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INTERACTION OF ALKALI- AND ALKALINE-EARTH-IONS IN SIMPLE SILICATE GLASSES¹
(Presented in the Glass Division of the 58th Annual Meeting (1956) of the
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ABSTRACT

The effect of the presence of additional alkali- and alkaline-earth- ions in a glass on the diffusion rate of an alkali ion in it is discussed. The theoretical basis for this effect and its importance in determining the atomic structure of a glass are considered. The role of the individual ion diffusion rates in determining the total alkali extraction (which is also a measure of chemical durability) from a mixed alkali or alkali-alkaline-earth-silicate glasses is brought out. The necessity of an exhaustive study of this interaction of the positive ions in a glass, along the lines of the work done by the authors is pointed out.

The authors believe that this complex effect of the positive ions on one another further points towards a preferential, (rather than a random) arrangement of the positive ions of the so-called non-glass forming oxides, proposed by the authors in some of their earlier work.

I. INTRODUCTION

It is a well-known experimental fact that the introduction of calcium or some other di- or tri-valent positive ions in an alkali-silica glass immensely improves its chemical durability. The authors in an earlier paper (Ref. 3) further showed that the effect of the introduction of the calcium ions in an alkali glass on the extraction of the different alkali ions is not identical. The literature does not indicate any successful attempt to explain these effects on the basis of the structure of glass. In fact, these experimental facts can hardly be explained if one is to accept the role assigned to the alkali- and alkaline-earth ions in the glass structure according to the classical Zachariasen-Warren "Random Network Theory," according to which these ions merely fill the holes in the tetrahedral-silica structure and are randomly distributed. However, the authors, in some of their earlier work (Ref. 2) have advocated a preferential, rather than a random, distribution of these ions in the glass structure and have indicated a definite structural role for them. In this paper, it is intended to explain the alkali-extraction results obtained by the authors in light of the structural concepts advocated by them.

II. STRUCTURAL CONCEPTS

According to the structural concepts presented by the authors it was postulated that there would be a high probability for a part of the X-ion (Li, Na, K, Rb, or Cs) content of the glass to exist in the form of what were called doublets, triplets, etc. Further, it was postulated that the Y-ions (Be, Mg, Ca, Sr, or Ba) in appreciable proportions exist in a glass only in combination

with X-ions forming X:Y:X triplets, X:Y:X quadruplets, etc., and that the X:Y:X triplets would be the shortest of these combinations possible. Any particular X:X or X:Y association is, of course, through a pair of singly associated oxygens. Any X-ions not forming a part of such associations would be associated with doubly associated (commonly known as double bonded) oxygens only. Figure 1 shows a two-dimensional view of the structure of an X_2O -YO-SiO₂ glass illustrating an X:X doublet, an X:Y:X triplet, and an X ion associated with doubly associated oxygens only.

According to this theory, the positions or "holes" available for the residence of an X- or a Y-ion can be classified into three types depending on their oxygen surroundings.

Type "A" holes are those containing only doubly associated oxygens (and no singly associated oxygens) in their environment. This type of a hole would represent the least stable residence for an X or Y ion.

Type "B" holes are those containing, on an average, one pair of singly associated oxygens in addition to some doubly associated oxygens in their environment. This type of a hole represents a more stable residence than an "A" type hole for an X or Y ion.

Type "C" holes are those containing, on an average, two or more pairs of singly associated oxygens in addition to some doubly associated oxygens in their environment. Of the three types of holes defined, this type represents the most stable residence for an X or Y ion.

It was postulated, from immiscibility considerations, that the Y-ions invariably occupy holes of the type "C", with X-ions flanking them to give X:Y:X triplets and other higher groupings.

LEGEND

• SILICON

○ OXYGEN (WITH SILICON)

⊕ ADDED OXYGEN

⊗ X ION

⊙ Y ION

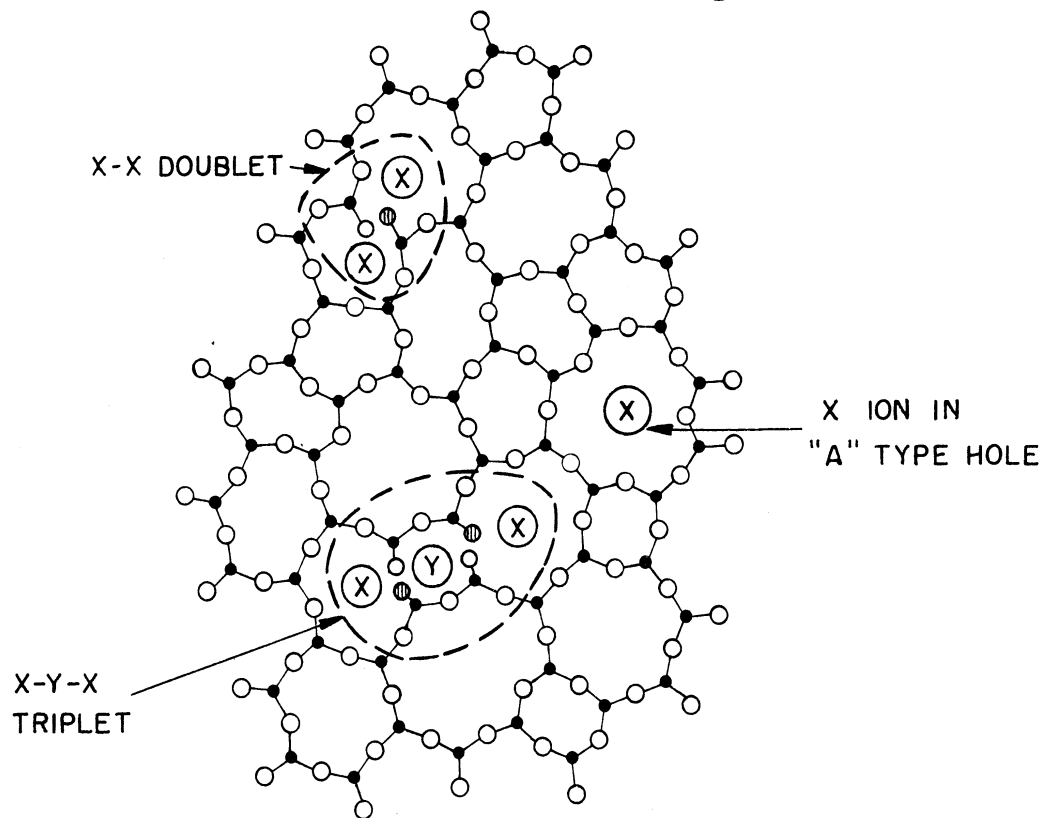


Fig. 1

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the authors' experimental values for K^+ , Na^+ , and total alkali ($K^+ + Na^+$) extraction rates at $50^\circ C$ for the series of glasses of the composition 18% ($K_2O + Na_2O$), 82% SiO_2 by weight plotted against weight percent of Na_2O and K_2O in the glasses. Figure 3 shows the corresponding results for the series of glasses in which the SiO_2 was reduced to 77%, the balance being replaced by CaO , giving glasses of the general composition 18% ($K_2O + Na_2O$), 5% CaO , 77% SiO_2 by weight.

The considerably-higher alkali extraction in a K_2O-SiO_2 glass as compared to a corresponding Na_2O-SiO_2 glass exhibited in Figure 2 can be explained if it were postulated that the Na^+ ions occupy the "C" type positions in preference to the K^+ ions. The introduction of calcium in the glass seems to reverse the effect. It was originally postulated on the basis of immiscibility data that the divalent ions mostly occupy the "C" type positions. The presence of the Ca^{++} ions in the "C" type positions forces more and more of the Na^+ ions to be present in the "A" type positions whereas the K^+ ions stay in the "B" type positions. This can explain the strange effect of the Ca^{++} ions on the extraction of the K^+ and Na^+ ions.

The peak in Fig. 2 and the valley in the alkali-extraction curves for $Na_2O-K_2O-Ca-SiO_2$ glasses reported by Sen and Tooley (Ref. 4), could probably be explained on the basis of the preferences of the various ions to occupy the "C", "B", and "A" type positions in the glass structure. However, before we go too far along this line, it must be pointed out that it is inherently wrong to use constant weight percent alkali glass alkali-extraction curves to explain the ionic structure of the glass. It was felt by the authors that for structural interpretation of alkali-extraction results, or in other words, to use alkali-extraction results to predict the tenaciousness with which a particular type of ions are held in the glass structure, it is necessary that the alkali-extraction

