Although the material "glass" has now been known for some thousands of years, the variations in which it may be obtained are not by any means exhausted. This is evident from the fact that during the last decades many kinds of glass with new properties have been developed and found application in various technical directions. For the man of science it is gratifying to see that now, after centuries of empiric rule in this domain, in many cases theoretical conceptions as to the structure of glass are serving as a guide to the development of new materials.

Introduction

For many uses of glass, particularly in the field of electrotechnology, the requirements which have to be met nowadays go far beyond the properties that are usually to be found in normal kinds of glass. To illustrate this we have only to take a few cases occurring in the field of activity of our laboratories. For radar transmitting valves a glass is required which shows no excessive dielectric losses in an alternating field with frequencies in the order of \(10^{10}\) c/s (3-cm waves). For the transmitting valves used for normal radio broadcasting at frequencies round about \(10^6\) c/s (300 metres) the glass must likewise not have too high dielectric losses, whilst it must also have a low softening point for easy manufacture. The development of the cathode-ray tubes for television receivers particularly involves special glass-technical problems. For the small projection-television tubes, in which electrons are accelerated by voltages of 25 kilovolts or higher, a glass is required which is able to withstand lengthy bombardment by the electrons and by X-rays without being subject to discoloration.

It was fortunate that at the moment when such very special requirements as these were placed before the glass technologist some insight had already been obtained into the structure of glass in general. This suggested the lines on which further work could be done to reach the desired results.

The foundations for our present-day knowledge of the structure of glass were laid by Zachariasen \(\textsuperscript{1}\), who in 1932 wrote a classical article on the subject. The theories he expounded have already been set forth in this journal \(\textsuperscript{2}\), so that it will suffice to recall them here quite briefly. We shall then proceed to deal with the refinements which Zachariasen's theory has subsequently undergone on various points and which are due mainly to the work of Warren and Weyl in the U.S.A. and of Dietzel and Smekal in Germany. It is due to these refinements in particular that we are not only able to grasp a number of peculiarities in the already known physical properties of glass but are now better prepared to cope with the new requirements of technical science.

Zachariasen's theory

There are a number of oxides, called glass-forming oxides, which may occur in the vitreous as well as in the crystalline state (\(\text{SiO}_2, \text{B}_2\text{O}_3, \text{P}_2\text{O}_5\)). According to Zachariasen, in the crystalline and in the vitreous state these oxides are built up of the same elements, namely polyhedrons (tetrahedrons or triangles) of oxygen ions with the highly charged cations \(\text{Si}^{4+}, \text{B}^{3+}, \text{P}^{5+}\) at their centres. The only difference is that in the crystalline state these polyhedrons are arranged regularly, whereas in the vitreous state they are not. A schematic representation of this is given in fig. 1.

For the network of oxygen polyhedrons to occur in these two forms it is necessary that the structure of the oxide in the crystalline state satisfies a number of conditions given by Zachariasen, which (see the article quoted in footnote \(\textsuperscript{2}\)) involve the following.

1. Every oxygen ion must be bound to not more than two positive ions which must be highly charged and small.
2. The number of oxygen ions which surround such a positive ion (forming a polyhedron) must be neither very large nor small (3 or 4).
3. The oxygen polyhedrons adjacent to each other must have common corners (bridging oxygen ions), but no common edges or faces.
4. Each polyhedron must have at least three oxygen ions in common with neighbouring polyhedrons.

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\(\textsuperscript{1}\) W. H. Zachariasen, J. Amer. Chem. Soc. 54, 3841, 1932.
\(\textsuperscript{2}\) J. M. Stevels, Philips Techn. Rev. 8, 231—237, 1946.
We shall not enter into the arguments on which these rules have been formulated. Suffice it to say that oxides which in the crystalline state satisfy these conditions have a very open structure, so that the polyhedrons need not necessarily arrange themselves according to a periodic pattern when, upon cooling of the melt, the solid phase is formed.

