(6) Smelting tests indicated that oversmelting, as evidenced by yellow-to-brown coloring of the frit, is detrimental to reflectance; color of fired enamel is not affected by oversmelting; correct smelting temperature seemed to be 2150°F. and glass should be poured as soon as all material is in solution. Undersmelting as indicated by some undissolved particles imbedded in the frit did not affect reflectance or color of fired enamel. The yellow coloring of glass is due in part to reduction of TiO_2 to a lower oxide.

(7) Firing time and temperatures are important since opacity is produced in the enamel during the firing process; optimum time and temperature are indicated for this type of enamel, above which optimum the reflectance is not increased appreciably for feasible increases in time or temperature.

(8) Opacifying crystals in these titanium enamels were either rutile or anatase; in the large majority of cases, rutile was found; effect of composition on form of TiO_2 that recrystallizes in firing is not definite from results of this investigation. It has been determined that the crystal form of TiO_2 added to the smelter does not control the form of TiO_2 recrystallizing.

Acknowledgment

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FUNDAMENTAL CONDITION OF GLASS FORMATION*

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Abstract

The fundamental condition for glass formation is the existence of strongly bonded large networks or long chains of atoms in the liquid. Such chains or networks prevent or hinder the orderly orientation of atoms in the chains or networks themselves and also that of atoms, not in the networks in the liquid, near the melting point or liquidus temperature. A liquid structure will persist when the liquid is cooled below the melting point or liquidus temperature and will continue until free, long-range movement of atoms becomes impossible. In order to obtain such long chains or large networks, it is necessary that (1) the bond strength of atoms in the chains or networks be very strong; (2) the small ring formation of these strongly bonded atoms be at a minimum; and (3) the relative numbers of various atoms in the chains or networks be such that at least a continuous chain is configuratively and structurally possible; at the same time, the coordination numbers of the glassforming atoms should be as small as possible to keep the bond strong. The general treatment is applied to all kinds of glasses, particularly oxide glasses. The bond strengths of all M—O single-bond linkages in these glasses are calculated and tabulated here for the first time. The bond strength of all the glassformers was found to be greater than 80 kilocalories per Avogadro bond, that of the intermediates between 60 and 80, and that of the modifiers below 60; the transition is continuous, and the division into glassformers, intermediates, and modifiers is arbitrary.

I. Introduction

Glass is a vitreous substance which, if defined simply, is called a "frozen" or "rigid" liquid. In other words, the arrangement of all the atoms or molecules in a glass or vitreous substance possesses a permanence similar to that in crystalline solids and a randomness similar to that characteristic of liquids. This definition or concept of a vitreous substance is qualitative, but at the present time, there are no quantitative ways of defining different degrees of permanence and randomness.

The writer will discuss here a fundamental condition for the formation of the vitreous state of all materials, with special reference to glass or inorganic vitreous substances. Within certain limits and for convenience, the words "glass" and "vitreous substance," will be regarded as synonyms.

Glass is a thermodynamically unstable substance and tends to crystallize. Its formation is essentially a rate process, that is, a glass is formed if the rate of cooling below the melting point or liquidus temperature of the substance under consideration is faster than the rate of crystallization. Once a "glass" is formed, and since the term glass implies rigidity or very high viscosity, the rate of crystallization becomes so slow that the glass is relatively stable even if the rate of cooling should become zero. Since every liquid at any temperature below its melting point (or liquidus temperature, for a complex liquid) has a definite rate of crystallization at that particular temperature, it is theoretically possible to convert it into a glass by applying a rate of cooling faster than that of crystallization.

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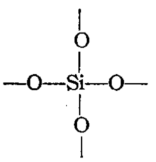
The rate of cooling, however, is limited by present-day laboratory techniques and by the amount of the substance and it is not possible to make a glass, particularly in sizable pieces, out of every substance. Even if a very high rate of cooling could be achieved and a small amount of glass could be obtained from every known substance, the differences in the melting points or liquidus temperatures of the starting liquids and those in degrees of permanence and randomness of the resulting glasses will emerge as another difficulty in a generalization and interpretation of the experimental facts. With the present technique and knowledge, the subject apparently cannot be treated comprehensively and quantitatively.

