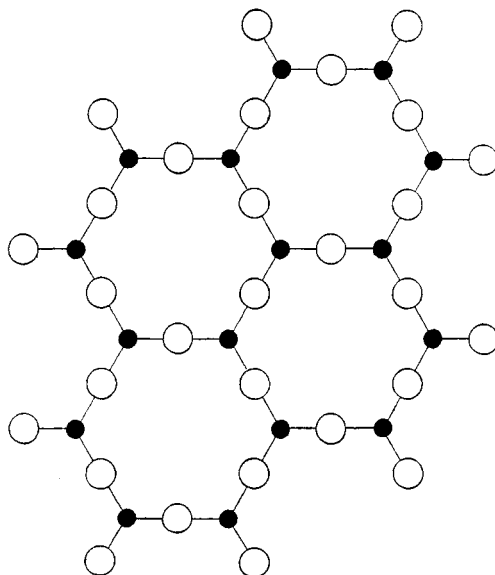

Fig. 1a.

It is somewhat difficult to illustrate the principle in drawings because of the three-dimensional arrangement.   I have therefore tried to make use of two-dimensional analogies in Figs. 1a and 1b.   Figure 1a shows the lattice of a

two-dimensional crystal of composition A_2O_3, while Fig. 1b represents the glass network of the same compound.   It is probably obvious from the draw-
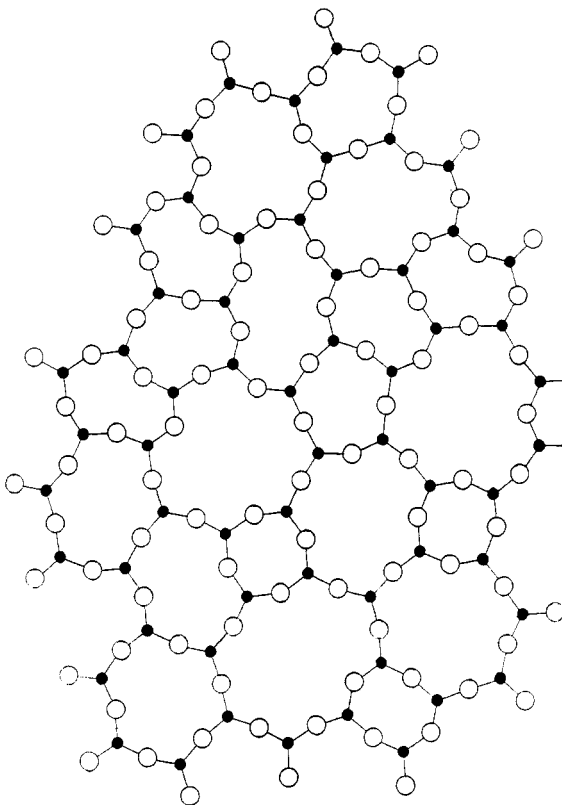

Fig. 1b.

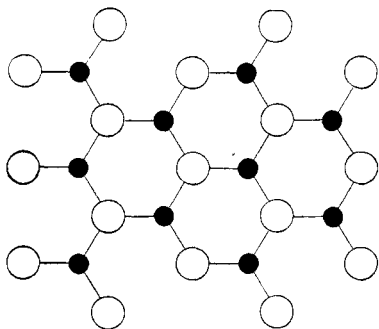ings that the potential energy cannot be very different in the two cases.   In Fig. 2 is shown the two-dimensional lattice of a crystal AO in which three oxygen atoms surround atom A and *vice versa*.   In this case it is impossible to form a two-dimensional glass with an energy content comparable to that of the crystal.   The requirement of a small potential energy will necessarily lead to a periodic network.   Analogous results we will obtain if we extend our considerations to three dimensions.   It is as a matter of fact possible from simple considerations to give a series of requirements which must be satisfied if the ox-

Fig. 2.

ide is to form a glass with energy comparable to that of the crystalline form. These simple rules are: (1) an oxygen atom is linked to not more than two atoms A; (2) the number of oxygen atoms surrounding atoms A must be small; (3) the oxygen polyhedra share corners with each other, not edges or faces.