The structure of the many glasses that can be made by fusing these glass-forming oxides together with a large number of metallic oxides, such as CaO, BaO, PbO, Na₂O, is likewise described by the theory of Zachariasen. While the metal ions find a place in the interstices of the open network just mentioned, the added oxygen ions are taken up through a number of oxygen bridges in the network being broken, each bridging oxygen ion being replaced by two non-bridging oxygen ions. Obviously any continued change of this nature will greatly influence the properties of the glass.

The structure of borate glasses

It will be obvious that the addition of metallic oxides to a glass-forming oxide cannot be continued at will. It has already been pointed out that the breaking down of oxygen bridges greatly influences the properties of a glass, and one can imagine that if this is carried too far the typical vitreous structure of coherent tetrahedrons or triangles ultimately becomes unstable. It can readily be understood that a network completely spatially bonded is no longer possible as soon as the number of contact points (bridging oxygen ions) per polyhedron, denoted by Y, becomes less than two. "Islands" are then formed, which in themselves may consist of a rather large number of polyhedrons. The smaller the value of Y, the smaller are the islands. For Y = 1 these islands average two polyhedrons, whilst for Y = 0 the "structure"

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consists of isolated polyhedrons. Obviously the structures with small \( Y \) values will have a strong tendency to order themselves, thus readily changing into the crystalline state.

The number of contact points per polyhedron, \( Y \), can quite easily be calculated from the composition of the glass. In this connection the composition is characterized by the ratio \( R \) of the total number of oxygen ions to the total number of network-forming ions. For glasses with tetrahedrons as elements, i.e. with network-forming ions having a coordination number of 4 (silicate and phosphate glasses), the relation is \( Y = 8 - 2R \), whilst for glasses with triangles as elements, i.e. with network-forming ions having a coordination of 3, the rule is: \( Y = 6 - 2R \).

Silicate glasses can, indeed, only be formed as long as \( R \leq 3 \); in other words, as soon as \( Y \leq 2 \) (i.e. as soon as islands begin to form) it is no longer possible for the melt to solidify in the vitreous state. With phosphate glasses it appears that one can go a little farther in adding metallic oxides, as far as \( R = 3.2 \). Then \( Y = 1.6 \), which means that it is possible to reach the vitreous state notwithstanding the occurrence of (not too small) islands.

With borate glasses, considering that the \( \text{B}_2\text{O}_3 \) structure consists of triangles, one would expect the addition of metallic oxides to cause formation of islands \( (Y<2) \) as soon as \( R > 2 \). With borium-containing glasses, however, a peculiar complication arises, in that in such glasses metallic oxides may be taken up according to a mechanism differing somewhat from that described above. When metallic oxides are added to \( \text{B}_2\text{O}_3 \) — for instance Na\(2\text{O} \)— the Na\(^+\) ions will find a place as network modifiers but the mechanism of bridge breaking does not take place. The excess of added oxygen is taken up owing to the property of the B\(^3+\) ion being able to occur in the centre of an oxygen triangle but also in the centre of an oxygen tetrahedron. Thus the network is then built up from both oxygen triangles and oxygen tetrahedrons, while there is not a single non-bridging oxygen ion. Such a structure is represented in fig. 3.

\[ Y = 8 - 2R, \quad \ldots \ldots \quad (1) \]

It is remarkable that this process of taking up oxygen, whereby a change takes place in the coordination number for some of the B\(^3+\) ions and the network gains more and more in strength, continues until a certain concentration is reached, which, for the system Na\(2\text{O}-\text{B}_2\text{O}_3\), is 18 mol. \% Na\(2\text{O} \). With greater concentrations of Na\(2\text{O} \) the previously described bridge-breaking mechanism comes into action again, non-bridging oxygen ions then being formed. These ranges of concentrations have been named respectively the accumulation region and the destruction region.

\[ Y = 6 - 2R, \quad \ldots \ldots \quad (2) \]