II. Discussion

As already mentioned, one difference between crystals and liquids or glasses is the arrangement of atoms or ions within a certain range or distance. This range is difficult to define, but it is approximately of the order of a few tens or thousands of angstroms. The crystals have an orderly arrangement extending from this range up; the glasses have a scattered orderly arrangement from this range down to a few angstroms. Some glasses have no such small range of orderly arrangement. The fundamental building units of crystals and glasses, particularly at the melting point or liquidus temperature, are essentially the same. For example, the fundamental building units for crystalline and elastic sulfur are —S—S— and those for crystalline and vitreous silica are



$$\begin{array}{c} | \\ \mathrm{O} \\ | \\ -\mathrm{O}-\mathrm{Si}-\mathrm{O}- \\ | \\ \mathrm{O} \\ | \end{array}$$

or simplified, the (SiO_4) unit. In crystalline silica, the (SiO_4) unit will repeat itself in a regular pattern up to sizes large enough to be visible to the eye, while in vitreous silica the orderly arrangement may end at a few angstroms or a few thousand angstroms.

From a geometrical point of view, any substance, simple or complex, may be considered a packed aggregate of atoms or ions. Each atom or ion is connected with a definite number of atoms which, in turn, are surrounded by others. The number of immediate neighbors, which is called the coordination number, and the strength and direction of linkage or bonding are characteristic of the individual atoms or ions in the particular substance. The charges and sizes of the various atoms are essentially the deciding factors. These also determine the compactness of packing. If the atoms can be distinguished as positive or negative, the packing is usually such that each positive atom will be surrounded by a definite number of negative atoms as immediate neighbors and each negative atom by a definite number of positive atoms.

Consider, for example, a two-dimensional case of a uniatomic substance and assume it to be composed of a large crowd of closely and randomly packed "handless soldiers". When it is cooled below the melting point, which is equivalent to the call for orderly arrangement of the soldiers in a pattern, say of hexagonally closed packing, the movement of the individual soldiers will be relatively slight because the regular pattern of the whole group can easily be obtained by moving each soldier a little in his immediate neighborhood without passing through other soldiers in the crowd. Such an orderly arrangement calls for very little disturbance of the group. An orderly arrangement is thus reached before an infinite number of enemy bullets kill all the soldiers and "freeze" them in the originally disorderly formation.

Now, one half of the soldiers may be assumed to have two hands and they join hands in the crowd in groups of several hundred or more soldiers. The rearrangement of the soldiers will not be so easy as it was before, during the call for orderly arrangement, and it will take a much longer time. In other words, the rate of orderly arrangement is slowed down because half of the soldiers have joined hands in groups. When the enemy bullets come at the later period, the dead or "frozen" soldiers will not be in the orderly pattern. This formation of soldiers is called "glass" formation.

The joining of hands, however, is a necessary but not a sufficient criterion for glass formation. If two or three, that is, a very small number, of soldiers join hands to form a ring, it is possible that the orderly arrangement of the whole group can be attained relatively easily because the obstacle (linked) groups are small in size and localized. It is important to note that the strength of the hand clasp or link is also a deciding factor in glass formation. The soldiers with weak hands can break and re-form or readjust their hand linkages without causing much movement of the individual soldiers in the crowd and an orderly arrangement is easy; the result is a crystalline, not glassy, body. The soldiers with strong hands, however, resist the breaking of connections and make glass formation easy.

Similar treatment may be extended to three dimensions by imagining the soldiers as round with a definite number of hands extended in different directions. These soldiers are called "atoms" and their hands, chemical "bonds."

It is clear, therefore, that the fundamental condition for glass formation is the existence of strong and large networks or even long chains formed by joining atoms together through two or more strong chemical "bonds" in the main body of the atomic crowd in which other atoms are linked together with much weaker "bonds." These strong atomic chains or networks prevent or hinder the orientation or orderly arrangement of all the atoms in the crowd and are thus responsible for the formation of glass. In order to form these strong and large networks or chains, the atoms must have a minimum number but at least two strong chemical bonds, and these bonds *must not join in* such a fashion that small rings result.