If we further require the network to be three-dimensional, (4) at least three corners in each oxygen polyhedron must be shared.

Oxides X_2O or XO do not satisfy these requirements under any conditions. Under certain conditions other oxides, however, will fit our rules. We find readily the requirements (1), (3) and (4) are satisfied by oxides: A_2O_3 if the oxygen atoms form triangles around each atom A; AO_2 and A_2O_5 if the oxygen atoms form tetrahedra around each atom A; AO_3, A_2O_7, AO_4 if the oxygen atoms form octahedra around each atom A; AO_4 if the oxygen atoms form cubes around each atom A.

Whether all of these oxides satisfy the requirement expressed in Rule 2 cannot easily be decided. However, as no oxide AO_3, A_2O_7 or AO_4 to my knowledge has been prepared in the vitreous state, we may take that as an indication that only oxygen triangles and tetrahedra agree with Rule 2.

From crystal structure data we have quite extensive information about the oxygen polyhedra which are formed around the different cations.

Of trivalent cations only the following have been found within oxygen triangles in crystal lattices: B^{+3}, As^{+3}, Sb^{+3}. There is no available information about P^{+3}; but I do not think that there can be much doubt that the coördination number is three for this ion also. One important fact is worth mentioning. Whereas boron is lying in the plane of the three surrounding oxygen atoms, arsenic, antimony and probably also phosphorus are displaced out of the plane. The configuration around the latter ions is as a matter of fact a hybrid between a triangular and octahedral configuration. In As_4O_6 and Sb_4O_6 there are six oxygen atoms around As or Sb, three of the oxygen atoms being closer to the cation than the rest. In As_4O_6 the two distances are 2.01 Å. and 2.78 Å.; in Sb_4O_6 the two distances are more nearly equal, namely, 2.22 Å. and 2.61 Å. The approximation to the coördination number three is thus closer for As^{+3} than for Sb^{+3}, and we must expect that for P^{+3} the approximation is still closer than for As^{+3}.

In the series P_2O_3, As_2O_3, Sb_2O_3 the ability to form glass therefore will decrease in the order given. B_2O_3, however, should form glass with greater ease than any other oxide.

No other sesquioxide than the four given can be expected in the vitreous form.

Of the quadrivalent cations only Si^{+4} and Ge^{+4} are surrounded by oxygen tetrahedra in crystal lattices. SiO_2 and GeO_2 consequently may occur in

the vitreous state. The ability to form glass will be less than for B_2O_3 because of the greater coördination number.

The pentavalent cations P^{+5} and As^{+5} are always surrounded by oxygen tetrahedra, probably also V^{+5}. It is possible that also Sb^{+5}, Cb^{+5} and Ta^{+5} may occur with coördination number four with respect to oxygen. The available crystal structure data are, however, too few to allow definite conclusions.

Summarizing our results we conclude that B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, P_2O_3, As_2O_3, Sb_2O_3, V_2O_5, Sb_2O_5, Cb_2O_5, Ta_2O_5 may occur in vitreous forms. From lack of the necessary crystal structure data we may have included in the list some oxides which do not belong there.

References to the literature show that B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, and As_2O_3 have actually been prepared in the vitreous state. Indications that also V_2O_5 and Sb_2O_3 can form glass are found, while we have not been able to procure any data for P_2O_3.

We feel that this surprising agreement cannot be due to mere coincidence, but rather that it must be ascribed to the fact that our reasoning is closely connected with fundamental principles of the atomic arrangement in glass.

It is a simple task to extend our results also to fluorides. We find that BeF_2 is the only fluoride which can be expected to form glass, again in complete agreement with observations.

4. **Oxide Glasses in General.**—From our discussion of the vitreous oxides we have seen that the formation of vitreous networks of low potential energy could take place only under certain conditions. We found that we could build up a vitreous network of oxygen tetrahedra or of oxygen triangles, while oxygen octahedra or oxygen cubes would lead to a periodic network. We found further that the presence of oxygen tetrahedra or of oxygen triangles is not the only condition. In order to prevent the regular lining up of the polyhedra when building the network we had to require that the polyhedra have only corners in common and that oxygen atoms do not belong to more than two polyhedra. For the vitreous oxides these rules led to very simple conclusions, since in a given oxide we have only one kind of oxygen polyhedra present.