The state of affairs outlined here implies that in such a borate glass relatively more metallic oxides can be taken up before island formation arises. In the accumulation region, where no non-bridging oxygen ions occur, \( Y \) always equals \( 2R \) (cf. footnote \(^5\)), so that the average number of contact points per polyhedron increases with increasing \( R \) ! In the destruction region the ratio of the number of triangles to the number of tetrahedrons remains constant, such that the average coordination number of the B\(^3+\) ion \( Z = 3.22 \). In this region, therefore, the relation (cf. footnote \(^5\)) is:

\[ Y = 6.44 - 2R, \quad \ldots \ldots \quad (3) \]

Island-forming \( (Y<2) \) will then not take place until \( R > 2.22 \). Actually it appears that most borates may become vitreous up to \( R = 2.4 \), so that here again, just as in the case of phosphate

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\(^5\) Denoting the average number of non-bridging oxygen ions per polyhedron by \( X \) and the total number of oxygen ions per polyhedron (the coordination number) by \( Z \), then, as may be verified by simply counting the ions, \( X + \frac{1}{2} Y = R \) and \( X + \frac{1}{2} Y = R \), from which it follows that \( Y = 2Z - 2R \).
glasses, a small degree of island-formation is no hindrance to vitrification.

The foregoing is illustrated graphically in fig. 4. Of particular importance in practice are the consequences that the changing of the coordination number and the accompanying strengthening of the network have for the physical properties of this group of glasses. By way of example, in fig. 5 the coefficient of thermal expansion of the pure sodium-borate glasses is plotted as a function of their composition. This curve shows a minimum just at the composition where, according to the foregoing considerations, the network has the strongest structure.

Something similar is found in the case of borosilicate glasses. On the boundary line between the accumulation region and the destruction region (fig. 6) are the glasses which, compared with other borosilicate glasses, are characterized by a maximum strength of structure (small expansion coefficient and high softening point), for example the "Pyrex" glasses.

The changing of the coordination number of the $B^{3+}$ ion is therefore responsible for the fact that, under suitably chosen conditions, the incorporation in glass of $B_2O_3$, which itself has a very high expansion coefficient and very readily melts, results in a reduction of the expansion coefficient and a raising of the softening point. Various other
properties of the glass are likewise influenced by the structural change described, as for instance the dielectric losses. This will be discussed in greater detail in another article to be published shortly in this journal.

The conceptions of network-forming and network-modifying ions

Zachariasen thought that the positive ions could be divided into two groups, which in the foregoing have been denoted as network formers and network modifiers, but it has meanwhile become apparent that this division does not hold in all cases. It is now known that there are a large number of ions which may occur in glass in both forms, and often simultaneously. This means that in glass there are some ions of a certain type which have 4 oxygen ions surrounding them, thus being situated in the centre of the tetrahedrons forming the network typical for glass, while other ions of that type are surrounded by a larger number of oxygen ions. In some cases the position of the "equilibrium" between the two forms may be roughly determined by the colour of the glass, as is the case, for instance, with the nickel ion. Ni\(^{2+}\) ions may occur in a glass mainly as network formers, in which case the glass has a purple colour; under other circumstances these Ni\(^{2+}\) ions mainly occur as network modifiers, the glass then being yellow. Such differences in colour in cases where the coordination number is changed have been found, for example, with Cu\(^{2+}\), Co\(^{3+}\), Fe\(^{3+}\), Fe\(^{2+}\), Mn\(^{2+}\), Mn\(^{3+}\) and U\(^{6+}\). But it is also possible to detect these changes in the coordination number among non-colouring ions, by a method which has recently been indicated \(^3\) and which will be discussed in our next article.