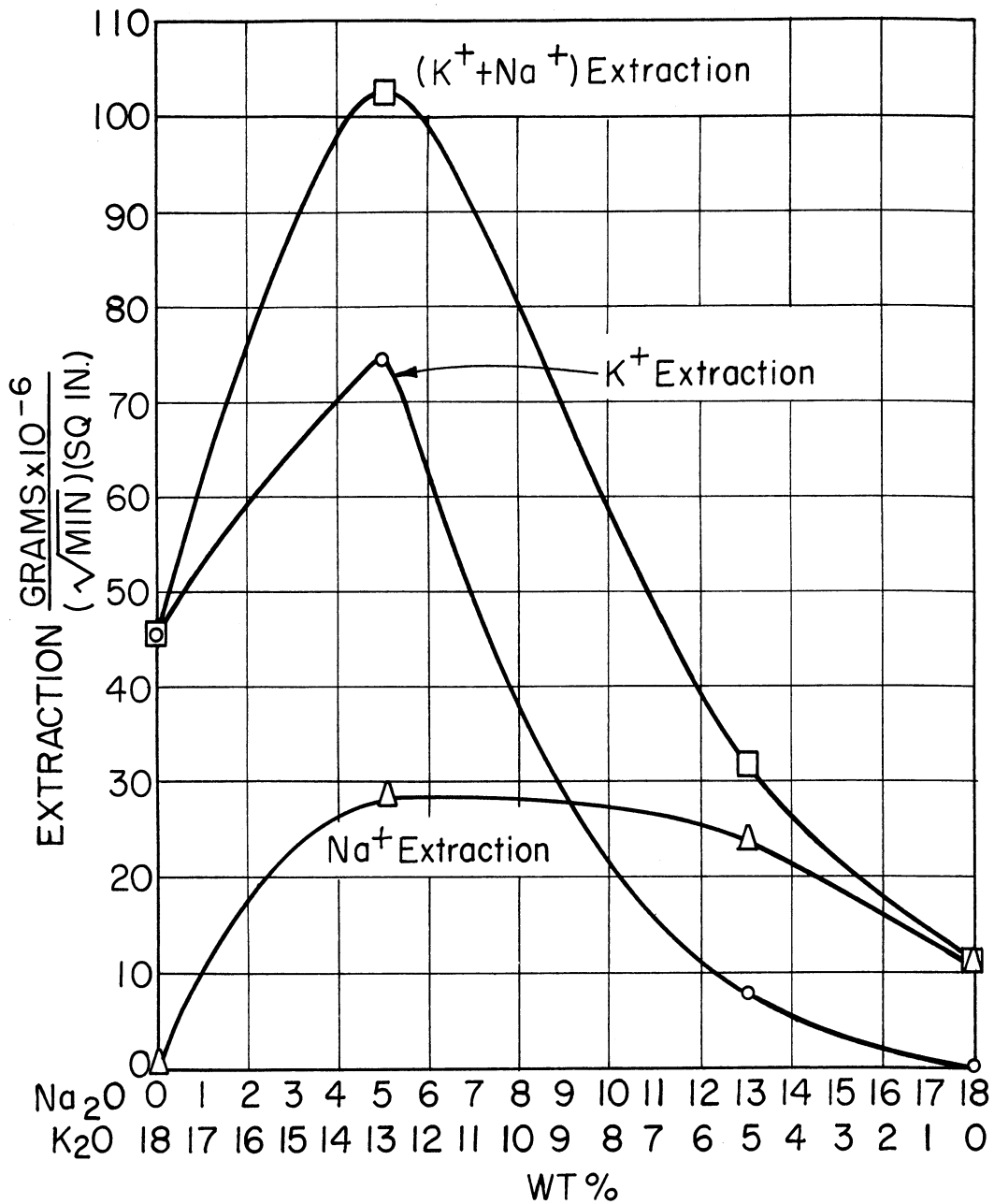


Fig. 2 Alkali extraction rates at 50°C for the series 18% ($\text{K}_2\text{O} + \text{Na}_2\text{O}$), 82% SiO_2 by weight.

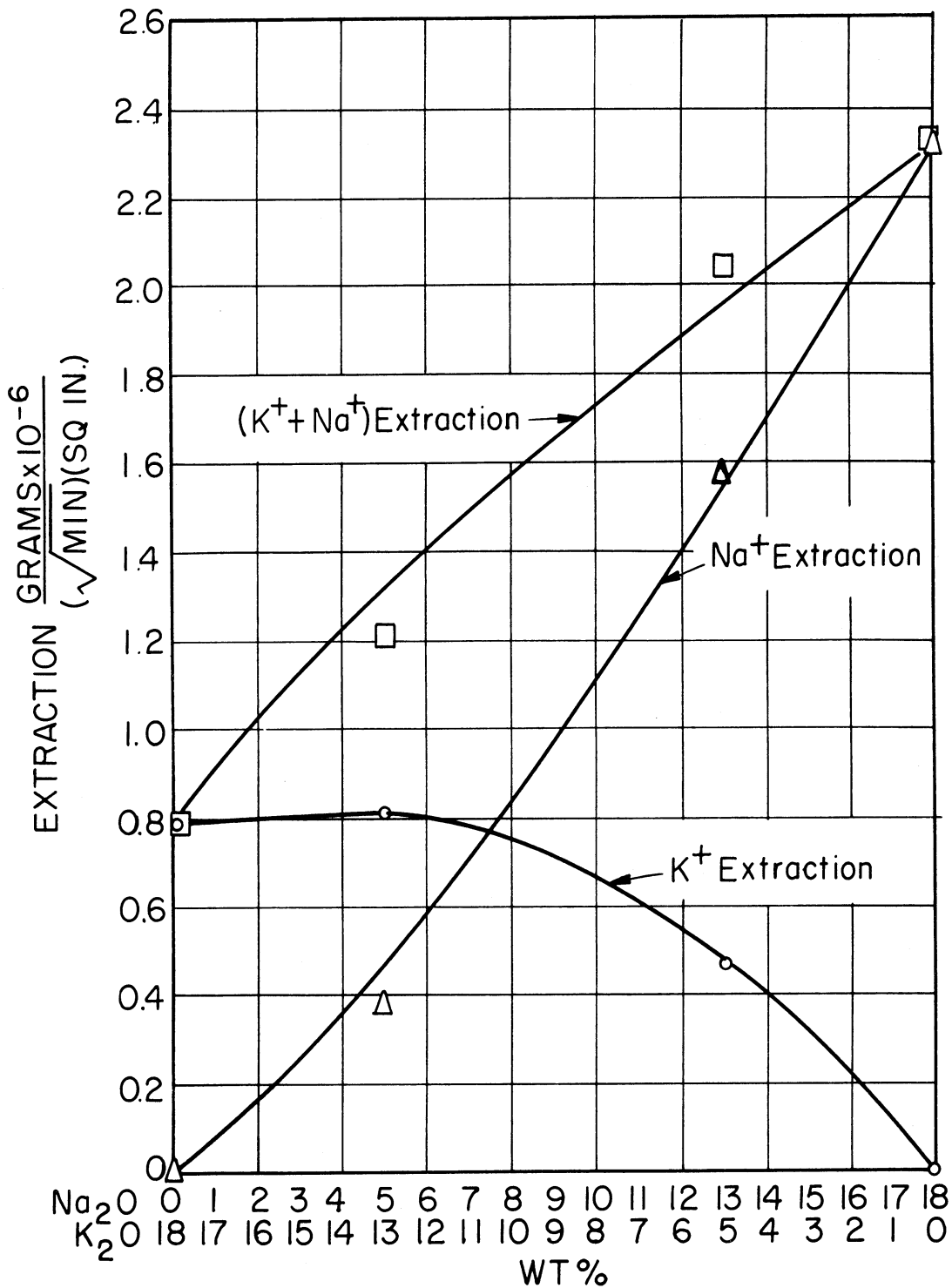


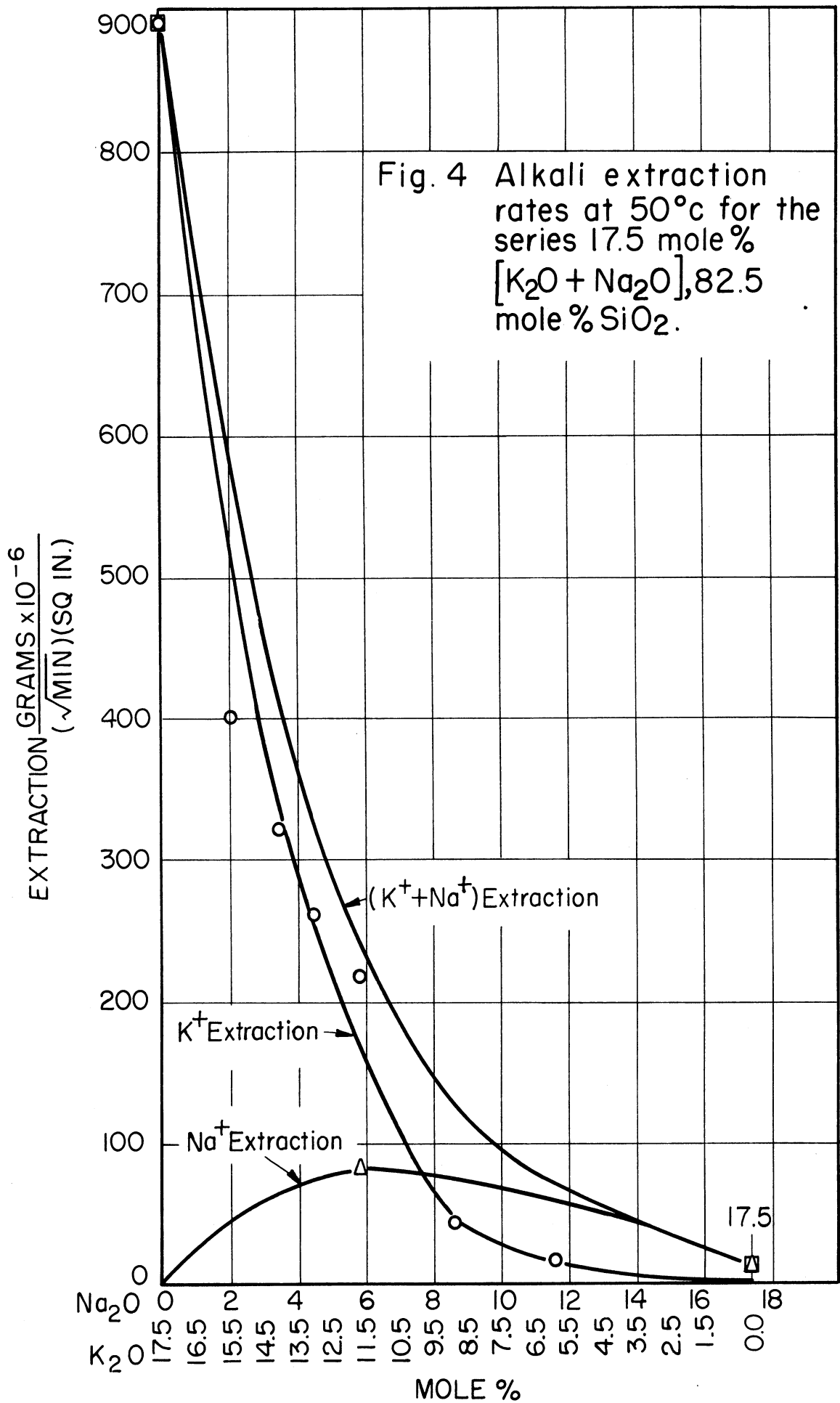
Fig. 3 Alkali extraction rates at 50°c for the series 18% (K₂O+Na₂O), 5% CaO, 77%SiO₂ by weight.