In oxide glasses of the general type the circumstances are much more complicated. The rules we found for the individual oxides therefore must be somewhat modified. These modifications are fairly obvious from the discussions in the preceding chapter.

An oxide glass may be formed (1) if the sample contains a high percentage of cations which are surrounded by oxygen tetrahedra or by oxygen triangles; (2) if these tetrahedra or triangles share only corners with each other and; (3) if some oxygen atoms are linked to only two such cations and do not form further bonds with any other cations.

In reality this means that the glass must contain appreciable amounts

of the cations which can form vitreous oxides or of other cations which are able to replace any of the former isomorphously. These glass-forming cations are: B^{+3}, Si^{+4}, P^{+3}, P^{+5}, As^{+3}, As^{+5}, Ge^{+4} and possibly also V^{+5}, Sb^{+5}, Cb^{+5}, Ta^{+5} and in addition Al^{+3} which is capable of replacing Si^{+4} isomorphously. It is worth mentioning that Al_2O_3 alone cannot form glass.

These results are in excellent agreement with observations. We know of no oxide glass which does not contain appreciable quantities of one or another of the cations listed. These cations are responsible for the glass-forming ability, and they compose together with oxygen atoms what we may conveniently call the vitreous framework of the glass.

The chemical composition of a glass we can express by a gross "chemical formula" of the form A_mB_nO. In this formula m and n are in general not integers, but represent merely the number of atoms A and B per oxygen atom. By atoms B we will understand the glass-forming cations listed above, while all other cations in the glass are grouped together as atoms A. Cations B may be surrounded by oxygen tetrahedra or by oxygen triangles; accordingly we may for convenience use the terms tetrahedral or triangular glasses.

It may be expected quite generally that the glasses would have the most advantageous properties (e. g., from the point of view of devitrification difficulties and with respect to strength) if the tetrahedral or triangular network had three-dimensional extension. For a tetrahedral glass this will mean that at least three corners in each tetrahedron are shared with other tetrahedra, or rather that the value of n in the gross formula will lie between 0.33 and 0.50. For a triangular glass n analogously will be 0.67.

We have calculated the gross chemical formula for practically all the glasses whose chemical compositions are given in "International Critical Tables." For nearly all of these glasses n lies around 0.40; in a few cases n is slightly greater than 0.50, namely, if the B_2O_3 content is high. That this agreement is due to coincidence is hard to believe.

When we build up the three-dimensional framework of oxygen atoms and atoms B, the valences will in general not be balanced, so that we must introduce additional cations. Because the oxygen polyhedra in this framework are tetrahedra or triangles, holes necessarily must exist in the network. These holes will be bounded by oxygen atoms, so that they are excellently suited as positions for the cations A. Furthermore, since the framework itself is without periodicity and symmetry, the holes must be statistically distributed and there will be no restriction on behalf of symmetry as to which and how many of these holes are to be filled by cations A. In agreement with previous results this shows that the chemical composition cannot be expressed by a rational chemical formula. Continuing our argument, we can make some statements as to the nature of atoms A. We will simply require that the introduction of the cations A

into the framework does not cause great increase of the potential energy. The fact that the cations A go into the holes is in agreement with this requirement. We must not be deceived by our reasoning and think that the framework is first formed and that then the holes are filled. Naturally the holes are being filled as the framework is being formed, so that the dimensions of the holes are determined by the size of the cations occupying them. When the cations A are put into the network, repulsive potentials will arise between cations A and B. These repulsive potentials according to our requirement must be small. The holes are to a great extent bounded by edges of the oxygen triangles or tetrahedra or by tetrahedral faces, and furthermore the cations B carry charges 3, 4 or 5. In order to make the repulsion between cations A and B small, the charge on cation A must be small and the distance between the cations large. We increase the distance if we enlarge the holes. But as we have stated earlier that the dimensions of the holes are determined by the size of cations A, it follows that cations A must be large. Consequently: *Cations A must be large and carry a small charge.* Small and highly charged cations like Ti^{+4}, Mg^{+2} will on the other hand tend to produce devitrification. The cations A which are present in typical oxide glasses agree with our result: they are chiefly Na^+, K^+, Ca^{+2}, Ba^{+2}, Pb^{+2}.