The subject may now be discussed in terms used in actual glassmaking with all types of materials.

Glasses may be divided into two classes,[1] namely, (1) elementary glasses, in which all the atoms are the same or alike in chemical nature and (2) compound glasses in which persistently positive and negative atoms can be distinguished and which can be further classified as organic-, oxide-, fluoride-, chloride-, or sulfide-type glasses.

Almost all of the metallic elements have either cubic or hexagonal packing of their atoms according to X-ray studies; in other words, the coordination numbers of metals are either 8 or 12. The binding strength per "bond" is relatively small, roughly in the order of a few kilocalories to maximum about 20 kilocalories per Avogadro bond. This is similar to the situation of handless soldiers or soldiers with eight or twelve weak hands. Crystallization or orderly arrangement is easy, and glassy metals or alloys are formed with great difficulty.

Among the nonmetals, sulfur is an interesting example. It is known that each sulfur atom links with only two other sulfur atoms with an angle about 106 degrees. The strength of the —S—S— bond is about 63.8 kilocalories per Avogadro bond.[2] These are good conditions for the formation of strong chains or rings which would form a glass easily except for the fact that eight sulfur atoms always have a tendency to form a closed ring. These 8-atom rings break up at high temperatures and, under quick cooling, the sulfur forms an elastic glass. Similar reasoning may be applied to other elements when their structure is known.

III. Calculation of "Bond Strength" of Glass Components

Compounds are generally divided into organic and inorganic groups. In organic chemistry, it has been recognized that the strong long-carbon chains, single, branched, or interlinked, (58.6 kilocal. per —C—C—), are usually responsible for the formation of innumerable polymer plastics. Such chains offer strong resistance to the orientation necessary for crystallization.

Among the inorganic compounds, such as oxides, sulfides, fluorides, and chlorides, there are positive and negative atoms packed together. A detailed discussion of oxides should suffice to illustrate the glass formation of the inorganic compounds.

The coordination numbers of positive and negative atoms and the bond strengths between them in the liquid are the primary concerns in determining the glass formation of an oxide, whether simple or complex. The coordination numbers are usually related to the relative sizes and charges of the positive and negative atoms and they can be obtained from direct X-ray examination of crystals or, more laboriously, of glass. As a first approximation, the bond strength can be determined from the heat of dissociation of the simple oxide (or oxide component in a complex oxide) into gaseous atoms as suggested by Pauling.[2]

TABLE I

CALCULATED BOND STRENGTH OF OXIDE COMPONENTS

M in MO_k	Valence	Dissociation energy per MO_x, E_d, (kilocalories)*	Coordination No.†	Single-bond strength B_{M-O} (kilocalories)
		Glassformers		
B	3	356	3	119
Si	4	424	4	106
Ge	4	431 (?)	4	108
Al	3	402–317	4	101–79
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

* ϵ' values of reference 3; a few values slightly modified by the author.

† Based on either known or assumed values.

Sun and Huggins[3] have calculated the heat of dissociation of various oxides or oxide components in crystals and glasses into gaseous atoms (not ions) from the corresponding lattice-energy data calculated by Huggins and Sun.[4] The bond strengths for the various M—O single bonds are calculated by using the coordination numbers, known or assumed, for the metals in oxides or oxide components. The M—O bond strengths are obtained simply by dividing the dissociation energy of the oxide, MO_x (in which x equals n/m for the oxide M_mO_n) by the oxygen coordination number of the

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[1] K.-H. Sun, "Glassforming Substances," *Glass Ind.*, **27** [11] 552–54, 580–81 (1946).

[2] Linus Pauling, Nature of Chemical Bond and Structure of Molecules and Crystals, 2d ed. Cornell Univ. Press, Ithaca, N. Y., 1940; 429 pp.; *Ceram. Abs.*, **19** [1] 28 (1940).

[3] K.-H. Sun, and M. L. Huggins, "Energy Additivity in Oxygen-Containing Crystals and Glasses, II," *Jour. Phys. Colloid Chem.*, **51** [2] 438–43 (1947).