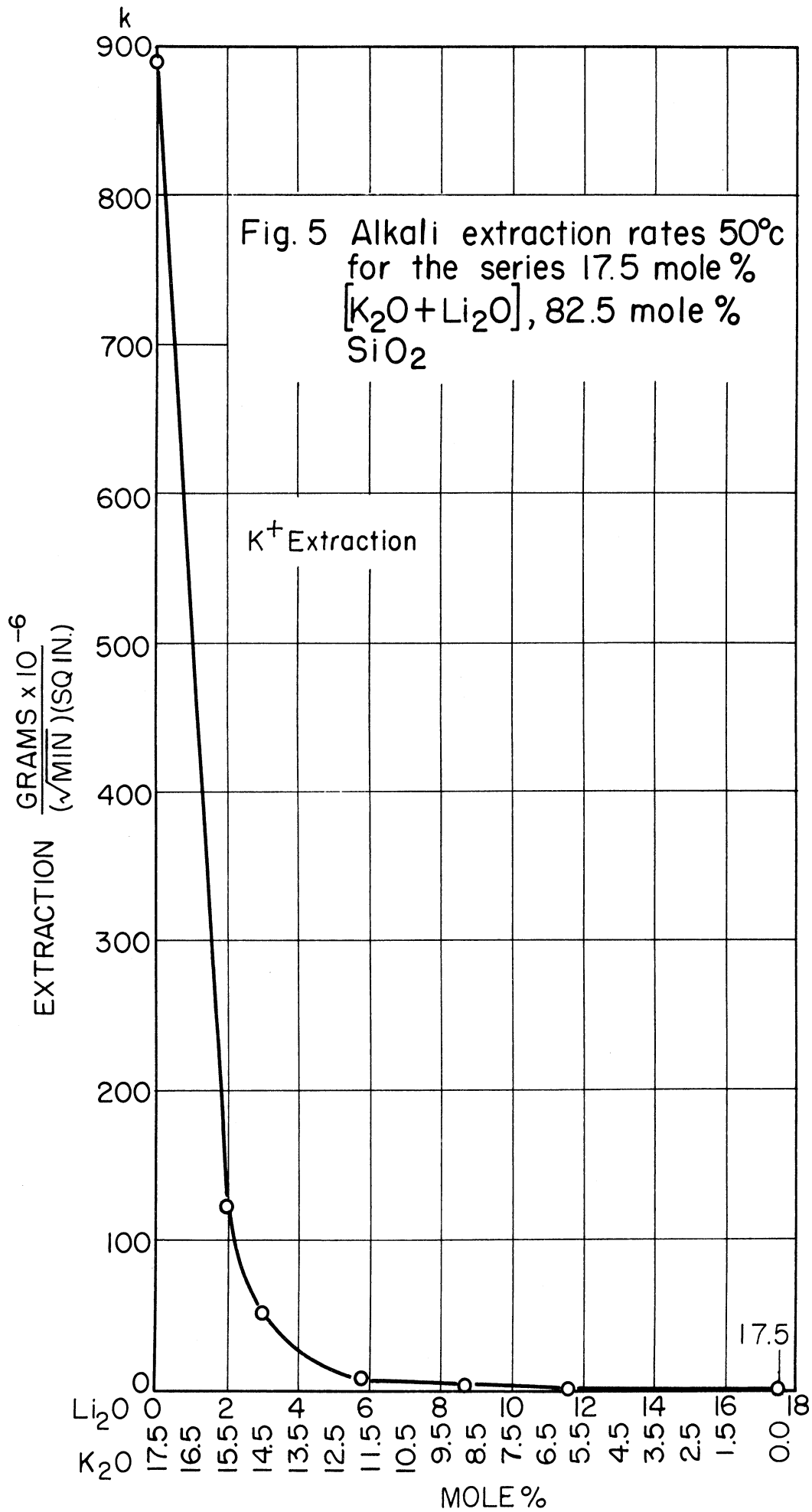
results be obtained on a series of constant-mole percent alkali-glasses. The experimental work on constant weight percent alkali glasses, represented by Figs. 2 and 3, was conducted by the authors to obtain results comparable with the ones reported in the literature. For structural interpretation of the alkali-extraction data, the authors carried out extraction tests on constant mole percent alkali-glasses. The nature of the curves so obtained is substantially different from the curves in Fig. 2 and 3 obtained with the constant-weight-percent alkali-glasses.

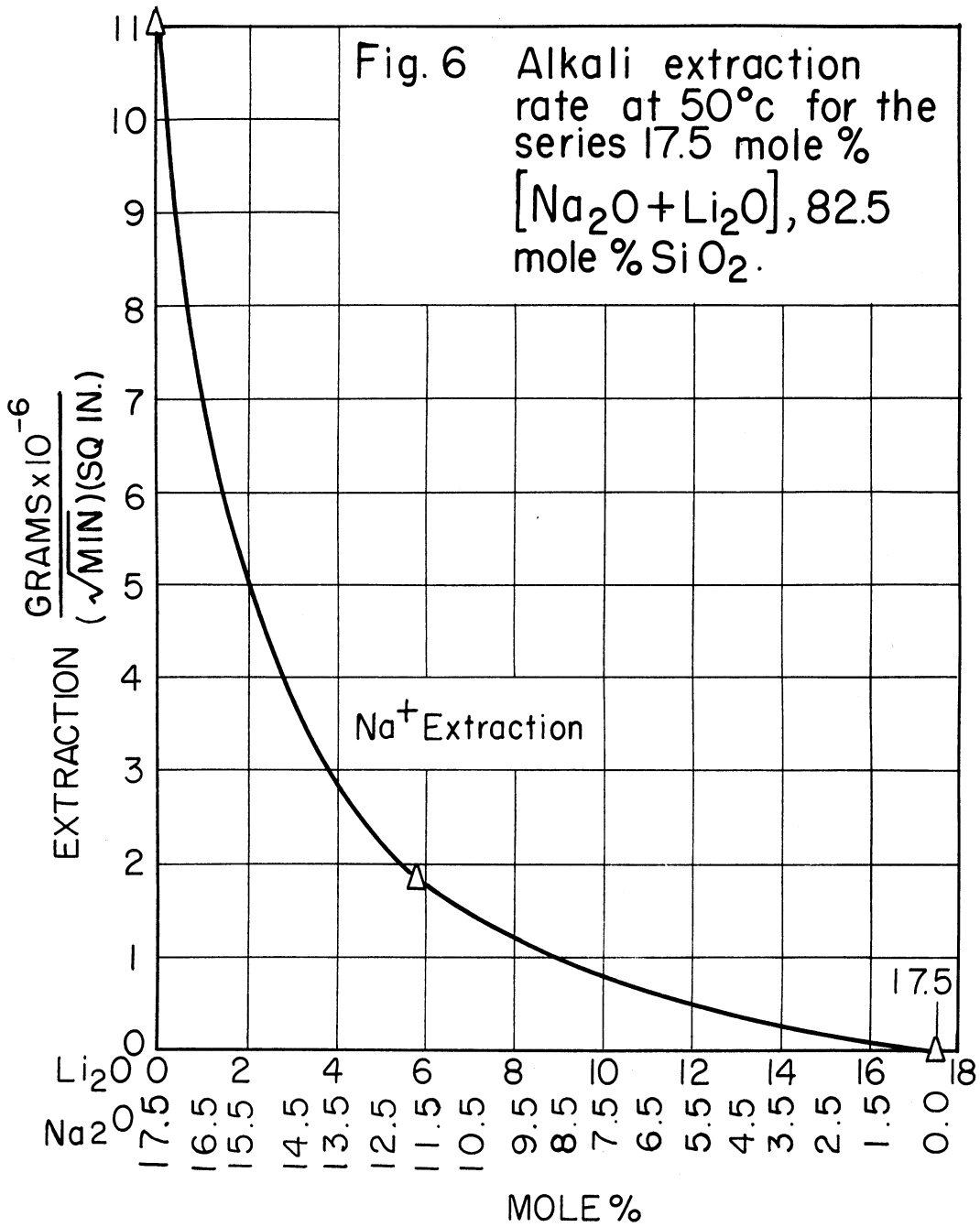
Figure 4 gives a plot of the authors' experimental values for K^+ , Na^+ , and total alkali ($K^+ + Na^+$) extraction rates at $50^\circ C$ for the series of glasses of the composition 17.5 mole % ($K_2O + Na_2O$), 82.5 mole % SiO_2 plotted against the mole percent of Na_2O and K_2O in the glasses. The figure 17.5% was chosen because 17.5 mole percent of Na_2O is equivalent to 18 wt percent (the value in the constant weight percent alkali series).