Our fundamental ideas of the atomic arrangement in glasses thus have led to an explanation of the more prominent features of the chemical composition of oxide glasses.

Some conclusions regarding the relation between different properties and the chemical composition also may be drawn.

The rigidity which glasses possess over large ranges of temperature must be attributed to the fact that no appreciable migration of the atoms occurs at relatively low temperatures. The cations A, especially if they are alkali ions, will be bound less tightly to the surrounding oxygen atoms than the cations B. As the temperature rises we must therefore expect to get an increasing number of migrating atoms A, without any appreciable breakdown of the vitreous framework proper. Univalent cations will, of course, migrate with greater ease through the framework than the divalent cations, and again smaller cations will migrate more easily than large cations with the same charge. Thus Na^+ migrates more easily than K^+, both these ions more readily than say Ca^{+2}. The electric conductivity of a glass for these reasons must be chiefly electrolytic, the charge being carried by cations and for the most important part by the alkali ions. Owing to the increasing number of detached atoms with increasing temperature, the conductivity will also increase with the temperature. These conclusions seem to be substantiated by actual observations. Glasses rich in alkali invariably are relatively good conductors. Pyrex glass containing negligible amounts of cations A has a very low conductivity.

At higher temperatures breakdown of the vitreous framework proper will begin, and large parts of the framework may start migrating. As a matter of fact we must expect that even in the melt oxygen atoms and atoms B to a very great extent are linked together so as to form rather large groups, the degree of polymerization being, of course, a function of the temperature. In melts where there are highly associated groups like that the viscosity will be high.

It must be remembered that the conditions which we have given for the glass formation are not the only ones. Whether a substance will form a glass or not naturally will depend also on the conditions under which the melt is cooled down. We have stated therefore that certain substances *may* form glass, namely, when the melt is cooled under conditions favorable for glass formation.

Summary

It is shown that the following picture of the atomic arrangement is in complete agreement with the characteristic properties of glasses. The atoms in glass are linked together by forces essentially the same as in crystals. Over large ranges of temperature the atoms are oscillating about definite equilibrium positions. As in crystals extended three-dimensional networks are formed. The principal difference between a crystal network and a glass network is the presence of symmetry and periodicity in the former and the absence of periodicity and symmetry in the latter.

A glass network with an energy content comparable to that of the corresponding crystal can be formed only under certain conditions. These conditions are deduced for oxide glasses. It is found that the following oxides may be expected to occur in vitreous forms: B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, P_2O_3, As_2O_3, Sb_2O_3, V_2O_5, Sb_2O_5, Cb_2O_5, Ta_2O_5. Analogously it is deduced that BeF_2 is the only fluoride which can be prepared as glass. In a similar manner it is found that an oxide glass of the general type must contain appreciable amounts of one or more of the following types of cations: B^{+3}, Si^{+4}, Ge^{+4}, P^{+5}, As^{+5}, As^{+3}, P^{+3}, Sb^{+3}, V^{+5}, Sb^{+5}, Cb^{+5}, Ta^{+5}, Al^{+3}. The gross chemical composition of a glass can be expressed by a formula A_mB_nO, where B represents the cations listed above and where A represents all other cations present. m and n give the number of cations A and B per oxygen atom. It is concluded that a glass will have the most advantageous properties if n has a value of about 0.5. Cations A must carry a small charge and have a large radius.

These restrictions concerning the chemical composition are in complete agreement with empirical facts.

Some conclusions with respect to other properties of oxide glasses are given.

CHICAGO, ILLINOIS