[4] M. L. Huggins and K.-H. Sun, "Energy Additivity in Oxygen-Containing Crystals and Glasses," *Jour. Phys. Chem.*, **50** [4], 319–28 (1946).

metal, M. Table I gives the dissociation energy, E_d, for the oxide MO_x, the valence of M, the oxygen coordination number of M adopted, and the bond strength B_{M-O}, for the bond M—O. The bond strengths depend on the oxygen coordination number of the metal used in the calculations, and they may vary somewhat. For example, boron takes an oxygen coordination number 3 in pure B_2O_3 glass and as much as 20% or more of it takes coordination number 4 in complex borate glasses. The bond-strength values will be subject to change when more definite values of the oxygen coordination numbers are available.

The bond strengths for P—O, V—O, As—O, and Sb—O are calculated by dividing the dissociation energy of $MO_{2.5}$ (in which M is P, V, As, or Sb) by 5 instead of 4, because one of the four oxygens surrounding the M atom behaves very much like a double bond. For the first approximation, one double bond may be assumed to be equivalent to two single bonds. The minimum M—O single-bond strength, therefore, is calculated by dividing the total energy by 5. The values obtained by dividing the dissociation energy by 4 are also given as the upper limit for P_2O_5.

The coordination number adopted for thorium and a few other elements may be too small. If a larger value is assumed, the bond strengths will be correspondingly smaller. The bond strength for Ge—O is slightly larger than it should be because of the uncertainty of the original heat data of GeO_2 used.

Based on the earlier discussion, a good glass must contain many bonds or linkages of the types that have high bond strengths in the neighborhood of 100, such as those of P—O, B—O, Si—O, and Ge—O. These bonds will link the atoms together to form a strong three-dimensional network, a fundamental condition for glass formation. The introduction of bonds such as Ti—O and Be—O will weaken the glass structure somewhat because of the lower bond strength but not so much as the introduction of bonds such as Na—O, K—O, etc. The weak bond strengths of Na—O and K—O explain why it is almost impossible to quench Na_2O into a glass.

The term, "bond," is used merely for convenience; actually, it refers to the probability of the localized concentration of electron clouds in certain definite directions between atoms. Atoms, such as in divalent lead in oxides, are easily deformed or polarized. A recent study of Fajans and Kreidl[5] has shown that the six S^2 electrons of the divalent lead ions are easily loosened in the glass. It is not impossible for the divalent lead atom to orient itself in such a way that strong binding forces are developed between two nearest oxygens in glass. If this is the case, the coordination number 2 may be considered for the divalent lead. Zinc and cadmium behave similarly to divalent lead. For the sake of speculation, the bond strengths of these metals with oxygen are also calculated by using coordination number 2.

The list in Table I may be useful as a guide for glassmaking with oxide glasses.

The discussion so far has been limited to a theoretical treatment. When these results are compared with the experimental data and with the rules for glass formation drawn up by various investigators, the agreement is remarkable. Section III will be devoted to such a comparison and discussion.

IV. Comparison and Discussion of Data

Glass chemists divide glassmaking components into three classes based on the function of the component in the glass structure as follows:

(1) Glassformers, which constitute the backbone of glass and usually can form a glass with ordinary laboratory techniques; B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, Sb_2O_5, V_2O_5, ZrO_2, P_2O_3, Sb_2O_3, and Bi_2O_3 are in this class, and the first four are particularly important in glassmaking.

(2) Modifiers, which do not form a glass under ordinary conditions but are introduced into glass to modify its properties; they usually weaken the glass structure; Na_2O, K_2O, CaO, SrO, and BaO are examples.

(3) Intermediates, which occupy a position somewhere between the glassformers and the modifiers; Al_2O_3, BeO, ZnO, CdO, PbO, and TiO_2, belong to this group. An analogy may be drawn in the field of plastics with respect to such a classification. The long chainforming substances, such as styrene and the vinyl derivatives, correspond to the glassformers; the plasticizers to the modifiers; and the vulcanizers, to a certain extent, to the intermediates.