A comparison of Figs. 2 and 4 shows a striking difference. The K^+ extraction curve in Fig. 4 does not show a maximum as it does in Fig. 2. It is a smooth curve of roughly a hyperbolic nature. The Na^+ extraction curve does show a maximum, however. The total ($K^+ + Na^+$) extraction curve in Fig. 4 also does not show a maximum and in this respect is in direct contrast with the corresponding curve in Fig. 2.

Figure 5 shows the K^+ ion extraction results for a series of 17.5% ($K_2O + Li_2O$), 82.5% SiO_2 (by mole percent) glasses, and Fig. 6, the Na^+ ion extraction for a series of 17.5% ($Na_2O + Li_2O$), 82.5% SiO_2 (by mole percent) glass. Both these curves are similar in nature to the K^+ ion and the total-alkali-extraction curves in Fig. 4. In the case of the Li_2O -containing glasses, the Li^+ ion extraction was not measured because the values were very low and reliable results could not be obtained with the flame spectrophotometer. However, the nature of the Li^+ ion extraction curve should logically be similar to the Na^+ ion extraction curve in Fig. 4 for the K_2O - Na_2O - SiO_2 glasses.







Since the lithium extractions are relatively low, the K^+ ion and the Na^+ ion extraction curves in Figs. 5 and 6 respectively can be treated as the total alkali-extraction curves for purposes of comparison.

It is interesting to note that the general shape of the alkali extraction curves reported in Figs. 4, 5, and 6 is similar to that of the alkali extraction curves for glasses containing the divalent oxides (with the alkali extraction plotted against more % of the divalent oxide in the latter case). A comparison of Fig. 7, showing the chemical durabilities, expressed as total weights in milligrams of dissolved material, reported by Enss (Ref. 1) for a series of glasses obtained from a parent glass having the percentage composition by weight: SiO_2 , 82%, Na_2O , 18% (on a molar basis this comes to SiO_2 82.5%, Na_2O 17.5%-- the parent glass used in the author's studies) by stepwise replacement of SiO_2 by CaO , with Figs. 4, 5, and 6 illustrates this similarity.

In their earlier work (Ref. 2) the authors have postulated and substantiated that the stable residence for a divalent (Y-type) ion is a type "C" hole. In the presence of Y-type ions the alkali ions would occupy the "B" type holes in preference to the "A" type holes. Thus, on the addition of Y-type ions to an X_2O-SiO_2 glass, the alkali extraction decreases rapidly until an X:Y ratio of 2:1 has been reached (the "B" type holes in a glass being twice as numerous as the "C" type holes if the triplets are the largest groupings in the structure). Any further addition of the Y-type ions should have little effect on the alkali extraction. If triplets (X:Y:X) were the only type of combinations in an $X_2O-YO-SiO_2$ glass, there should be a sharp break in the alkali-extraction curve at an X:Y ratio of 2:1. The sudden change in slope of the curve in Fig. 7 indicates that triplets are the major type of combinations present.

The similarity of the alkali-extraction curves in Figs. 4, 5, and 6 with the chemical-durability curve in Fig. 7, indicates that some of the X-type

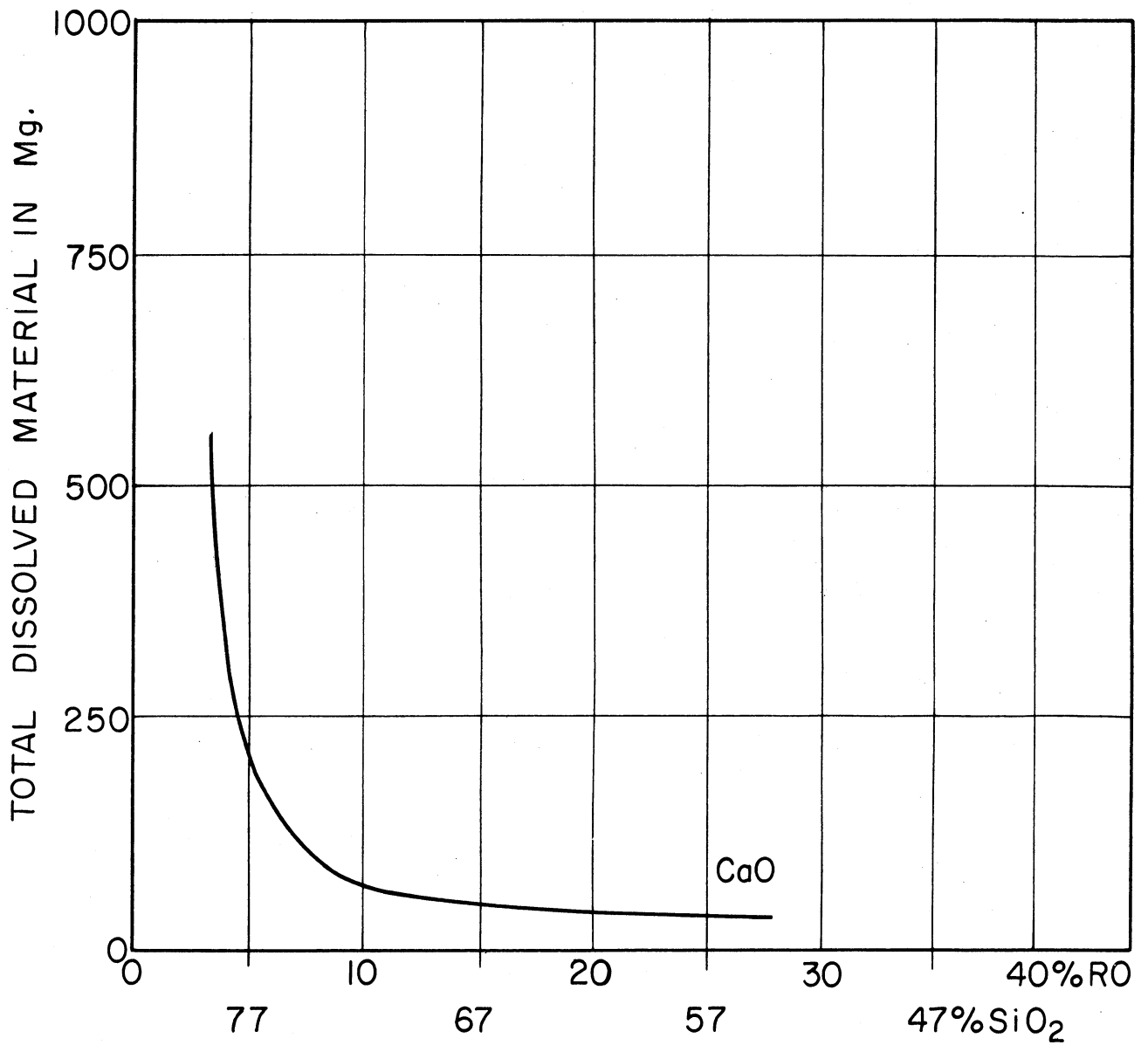


Fig. 7 Chemical durability of glasses of the formula, in percentage by weight, $18\text{Na}_2\text{O} + 82(\text{SiO}_2 + \text{CaO})$ -after Enss.

(monovalent) ions can play the same role with respect to the other X-type ions as do the Y-type ions with respect to the X-type ions. In other words, triplets of the type $X_1:X_2:X_1$ are probable. In a glass containing two (X_1 and X_2) of the X-type ions the ion which is closer, in its characteristics, to the Y-type ions would have a greater probability of existing in the "C" type rather than the "B" type position in a triplet. A look at the periodic table of elements and reference to data on ionic radii and electronegativities shows that the order of the alkali ions in their closeness in characteristics to the Y-type ions is: Li, Na, K, Rb, and Cs. It must be pointed out that the effect, in reducing the alkali extraction of glass, of an alkali ion on another alkali ion would be less than that of the Y-type ions. The degree of this effect should naturally depend on the difference in characteristics of the two types of alkali ions in the glass; the effect being more pronounced with the two ions being farther in their characteristics. Thus, replacement with Li_2O of K_2O in a $\text{K}_2\text{O}-\text{SiO}_2$ glass would reduce the alkali extraction considerably more than its replacement with Na_2O . This is substantiated by comparing Fig. 4 with Fig. 5 which are for $\text{K}_2\text{O}-\text{Na}_2\text{O}$ and $\text{K}_2\text{O}-\text{Li}_2\text{O}$ combinations respectively. Similarly, replacement with Li_2O of $\text{K}_2\text{O}-\text{SiO}_2$ glass would reduce the alkali extraction much more than the replacement of Na_2O in an $\text{Na}_2\text{O}-\text{SiO}_2$ glass. A comparison of Fig. 5 with Fig. 6 substantiates this conclusion.