The "equilibrium" between the forms of coordination depends not only upon a number of external factors (temperature and furnace atmosphere when making the glass, and the rate of cooling) but also to a large extent upon the quantities of the different ions contained in the glass. The simple theory of Zachariasen could not furnish any explanation for this, but it has been made comprehensible by means of a "competition principle". In general, the small, highly charged cations which are capable of attracting the oxygen ions close to them, and strongly binding them, will easily surround themselves with only four oxygen ions (or three in the case of B\(^{3+}\)). The larger and less charged cations are then surrounded by a larger number of oxygen ions, to which they are less strongly bound. In principle, however, also these latter cations may be surrounded by only four oxygen ions, thus entering into competition with the small, highly charged ions, in which they may be successful, for instance, when relatively few oxygen ions are present.

Various investigators have attempted to express this "competition capacity" of the ions numerically. A suitable measure has been found to be the "field strength" of the ion at the centre of an adjacent oxygen ion, \(z/a^2\), where \(z\) is the charge of the ion and \(a\) the distance between the centres of the two adjacent ions \(^7\). When the ions are arranged in the order of their calculated field strength (see table I) their sequence gives an idea of the preference that the various ions have for occurring either as network formers or as network modifiers. When different cations occur in a glass simultaneously, those with the highest \(z/a^2\) value will preferably occupy the network-forming positions (smallest coordination numbers), while those with the lowest \(z/a^2\) value show a preference for the network-modifying positions (largest coordination numbers).

Table I. The "field strength" \(z/a^2\) for a number of cations, according to Dietzel \(^7\); \(z\) = charge of the ion, expressed in elementary charges; \(a\) = distance (in Angstrom) from the centre of the ion to the centre of an adjacent oxygen ion. (If the cation is rather large it then no longer fits in the interstice of a tetrahedron formed by four oxygen ions, and for this reason alone the natural coordination number is greater than four).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Coordination number</th>
<th>3</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(^{2+})</td>
<td></td>
<td>0.87</td>
<td>0.87</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td>Mn(^{3+})</td>
<td></td>
<td>0.87</td>
<td>0.87</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td>Li(^{+})</td>
<td></td>
<td>0.23</td>
<td>0.23</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td></td>
<td>0.19</td>
<td>0.19</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>K(^{+})</td>
<td></td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>Zr(^{4+})</td>
<td></td>
<td>0.51</td>
<td>0.51</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td></td>
<td>0.59</td>
<td>0.59</td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td></td>
<td>0.61</td>
<td>0.61</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>Ni(^{3+})</td>
<td></td>
<td>0.61</td>
<td>0.61</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td></td>
<td>0.97</td>
<td>0.97</td>
<td>0.84</td>
<td>0.84</td>
</tr>
<tr>
<td>Si(^{4+})</td>
<td></td>
<td>1.57</td>
<td>1.57</td>
<td>1.57</td>
<td>1.57</td>
</tr>
<tr>
<td>B(^{3+})</td>
<td></td>
<td>1.65</td>
<td>1.65</td>
<td>1.65</td>
<td>1.65</td>
</tr>
<tr>
<td>P(^{5+})</td>
<td></td>
<td>2.08</td>
<td>2.08</td>
<td>2.08</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Some striking examples can be given to illustrate this.

When silicon ions and phosphor ions enter into competition with each other, as in the glass of the composition SiP\(_2\)O\(_7\) (i.e. SiO\(_2\)P\(_2\)O\(_4\)), from the table

\(^3\) J. M. Stevels, Verres et Réfractaires 2, 2, 1948.

it is to be predicted that the phosphor ions will "win". For this glass it is difficult to determine directly with what coordination numbers the ions Si$^{4+}$ and P$^{5+}$ occur in it. The crystalline SiP$_2$O$_7$, which is isomorphous, as. By X-ray diffraction analysis it was found that each P$^{5+}$ion is indeed surrounded by four bridging oxygen ions and each Zr$^{4+}$ion by six bridging oxygen ions. Since it may be assumed that the coordination numbers will be the same in the vitreous state and in the crystalline state, we have here a case where Si$^{4+}$ occurs in a coordination of 6, i.e. the Si$^{4+}$ion, the network former par excellence, occupies only a network-modifying position.