Since, in a glass, the identity of oxide-forms disappears entirely and the resulting glass is a packing of positive atoms and negative oxygen atoms, the comparison of the bond strengths of various M—O bonds suffices to determine the properties of each oxide and offers a means of classifying oxides. An analysis of this classification with respect to the bond strength of various M—O combinations (Table I) shows that the bond strengths of all the so-called glassformers are above 80 kilocalories per Avogadro bond, those of the intermediates are between 60 and 80, and those of the modifiers are below 60. The transition is gradual, and it is the classification of glassformers, modifiers, and intermediates which is arbitrary. The study of the bond strength, however, does present a semiquantitative means of distinguishing between the oxide components used by the glass chemists.

Other interesting points may be noticed by studying Table I.

Aluminum in Al_2O_3 crystal assumes an oxygen coordination number 6, the bond strength (67 kilocalories or lower) is relatively weak, and glass formation is difficult. In certain combinations, such as $12\,CaO \cdot 7Al_2O_3$, Al takes a coordination number 4, and its bond strength is high (101 kilocalories). Aluminates of these compositions form a glass.

The difference in the behavior between Li_2O and other alkali oxides long noticed by glass chemists may be attributed to the difference in their bond strengths.

The order of bond strength for the glassforming

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[5] K. Fajans and N. J. Kreidl, "Constitution of Extra Dense Flint Glasses"; for abstract, see *Amer. Ceram. Soc. Bull.*, **25** [3] 130 (1946); to be published later in *Jour. Amer. Ceram. Soc.*

elements and oxygen for the phosphate, borate, silicate, and germanate glasses is uncertain because the coordination of boron varies a great deal and the bond strength of P—O is not definitely known. It is possible that the order of the bond strengths may be arranged as P—O, Si—O, B—O (average in common borate glasses), Ge—O, and Al—O in decreasing order.

Although the bond strengths of V—O, As—O, and Sb—O are relatively high, they are not good glassformers. This may be due to small ring formation in these substances which would cause relatively easy crystallization.

There are rules formulated by various investigators in relation to glass formation. Sun and Silverman[6] suggested that, for all glassformers, the radius ratio of the positive atom to oxygen is smaller than 0.414, which is the limit for a tetrahedral linkage, MO_4. This rule actually states that all positive atoms of the glassformers have an oxygen coordination number of 4 or smaller which is necessary to secure maximum possible bond strength. The case of Al—O mentioned is a good sample of this rule interpreted in terms of the writer's bond-strength theory.

After a comprehensive study, Zachariasen[7] observed, "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." His first point coincides with the present view in that enough strongly bonded atoms must be present in order that a glass be formed. The second point emphasizes the undesirability of small ring formation between the strongly bonded atoms. The third point is again a natural consequence of the present discussion; namely, that in order to secure a strong M—O bond, it is important that the coordination numbers of the cation as well as of the oxygen be as small as possible but larger than 2.

V. Summary

Although only a brief treatment of oxide glasses has been given here, the general idea is applicable to other types of glasses. In short, the existence of strongly bonded large chains or networks of atoms in the liquid is the fundamental condition for the formation of a glass. Such chains or networks will not only prevent or hinder the orientation or arrangement of atoms in the chains or networks themselves but also in other atoms in the liquid. Thus, a liquid structure persists even after the liquid is cooled below the melting point or liquidus temperature to the extent that free long-range movement of atoms becomes impossible. To secure such long chains or large networks, (1) the bond strength of atoms in the chains or networks must be very strong; (2) small ring formation of these strongly bonded atoms should be at a minimum; (3) the relative numbers of various atoms in the chains or networks should be such that at least a continuous chain is configuratively and structurally possible; and (4) at the same time, the coordination numbers of the glassforming atoms should be as small as possible to keep the bond strong.

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[6] K.-H. Sun and Alexander Silverman, "Glassforming Nature of Oxides with Special Reference to Tantala, Titania, and Beryllia," *Jour. Amer. Ceram. Soc.*, **25** [4] 97–100 (Feb. 15, 1942).

[7] W. H. Zachariasen, "Atomic Arrangement in Glass," *Jour. Amer. Chem. Soc.*, **54** [10] 3841–51 (1932); *Ceram. Abs.*, **12** [4] 145; [12] 416 (1933).