The tremendously low alkali extraction of $\text{Na}_2\text{O}-\text{SiO}_2$ glass as compared with the corresponding $\text{K}_2\text{O}-\text{SiO}_2$ glass, and that of $\text{Li}_2\text{O}-\text{SiO}_2$ glass with respect to the corresponding $\text{K}_2\text{O}-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{SiO}_2$ glasses can be explained by an extension of the above theory. It has already been proved that the probability of an X-type ion existing in the "C" type positions decreases from Li to Na to K. It appears that these ions, to a lesser or greater degree, can form pure or self triplets (i.e., of the type $\text{Li}:\text{Li}:\text{Li}$). It would be reasonable to postulate that the ability to form these pure or self triplets would also decrease from Li to Na to K. Now, knowing that it is much harder to

extract the alkali ions in a triplet than those occupying the "A" type positions, the tremendous differences in the alkali extraction from K_2O-SiO_2 , Na_2O-SiO_2 , and Li_2O-SiO_2 glasses become obvious.

IV. CONCLUSIONS

The effect of the presence of additional alkali and alkaline-earth ions in a glass on the extraction rate of an alkaline ion from it is discussed. The theoretical explanation for this effect and its importance in determining the atomic structure of a glass is considered. It is pointed out that it is inherently wrong to use constant weight percent alkali glass alkali-extraction curves to explain the ionic structure of a glass, and that it is necessary to obtain the alkali-extraction results on a series of constant mole percent alkali glasses in order to be able to use the alkali-extraction results to predict the tenaciousness with which a particular type of ions are held in the glass structure. Experimental data on alkali-extraction for 17.5 mole % alkali, 82.5 mole % SiO_2 glasses containing combinations of K_2O-Na_2O , K_2O-Li_2O , and Na_2O-Li_2O are reported. It is shown that these alkali extraction results can be explained by the theory for the structure of glass presented by the authors in some of their earlier work. This affords a further substantiation of the concept of a preferential, rather than a random, arrangement of the positive ions of the so-called non-glass forming oxides.

V. REFERENCES

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AN ACCURATE METHOD FOR THE STUDY OF IONIC DIFFUSION IN GLASS¹

(Presented in the Glass Division at the 58th Annual Meeting (1956) of the American Ceramic Society - Paper No. 8)

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April, 1956

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ABSTRACT

The need for an accurate method to study the rates of diffusion of the alkali ions from an alkali-containing glass to a leaching solution is brought out, and a method for this purpose is proposed. It is pointed out that the existing methods for measuring chemical durability of glass which use a powder sample and give a value for total alkali extraction are not suitable for the purpose of studying individual ion diffusion rates. An accurate study of individual ion diffusion rates is extremely useful in the study of structure of glass. At the same time these diffusion rates can be used as a measure of the chemical durability of a glass.

The proposed method uses freshly-drawn cane of glass as the sample, a dilute solution of hydrochloric acid in double-distilled water as the leaching reagent, and a Beckman Model-B (Model DU can also be used) Flame Spectrophotometer for measuring the alkali concentrations in the leach solutions. With moderate care duplicable results can be obtained for glasses with a fairly wide range of chemical durabilities. The results are obtained as the extraction or diffusion rate of each ion separately in well-defined units [gms of ion/ $\sqrt{\text{min}}$ (sq. in. area)]. The uncertainty in determining the surface area of the reacting sample--a feature of most of the conventional chemical durability methods--is eliminated. Thus, it is possible to use the results for activation energy calculations.

Diffusion rate results for several glasses, obtained by this method, are reported.

AN ACCURATE METHOD FOR THE STUDY OF IONIC DIFFUSION IN GLASS

I. INTRODUCTION

The structure of glass has long been a subject of controversy. Though the Zachariassen-Warren "Random Network Theory" is now widely accepted, there are still doubts about the location of the positive ions of the so-called non-glass-forming oxides in the glass structure. Several workers (Gupta and Hess, Harleif, Lukesh) have indicated that the alkali-ions in glass are more apt to be preferentially located, rather than being completely randomly distributed as postulated by the Random Network Theory.

The authors undertook a study of this problem. It was felt that the best way of studying the location of the alkali ions in the structure would be to study a property of the glass affected mainly by the alkali ions. If it were possible to study the diffusion rates of individual ions in a glass, the results, it was felt, would be very useful in indicating the inter-relationship of these ions in the glass structure. A thorough survey of the literature was made to find the best way of studying the ionic diffusion rates. In alkali glasses, the electrical conductivity is essentially ionic, and could afford a measure of the diffusion rate. However, it would be useful only for overall diffusion rates and it would not be possible to get an idea of the diffusion rates of the individual ions from the conductivity measurements. The conventional methods of measuring chemical durability by alkali-extraction, though subject to the same limitations, if used as such, can, if properly modified, afford the

basis for a successful method to study these diffusion rates. The method proposed by the authors in this paper, and used by them in a series of diffusion rate studies on glass, is essentially a modified alkali-extraction test.

II. CRITERIA FOR A SUCCESSFUL METHOD

- A) The test should be fairly simple so that it can be duplicated easily.
- B) There should be a minimum of handling and treatment between the procurement of the glass sample and the actual diffusion test.
- C) The test should give accurate and duplicable results.
- D) The results from the test should be capable of being reported in well-defined physical units rather than on an arbitrary basis.
- E) The test results should approach true diffusion values as far as possible and it should be made sure that the factors altering the true diffusion rates are eliminated in the test.

III. THE PROPOSED METHOD

For convenience of discussion the proposed method can be divided into three parts or stages, namely:

- A) Sample preparation.
- B) Leaching test.
- C) Measurements and calculations.

A. Sample Preparation

In the author's studies it was contemplated to study the variation of ion-diffusion rates with variation in composition. Therefore, it was necessary to use glasses of widely varying compositions. Due to this reason it was decided to make the glasses as experimental melts from batches prepared from e.p. grade chemicals. However, if it is desired to measure the diffusion rates in an already prepared glass, a sample of the glass can be melted in place of the raw batch, the rest of the procedure remaining the same.

The various constituents of a glass batch, after being dried, were weighted in a laboratory balance and transferred to a porcelain tumbling jar. The jar was tumbled on rollers overnight for a thorough mixing. A portion of the mixed batch was taken in a platinum crucible and melted in a Sentry globar furnace located vertically. The crucible was supported on the end of a Silliminite (Mullite) refractory tube for ease in handling. The furnace was maintained at a temperature of 200-300°C greater than the liquidus point of the glass being melted. For the 18 wt % alkali-series of glasses, the melting temperature was around 1300°C. About 3-5 hours were found to be sufficient for melting and fining of the glasses. About the end of the fining period, the crucible was taken out of the furnace and checked for the completeness of firing. When the melt was sufficiently free of the bubbles, the crucible was taken out and a cane (thick fibre - of the order of 0.01 inches diameter) of glass was drawn by reaching in with a pyrex glass rod. An end piece of this cane was cut off and checked on a microscope with a magnification of 100 for any surface defects. If the glass had been fined to a fair degree, no surface defects were observed. If any surface defects were observed on a sample of the cane, the whole draw was discarded, the glass heated for some more time, and a new cane drawn and rechecked with the microscope. When a sample of the cane appeared

satisfactory on the microscope, the rest of the cane was used for the diffusion studies without any further treatment or handling. At no stages in the sample preparation was the cane to be used for the diffusion studies touched with the hands or brought in contact with any other contaminant. The total time elapsed between the drawing of the glass sample and the starting of the leaching test was of the order of 3-5 minutes.

B. Leaching Test

The leaching was carried out in a dilute solution of c.p. grade hydrochloric acid in distilled water passed through a "Deeminac" demineralizer (hereafter referred to as double distilled water--practically free of Na^+ K^+ ion contamination as indicated by a zero reading on a Beckman Model-B Flame Spectrophotometer set for maximum sensitivity). Thirty milliliters of a 0.02 normal solution of c.p. grade concentrated hydrochloric acid in double-distilled water were measured into a one-oz. polyethylene bottle provided with a polyethylene screw cap. After filling the bottle, the cap was put on and the bottle, with the liquid, brought to the operating temperature of 50°C by hanging in a constant temperature water bath. Then the cane of glass, already drawn, was cut up in small lengths into the acid solution in the bottles. The bottles, with the caps on, were put back into the constant temperature bath and 1 or 1.5 ml samples of the leach solution measured out of the bottles with a pipette at known intervals of time after the start of leaching. Before withdrawing the sample the tightly closed bottle was well shaken to assure a completely uniform solution. The samples were directly put into 5-ml Beckman sample beakers which are used for containing the samples while measuring the concentrations on a Beckman Model-B Flame Spectrophotometer.

In case the leaching temperature is to be higher than 70°C, it is recommended that a liquid with a higher boiling point than water (a glycol or

an oil) be used in the water bath. At these temperatures polyethylene containers should be replaced by vycor glass containers. A tight cover for the container is essential to eliminate evaporation during the leaching process.

The amount of the glass sample used and the total duration of the test would naturally depend on the durability of the glass. If high rates of extraction are expected a few short lengths cut from the glass cane should be sufficient to give appreciable readings on the spectrophotometer. However, for relatively durable glasses it might be necessary to use about 20-25 (or even a larger number) lengths to get measurable results on the Spectrophotometer. A total of about three hours of leaching time was found sufficient for all glasses studied to give sufficiently reliable results.

C. Measurements and Calculations

The Na^+ and K^+ ion concentrations in the leach solution samples were measured with a Beckman Model-B Flame Spectrophotometer using an oxy-hydrogen flame and standardized with standard NaCl and KCl solutions. The light intensity readings obtained from the spectrophotometer can easily be converted to parts per million (p.p.m.) of the respective ions by reading from calibration charts prepared for the instrument by using standard solutions. Due to the accurate nature of the work, the calibrations were checked everytime the instrument was used. The p.p.m. readings thus obtained were converted to $\text{gms} \times 10^{-6}$ of the ion extracted, knowing the amount of solution remaining when a particular sample was taken out and the amount of the ion in the preceding samples from the same bottle.