The opposite effect is seen in the following example. Of the compound 2CaO.SiO$_2$ only a crystalline form is known. This is in conformity with the aforementioned considerations about Y and R: for four oxygen ions there is only one network-forming ion, thus R = 4 and therefore, according to eq. (1), Y = 0. Though this substance is built up from SiO$_4$ tetrahedrons, these are all isolated and therefore arrange themselves into a well-ordered structure, with Ca$^{2+}$ions as "binder". The remarkable fact is that the entirely analogous compound 2ZnO.SiO$_2$ may indeed occur in the vitreous state. An explanation for this may find support in the fact that Zn$^{2+}$ stands some steps higher in table I than Ca$^{2+}$. It is therefore feasible that in the system in question Ca$^{2+}$ occurs exclusively with a coordination number six or higher, i.e. as a network modifier, whereas under suitably chosen conditions Zn$^{2+}$ may occur also with coordination number four, thus possibly playing the part of a network-forming ion. If in the compound 2ZnO.SiO$_2$ only 16.7% of the Zn$^{2+}$ions occur as network formers — instead of writing Zn$_2$SiO$_4$ the composition can then be better written as Zn$_{53}$ (Zn$_{17}$Si)$_3$O$_4$ — then the quotent R is already reduced to exactly 3 and thus vitrification is possible (Y = 2). Actually slightly more than 16.7% of the Zn$^{2+}$ions will be present as network formers. Vitrification in the system ZnO-SiO$_2$ continues until roughly the composition 2.2 ZnO.SiO$_2$ is reached. The condition $R \leq 3$ can then only be satisfied if at least 18.2% of the Zn$^{2+}$ions occupy a network-forming position.

Resuming, the following advances have thus been made upon the old theory. According to Zachariasen's criteria Zn$^{2+}$ and Ba$^{2+}$ ions should always behave as network modifiers. The new conception (the competition principle) makes it feasible that such ions may also occur as network formers, and that such is more likely to be the case the greater the concentrations in which these ions are present. This is of great practical importance; since the addition of one and the same ion to a glass may influence the properties to a different extent (or even in the opposite direction), depending upon the position it takes in the network: the Mg$^{2+}$ion, for instance, yields, as network modifier, a contribution towards the dielectric losses of a glass at 10$^6$ c/s, whereas as a network former it is harmless in this frequency range.

How the nature of the bond influences vitrification

The theory of Zachariasen has undergone a considerable evolution in recent years in yet another respect. Whereas Zachariasen never discussed the nature of the bond in vitreous systems and, moreover, regarded the elements (the polyhedrons) as being invariable, in recent years it has been pointed out, especially by German investigators, that the nature of the chemical bond in the elements is of great importance in determining whether a certain substance may or may not occur in the vitreous state. Smekal, to whose work this theory is mainly to be ascribed, has indicated that it is feasible that a condition for vitrification is that the system must contain "mixed" bonds. By this it is meant that, in addition to directed bonding forces (homopolar bonds, which are confined to certain mutual "valence angles", such as, e.g., in CO$_2$ or NH$_3$ or SiCl$_4$), also non-directed bonding forces (heteropolar bond or Van der Waals bond) must be in action. The two kinds of bonding forces may be united in one bonding direction, such as, e.g., in the Si-O bond, which is to be described as a combination of a force of the type of a homopolar bond and one of the type of a heteropolar bond, or they may be present in different bonding directions. The latter is found to be the case, for instance, in the vitreous selenium and in

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6) Here it is tacitly assumed that the limit found in practice for the occurrence of the vitreous silicates (R=3) would likewise apply for the glasses containing Si$^{4+}$ and few Zn$^{2+}$ ions as network formers. A priori this need not strictly be the case, it being possible for the limit to lie at a somewhat greater value of R (Y < 2) (cf. the phosphate and borate glasses). Then smaller percentages of network-forming Zn$^{2+}$ ions would be sufficient to account for vitrification in the case of the compositions mentioned.

the chain macromolecules, where in the direction of the chains a homopolar bond prevails while the chains are mutually kept together mainly by a Van der Waals bond 19).