The quantity ($\text{gms} \times 10^{-6}$) of the ion extracted was then plotted against the square root of time. Such plots were made for both Na^+ and K^+ ions separately for each test. Three or four tests were carried out simultaneously for each glass. The plot of the $\text{gms} \times 10^{-6}$ vs. \sqrt{t} min was invariably a straight line confirming that the rates being measured were in

fact rates of diffusion. Fig. 1 shows a sample plot representing the data for one of the runs on 18 wt % ko, 82 wt %, SiO₂ glass. The slopes of these lines were measured and gave the gms x 10⁻⁶/√min extracted for each test. The intercepts of the lines, representing the amount of extraction at zero time were slightly inconsistent, but that should not affect the diffusion rate results much.

The glass cane samples from each test bottle were taken out and their lengths and mean diameters measured. The surface area of the sample was then calculated considering them to be elliptic cylinders. The reproducibility of the overall results shows that this assumption was not too bad.

Knowing the rate of extraction of an ion and the surface area of the sample for a particular test the rates of diffusion of the ions can be expressed as gms x 10⁻⁶ of the ion/(√min)(square inch area). A summation of the rates of diffusion of all the alkali ions in a glass gives the total alkali extraction which is a good measure of the chemical durability of the glass.

IV. RESULTS

Table I shows the extraction rate results at 50°C obtained for some of the glasses studied by the authors. In addition to the experimental glasses, the table also shows results for the Na⁺ ion extraction rate for a Corning 0080 glass. Two values are reported for this glass. In one set of tests the commercial glass tubing was powdered and melted and the test performed in the normal way. For comparison, one set of tests was carried out on the commercial tubing. For this test the tubing was cut into two small lengths (to fit into the polyethylene bottles), washed with double

distilled water and acetone (c.p. grade), and used directly for the leaching test. The lower value for this set of tests, as compared to the set in which a fresh cane of the glass was used, is quite reasonable because the old surface would naturally be somewhat depleted in the diffusible ion. However, the fact that the value for the tests on the fresh cane is only slightly higher than that for the old surface (and was not multi-fold) shows that there were no great surface imperfections in the freshly drawn glass, thus, confirming the result of the microscopic examination.

V. DISCUSSION

As was mentioned earlier the method proposed in this paper is essentially a modification and refinement of the conventional chemical durability tests. In most chemical durability tests the leaching solution used is water. Water serves the purpose as long as it is aimed only to make an empirical study of the alkali-extraction. It is well established that when water is used as a leaching agent, the alkali extracted in the initial stages of the leaching process starts attacking the silica structure of the glass. This attack of the silica structure alters the rate of extraction of the residual alkali. Thus, in this case, the rates of extraction of the alkali-ions would not be a true measure of their rates of diffusion in the parent glass. This is demonstrated by the fact that the quantity extracted vs. square root of time plots are not straight lines. The best course, it appeared to the authors was to remove (by neutralization) the alkali ions as soon as they extracted. This can be achieved by using a small amount of an acid in the leaching solution, provided the potential rate of neutralization of the alkali by the acid used is faster than or equal to the rate of diffusion of the alkali ions. If this rate is less than the rate of ion-diffusion, it would control the rate of extraction of the ions measured in the test, and thus the measured rate values

will not be the true diffusion rates. It is known from previous experience that the rate of neutralization of NaOH and KOH with HCl is very fast and is in all probability much faster than the rate of diffusion of the ions in the glass. Thus, the use of HCl in the leaching solution helps the measurement of the true diffusion rates of the ions. The amount of the HCl is not very critical as long as sufficient HCl is present in the solution to neutralize all the alkali extracted during the test. However, the leaching solution should not be so concentrated a hydrochloric acid as to cause a direct chemical attack on the structure. The non-criticality of the HCl concentration was tested by using a 0.01 and a 0.05 normal solution for some extraction tests. The difference in the results of these tests with varying concentrations of HCl was quite insignificant and could not be attributed to the HCl concentration variation.

In most of the well-established chemical durability tests a powder sample of the glass is used. One of the main reasons for using a powder sample is to get a large surface area so as to give appreciable readings in the analysis of the leach solutions. This requirement, however, holds good only for the conventional gravimetric or volumetric analysis. Since, with a flame spectrophotometer, it is possible to measure concentrations down to small fractions of a part per million, a very large surface area is no longer necessary. Considering the uncertainty about the surface area of the sample and the pains to be taken in duplicating the powdering technique, it would be apparent that using a solid sample, wherever possible, would be much more desirable than the use of a powder sample.

The flame spectrophotometer used is claimed to have a sensitivity of 0.02 ppm for sodium (at a wavelength of 589 m μ) and that of 0.05 for potassium (at a wavelength of 768 m μ). The use of a photomultiplier tube in place of the regular tube in the instrument is claimed to increase the

sensitivity by a factor of about ten. Unfortunately, however, the photomultiplier tube is not useful at the most sensitive wavelength (768 m μ) for potassium ions. If it is desired to use the proposed method for glasses considerably more chemically durable than it is possible to study with this method, it would be wise to investigate the possibilities of improvement in the sensitivity of the concentration measuring device and to increase the quantity of the cane sample rather than to revert to a powder sample.

VI. CONCLUSIONS

The authors have proposed a method for the study of ionic diffusion in glass which is, in essence, a refinement of the conventional chemical durability methods. The proposed method uses freshly-drawn cane of glass as the sample, a dilute solution of hydrochloric acid in double-distilled water as the leaching reagent, and a Beckman Model-B (Model DU can also be used) Flame Spectrophotometer for measuring the alkali-ion concentrations in the leach solutions. With moderate care duplicable results can be obtained for glasses with a fairly wide range of chemical durabilities. The results are obtained as the extraction or diffusion rate of each ion separately in well defined physical units [gms x 10⁻⁶ of ion/($\sqrt{\text{min}}$)](sq in. area). The uncertainty in determining the surface area of the reacting sample--a feature of most of the conventional chemical durability methods--is eliminated. Since the results are in well defined physical units, a study of the diffusion rates at different temperatures can yield results useful for activation energy calculations.

In the present study the diffusion rates of K⁺ and Na⁺ ions only are studied. These are the two ions, that have appreciable diffusion rates, which are most commonly encountered in glasses. Other alkali-ions could also be studied, though the sensitivity of the flame spectrophotometer is not as

good for other ions as it is for K^+ and Na^+ ions. The study of the diffusion rates of divalent ions in glass is not practicable by the proposed method due to two reasons. First, because the diffusion rates for these ions are very small and second, because the sensitivity of the flame spectrophotometer for these ions is not sufficiently high. However, since the amounts of the divalent ions extracted from a glass are so small, one is rarely faced with the study of their diffusion rates.

The authors, in the present study, have not taken into consideration the interference of one ion on another during the flame-spectrophotometric analysis. For very accurate results corrections must be made in the results for this interference.

The importance of ion diffusion studies in determining the structure of glasses is brought out.

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Table I
Experimental extraction rate results

Glass	Rate of Extraction Grams x 10 ⁶ / ($\sqrt{\text{min}}$)(in. ²)	
	K ⁺ Extraction	Na ⁺ Extraction
18wt. % K ₂ O-82wt% SiO ₂ —Experimental	45.40	—
18wt. % Na ₂ O-82wt% SiO ₂ —Experimental	—	11.00
13wt% K ₂ O-5wt%Na ₂ O- 82 wt%SiO ₂ —Experimental	74.30	28.49
18wt% K ₂ O-5wt%CaO-77wt%SiO ₂ —Experimental	0.787	—
18wt% Na ₂ O-5wt%CaO-77wt%SiO ₂ —Experimental	—	2.3 18
Corning 008 glass - commercial tubing	n.m.	0.237
Corning 008 glass -remelted cane	n.m.	0.392

n.m.—Not measured

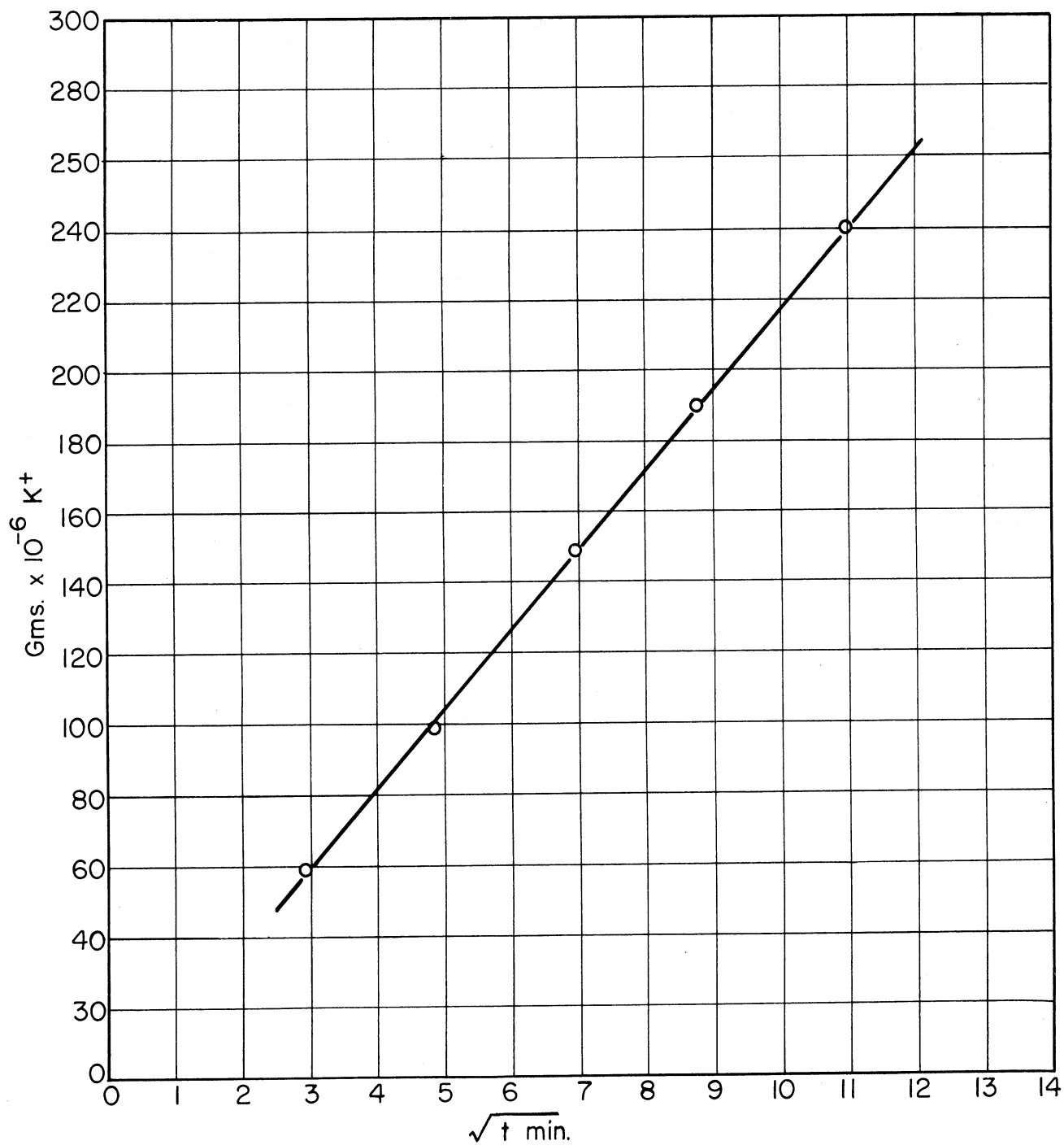


Fig. 1 Alkali extraction from 18wt% K_2O -82wt% SiO_2 glass.

CHEMICAL DURABILITY OF GLASS - A STUDY OF THE EXTERNAL FACTORS¹

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ABSTRACT

A mechanism for chemical attack on alkali-alkaline earth-silica type of glasses by reagents which do not affect the silica structure directly is presented. The proposed mechanism would apply to all cases of chemical attack on glass where the attack progresses essentially by diffusion of ions. The role of various factors, external to the glass, on the chemical attack is considered, and their importance brought out.

The proposed mechanism recognizes four essential external factors which control chemical attack. These are: 1) The existence of a Primary Water Layer on the glass surface, 2) The availability of positive ions (usually H-ions) to this primary water layer to replace those diffusing into the glass during counterdiffusion of X- (alkali) and H-ions, 3) The availability of either a diffusional or chemical means of removing X-ions from the primary water layer, and 4) The temperature as it affects the thermal energies of the ions involved and its effect on the other factors. The importance of some of these factors is experimentally demonstrated.

The structural role of the H-ions diffusing into the glass during counterdiffusion is given some thought. Various possibilities are discussed. However, the present knowledge on this subject allows one only to speculate regarding this structural role played by an incoming H-ion in a glass.

CHEMICAL DURABILITY OF GLASS - A STUDY OF THE EXTERNAL FACTORS

I. INTRODUCTION

To the layman, glass is one of the most inert materials. The housewife turns to her glass utensils when she wants to make sure that the food will not spoil. In the chemical and food industries, a recourse to glass is often had to avoid any serious corrosion or contamination. In spite of this good reputation enjoyed by glass for its chemical durability, glass technologists know well that this wonder material is attacked by water and by many other substances, both liquid and gaseous, although the rate of attack is rather slow except with hydrofluoric acid and with strong alkalies (in which case the basic silica structure is supposed to be dissolved by the reagent). A considerable amount of work has been done on this subject, and the literature (Ref. 6) is full of data obtained from chemical durability tests. However, most of the work reported consists of empirical determinations of the chemical durability of particular glasses with a view to pre-determine the corrosion resistance of the material. The subject of chemical durability of glass is important not only from the point of view of predetermining the corrosion-resistance of the material but also because the mechanism of the attack gives a good insight into the structure of glass and helps in explaining many of its characteristic properties. In spite of the large amount of work done on the chemical durability of glass, much attention has not been paid to gain structural information from the durability data and to a complete study of the numerous factors affecting chemical durability. Only recently has attention been directed to the mechanism of this phenomenon.

It is now well established that chemical attack on the more customary compositions of glass takes place, except in a very few cases, by means

of diffusion of ions. In the case of attack on ordinary glasses with hydrofluoric acid or with strong alkalies, the basic silica structure is supposed to be dissolved by the reagent. Similarly, in the case of attack on very high alkali glasses with water or with acidic reagents, the alkali is dissolved by the reagent. These exceptions in which case the attack is by actual solution rather than by a diffusion mechanism are not considered in this paper. The authors have developed a mechanism for chemical attack on glass, taking into account the several factors, both internal and external, which affect this phenomenon. Under the internal factors, the composition and structure of the glass are the most important. Under the external factors, which have hardly been given any consideration in the literature, factors like the existence of a necessary primary water layer, availability of positive ions for counter-diffusion, the availability of a means of removing the diffused X-ions (alkali ions---Li, Na, K, Rb, Cs) from the primary layer, are considered and their importance in the mechanism of chemical attack brought out. Temperature of attack acts as an internal as well as an external factor inasmuch as its effect is mostly to increase the rate of attack by accelerating the various component rates. Too much attention is not given this factor because it has already been given due consideration in the literature.

II. EXTERNAL FACTORS AFFECTING CHEMICAL DURABILITY

In a paper on the structure of high silica glasses by the authors (Ref. 3), it was shown that a part of the X-ions exercise a gross motion within the glass, moving from one set of associations to another. The situation for such an X-ion is quite different at the surface of a glass from that within the volume, as far as the transfer movements are concerned. Because of the discontinuation of the glassy oxygen environment, an X-ion at the surface is incapable of leaving the surface unless it has an extremely

high kinetic energy as compared with the average kinetic energy of X-ions at the temperatures usually involved in durability studies. Thus, unless there is a forced drift in a specific direction, the movement of the X-ions will be random and no net transport will take place. Consequently, our attention is drawn to the factors, external to the glass, which may establish a drift of X-ions to and through the surface of the glass.

A. The Necessary Primary Water Layer on the Glass Surface

One possible means for the X-ions to leave the glass surface is by diffusion through a layer of a second medium, of a structure similar to that of glass, in intimate contact with the glass surface. This second medium must be capable of attaching itself to the glass surface in such a fashion as apparently to continue the glass structure, so that the X-ions would not experience a discontinuity of the oxygen network on coming to the glass surface, but would keep on diffusing through this primary layer. Once an X-ion has diffused out into this primary layer the problem, in order to continue the chemical attack, is to remove it from this layer as fast as it comes into it, thus avoiding a build-up of X-ion concentration in the primary layer. This problem is treated in a subsequent part of this paper.

The work reported by Manley (Ref. 5) on adsorption of gases and vapors on glass indicates that in addition to the skin removable by pumping (termed a "secondary" skin), the glass possesses a "primary" and far more permanent one. In Manley's words "a nude surface, when brought into contact with a gas, first acquires a true, permanent and primary skin which under all conditions is retained even in the presence of high vacua." A high voltage discharge was found successful for removing a part of the primary skin from the glass surface (also referred to as denuding the glass surface). According to him the completed primary skin adsorbs a quantity of its parent

gas in much the same way as solids in general do. The so-called secondary skin is not a true skin, but a certain mass of gas, which varies with temperature, pressure, etc., condensed upon and co-mingled with the molecular groups forming the true and primary skin. The primary skin proposed by Manley if composed of a suitable material (of a structure similar to that of glass) could serve the function of the primary layer mentioned by the authors.

The extensive work of Langmiur (Ref. 4) on the evolution of vapors and gases from glass indicated that water vapor was the preponderant component in the evolved vapors. In light of this it would not be unfair to assume that glass normally has a primary layer consisting mainly of water on it. Thus there is a fair amount of evidence that glass surface invariably has a primary layer of water as its immediate neighbor. The thickness of the primary water layer on a glass surface can vary from unimolecular to several molecules depending on the temperature and pressure of the atmosphere and on certain characteristics of the glass surface. It is well known that water does have a structure similar to that of glass (as is shown by a comparison of the X-ray diffraction data for the two substances - Ref. 7). The constituent ions have only a general (or short range) order and constantly change their associations just as some of the constituent ions of glass do so we can be sure that water is an ideal material for this purpose.

Until now the authors have given the concept of the primary water layer only as a postulate and have shown that such a primary water layer does exist on a glass surface during normal conditions of chemical attack. The proof of the pudding, however, lies in experimentally proving the necessity of such a primary layer and to study some of its important characteristics as they affect the chemical attack on glass. The necessity of the primary water layer for chemical attack can best be shown by comparing

chemical attack on a glass with the primary layer on and on a corresponding denuded sample. A high voltage discharge (ionization)---using a Tesla coil---with the electrodes located inside or outside the reaction chamber to control the degree of ionization, can be used to help in the denuding of the glass sample.