These considerations are of great importance because they relate to all kinds of glasses, whereas Zachariasen's theories apply exclusively to kinds of glass formed by inorganic oxides.

The difference between Smekal's theory and that of Zachariasen may be formulated by saying that the latter theory ascribes the irregular structure of the network exclusively to the irregular packing of the oxygen polyhedrons. According to Smekal's theory, applied to the oxide glasses, the type of bond within the polyhedrons may change, in that the bond may bear a more homopolar or a more heteropolar character. Consequently, therefore, interatomic distances in those polyhedrons may change, and this may also contribute towards the irregular structure of the network in vitreous systems.

Inorganic glasses in which Zachariasen's rules do not hold

Having accepted this line of thought as being correct, one will not be surprised to find that inorganic systems exist which do not at all obey the rules given by Zachariasen and nevertheless occur in the vitreous state.

Excluding those resembling selenium (such as vitreous sulphur and tellurium), the earliest known example is the system of carbonates $K_2CO_3-MgCO_3$. According to Zachariasen's rules, as applied to the oxide $CO_3$, there would be no question of vitrification here; one would rather expect a regular crystal lattice formed by the positive metal ions and negatively charged $CO_3^-$ groups. It has now been found, however, that the heating of a mixture of $K_2CO_3$ and $MgCO_3$ in equimolecular quantities does indeed lead to vitrification. The glass certainly has a strong devitrifying tendency: at 300°C it completely devitrifies in an hour, but at temperatures below 150°C the vitreous state is maintained.

Quite analogous systems, such as $Na_2Ca(CO_3)_{2}$, $K_2Ca(CO_3)_{2}$, $Na_2Mg(CO_3)_{2}$, $NaLiCO_3$ and $KLiCO_3$, on the other hand, show no trace of vitrification.

Looking back at table I, it is seen that of all the cations in question here $K^+$ and $Mg^{2+}$ differ most in "field strength". The fact that of the systems mentioned only $K_2Mg(CO_3)_{2}$ forms a glass is an indication that the condition favourable for vitrification is created by the combination of a very weak and a much stronger cation. It may, therefore, be so interpreted that the greatly varying electric fields prevailing in the system deform the $CO_3^-$ groups in a different way, thereby, according to Smekal, promoting vitrification.

Something similar has been found with the nitrates. A mixture of equimolecular quantities of $Ca(NO_3)_{2}$ and $KNO_3$ becomes vitreous when cooled from the molten state, whereas such is not the case with the system $Ca(NO_3)_{2}-NaNO_3$. Apparently the difference in strength of the $Ca^{2+}$ ion and the $Na^+$ ion is not large enough for a sufficient deformation of the $NO_3^-$ groups. On the other hand the system $Mg(NO_3)_{2}-KNO_3$ would, indeed, be expected to occur in the vitreous state, and this has in fact been found to be the case. This is not so easily proved because it is difficult to obtain anhydrous $Mg(NO_3)_{2}$ in a chemically pure state. In the procedure followed by us a mixture of $Mg(NO_3)_{2}cdot 4H_2O$ was melted in a platinum crucible (the melting point is 92°C) and then carefully heated further, thereby removing all the water contained in it. As soon as the melt begins to give off nitrous vapour (at about 290°C) an equimolecular quantity of $KNO_3$ is added. The homogeneous melt of $KMg(NO_3)_{2}$ thereby obtained is quenched by decanting in droplets in liquid air. X-ray diffraction photographs showed that the product was vitreous.

With the sulphates there is a still more striking example. The system $K_2SO_4-MgSO_4$ does not, in any composition, yield a vitreous product, notwithstanding the great difference in strength between the $K^+$ and the $Mg^{2+}$ ions. When, however, the $Mg^{2+}$ ion is replaced by an ion with a still stronger field, viz. the $H^+$ ion, vitrification is possible: by heating $KHSO_4$ to just above the melting point and then quenching by decanting onto an iron plate, a glass is obtained. At a temperature of 70°C this glass can be drawn into threads.

Finally, a very striking confirmation of Smekal's theory has been found with normal oxide glasses themselves 12). According to what has been set forth above, in a system such as, for instance, $Na_2O-B_2O_3$ vitrification occurs as long as the amount of $Na_2O$ does not exceed a certain percentage corresponding to a value of $Rapprox 2.4$. The same limit is found for the system $K_2O-B_2O_3$. When examining, however, the mixed alkali borates, such as the system $Na_2O-K_2O-B_2O_3$, it is found that there are kinds of glass where $R$ is much greater

than the limit mentioned. The same phenomenon is found with the mixed alkali silicates and alkali phosphates, such as illustrated for some systems by the phase diagrams in figs 7 and 8. As far as the value of \( R \) is concerned, the area of vitrification would be expected to be bounded in each diagram by the broken line: as a matter of fact vitrification occurs within the whole of the hatched area. The most striking fact is that the relative increase of the vitrification area is on the whole larger the more the respective cations differ in "field strength"; for an example see table II. Herein lies the explanation for the whole phenomenon. The threshold value of \( R \) is related to the fact that with increasing number of oxygen ions the polyhedrons, originally considered as being entirely rigid, are ultimately no longer able to retain their mutual coherence in a network that is becoming more and more open. Owing to the great variations in the electric fields, however, the oxygen polyhedrons are themselves somewhat deformed. This deformation makes it possible for a coherent vitreous network to be formed also when the value of \( R \) is somewhat greater (smaller \( Y \)).

**Table II.** Relative expansion of the vitrification area in the phase diagram of mixed alkali borates, compared with the area in which the condition for \( R \) is satisfied \(^{11}\).

<table>
<thead>
<tr>
<th>System</th>
<th>Increase in ( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}_2\text{O}-\text{K}_2\text{O}-\text{B}_2\text{O}_3 )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{B}_2\text{O}_3 )</td>
<td>50</td>
</tr>
<tr>
<td>( \text{Li}_2\text{O}-\text{K}_2\text{O}-\text{B}_2\text{O}_3 )</td>
<td>100</td>
</tr>
</tbody>
</table>

In conclusion it may be said that due to recent refinements of Zachariasen's theory many details in the phenomenon of vitrification can now be better understood. In particular the existence of all sorts of glasses not fitting in the old scheme has become understandable, while the new conceptions may serve as a guide — and in many cases have already so served — when seeking new glasses possessing entirely new combinations of properties.

**Summary.** Zachariasen's theory indicates under what conditions oxides may occur in the vitreous state. These conditions are based upon a conception of the structure of glass as an irregular network of oxygen tetrahedrons (or triangles) in whose centres are situated the small, highly charged ions \( \text{B}^{3+}, \text{Si}^{4+}, \text{or } \text{P}^{5+} \) (network formers), while in the interstices of the network there may be taken up, as network modifiers, all sorts of large, less charged, cations surrounded by a larger number of oxygen ions. According to new conceptions this picture has to be refined in some respects. The coordination numbers are not fixed to the extent originally supposed. The number of oxygen ions surrounding \( \text{B}^{3+} \) may change from 3 to 4, thereby explaining various phenomena encountered with borate glasses. Further, under certain conditions typical network modifiers (with normal surroundings of, say, 6 or 8 oxygen ions) may act as network formers (with coordination number four), and vice versa. The behaviour of the cations in this respect is governed by a competition principle, to which expression is given by a classification according to the order of their "field strength". According to Smekal the occurrence of bonding forces of different types between the particles in the network is essential for vitrification. Many facts not covered by Zachariasen's theory, or in contradiction therewith, thus find a plausible explanation. A number of examples are given by way of illustration.