Experiments were conducted in which soda-lime-silica glass tubing (Corning 0080 glass) samples, rinsed with hot triple distilled water and subsequently rinsed with acetone, were subjected to different pretreatments (for controlling the primary water layer) and then reacted with HCl gas under various reaction conditions. A schematic flow sheet of the experimental set-up used is illustrated in Figure 1. The reason for selecting HCl gas as the attacking reagent was to make sure that only the internal factors and the primary water film were the important factors affecting the chemical attack. Since the reaction between Na and HCl is quite fast and since the use of HCl insures a steady supply of H-ions, adequate means for removing the X-ions from the primary water layer are insured. Thus, the primary water layer is left as the only important external factor. Since all the samples used were from the same batch of glass, the internal factors were eliminated as a variable and thus it was possible to study the primary water layer alone as a variable.

The various tests, along with the results of the reaction in each case, are listed in Table I. The degree of the reaction could be judged qualitatively by a visual observation of the intensity of the NaCl (reaction product) deposit on the reacted sample surface. Measurements of Na-ion, in the NaCl produced, made by rinsing the sample in a known amount of triple distilled water and analyzing the resulting rinse by means of a Beckman model DU Quartz Spectrophotometer with a flame attachment showed a direct correspondence with the visual observations. When no reaction was observed

TABLE I. SUMMARY OF EXPERIMENTAL RESULTS

Test Series No.	Pretreatment for at least 1 hr.		Chemical Attack			Time of React. min.	Visual Obs. of	Beckman Reading	
	Temp. °C	Vac Hg Press. Microns	Ioniz. for Denud.	Reagent	Humidity				Temp. of React. °C
A 1	500	90 μ	good	HCl	dry ²	400	10 cm	no reaction	0
2	500	90 μ	no	HCl	dry	400	10 cm	considerable reaction	17 ppm
3	500	2 x 10 ⁴ μ	no	HCl	very wet ³	400	12 cm	same as in Run A2	17 ppm
4	500	90 μ	no	no reagent	dry	400	9 x 10 ⁻³ cm	no reaction	0
B 1	400	1 μ	poor	HCl	dry	400	15 cm	considerable reaction	
2	400	0.1 μ	poor	HCl	dry	400	15 cm	some reaction (much less than in Bl)	
3	500	0.06 μ	poor	HCl	dry	400	15 cm	no reaction	
4	500	0.06 μ	poor	HCl	wet ⁴	400	15 cm	no reaction	
5	400	10 μ	poor	HCl	wet	400	15 cm	considerable reaction	
6	400	7.6x10 ⁵ μ	no	HCl	wet	400	76 cm	considerable reaction	

¹ The sample was denuded by means of high voltage ionization. A good degree of ionization was obtained with the electrodes inside the reaction tube, whereas situating the electrodes on the outside of the tube, for the same voltage, gave a poor degree of ionization.

² The gas after generation was passed over concentrated sulfuric acid and then dried by passing through a dry ice-acetone trap, thus giving a fairly dry gas.

³ Bulk liquid water was present in the reaction tube in this case.

⁴ The gas after generation was passed through concentrated hydrochloric acid and no subsequent drying treatment was involved. The gas in this case would contain a fair amount of water vapor.

visually, it was confirmed by a zero reading on the Beckman measurement. In the test series A the Beckman readings are also reported in Table I as parts per million (ppm) of Na-ions in the rinse solution made with 10 cc of triple distilled water, dissolving only the deposit on the inside surface of the standard sample tubing. The standard length of the samples was four inches. The tubing used was about 0.40 inch I.D. and 0.46 inch O.D. The Beckman instrument gave accuracies of ± 0.5 ppm of Na-ion concentration in solution.

From the data reported in Table I, the following inferences can be made:

1. A comparison of Runs B3 and B1 and of Runs A1 and A2 shows, without any doubt, that the reaction of HCl on glass can be stopped by means of a pretreatment of the sample consisting of heating at a very high vacuum with a poor degree of ionization or at a moderate vacuum with a good degree of ionization. The good degree of ionization was obtained by locating the electrodes inside the reaction tube, whereas locating the electrodes outside the tube gave the poor degree of ionization (same voltage was used for both cases). Run A2 indicates that the adsorbed water layer, which it is necessary to remove in order to stop the reaction, is not removed by a pretreatment at 500°C and 90 μ of Hg pressure if no ionization is used. Thus, the water layer in question must be a tenacious layer and of a primary nature. The necessity of the primary layer for chemical attack to proceed is, of course, evident.

2. Runs A1 and B3 show that the primary water layer can be removed by suitable combinations of temperature, vacuum, and ionization. It is planned to carry out further work to determine quantitatively the critical values of these variables which can affect the removal of the primary layer and thus stop chemical attack on glass.

3. A comparison of Run B4 with B3 shows that the water vapor in the reacting gas cannot take the place of the primary layer at the temperature of the reaction studied once the primary layer had been removed. In this connection it is planned to carry out further work to determine the possibilities if any, of making the primary layer removal permanent, thus imparting superior chemical durability to a glass with a composition which would normally give a poor durability on the basis of the internal factors alone.

4. The equal magnitudes of the reaction in Runs A2 and A3 indicate that the water content of the reacting gas does not determine the rate of attack on the glass. This, of course, would not be true if the reacting gas were deficient in H-ions for counterdiffusion with X-ions, thus causing a depletion of the primary water layer. In case of reaction with HCl we do not face this problem.

5. Run B2 indicates that a partial removal of the primary layer giving a partial reaction is possible. This indicates that below a certain thickness of the primary layer, the thickness of the primary layer also affects the reaction rate; the rate coming to zero when all or a certain critical thickness of the primary water layer has been removed.

B. Supply of Positive Ions for Counterdiffusion

When there is a layer of water on the surface of a glass and the X-ions diffuse out of the glass, H-ions of the water counterdiffuse into the glass to maintain electrical neutrality of the glass. If a continuous supply of H-ions is not available from the bulk of the attacking reagent to replace the ions which diffuse into the glass, the primary water layer would become depleted after a very short period of reaction and consequently the reaction will come to a stop. No significant reaction would be seen in such a case. This fact is supported by the result of Run A4 of Table I which shows that

no measurable reaction takes place in the absence of HCl even though the pre-treatment conditions are favorable to the presence of a primary water layer on the surface of the sample. Thus, if sufficient H-ions cannot be supplied for counterdiffusion, the rate of diffusion of X-ions out of the glass will drop, so as to correspond to that of the diffusion of H-ions into the glass.

One question which may logically be asked is whether any other positive ion can play the role of the H-ion or not. The answer to this question is closely dependent on the structural role that the H-ion plays after it has diffused into a glass. Burt (Ref. 2) reports that whereas sodium can easily diffuse into a soda glass, an attempt to try the same experiment with potassium or lithium as the diffusing ions ruined the glass. The reason for the failure of the K-ion to diffuse into glass and of the Li-ion making the glass opaque and extremely brittle on diffusion is the difference in sizes of Na-, K-, or Li-ions. K-ions are larger than Na-ions, which in turn are larger than Li-ions. In the diffusion described by Burt, the incoming Na-, K-, or Li-ion tends to take the position left by the outgoing Na-ion. H-ion is much smaller in size than the Na-ion and yet it is an experimental fact that H-ions can counterdiffuse with the Na-ions in glass and that the glass is not ruined in the process as it is in the case of Li-ion (smaller than Na) diffusion. This seems to indicate that the incoming H-ions do not simply take the positions of the outgoing X-ions, but that some complex mechanism is involved. Since an H-ion is very small and does not have an electron field of its own, it is possible that the incoming H-ions take positions in some much smaller positions than those of type "A" (maybe in the vicinity of "B" or "C" type positions - refer to Ref. 3 for definition of these positions), or that they actually enter the electron field of an oxygen, creating a complex OH body. The present state of our knowledge allows only to speculate regarding this structural role played by an incoming

H-ion in a glass. It, however, seems that some other positive ion cannot play the role played by the H-ion in the process of counterdiffusion during chemical attack on glass.

The authors strongly believe that a glass containing considerable hydrogen, gained by counterdiffusion, would, on heating, allow part of the Si-ions to become more-than-four-coordinated with respect to the oxygens or the complex OH bodies. It is further believed that this more-than-four-coordinated silicon structure would be retained on subsequent cooling and thus give a more compact glass than the parent material. Such a compacting of the glass structure is indicated in the data of Douglas and Isard (Ref. 3) by a drop in the water leaching rate of samples which had been water leached and baked or simply reacted with $\text{SO}_2\text{-O}_2\text{-H}_2\text{O}$ vapor at elevated temperatures. The drops in reaction rates reported are much more than what would be expected due to a decrease of the X-ion content of the glass during the initial reaction. Douglas and Isard have explained this drop of reaction rate on the basis of a compacting caused by the reaction of the indiffusing H-ions with the oxygens of the glass and a subsequent phase separation. This concept was developed by these workers on the basis of variation of reaction rates obtained by them with varying H_2O -content in the reacting $\text{SO}_2\text{-O}_2$ mixtures. However, the authors are convinced that the variation of reaction rate with varying H_2O -content of the reacting gas reported by Douglas and Isard is not due to any compacting but simply because in their system the removal of Na-ions from the primary layer is a controlling rate factor. This is reasonable to believe since the reaction of SO_2 and O_2 to produce SO_3 is a slow reaction and is dependent on several factors. That compacting is not responsible for the variation in reaction rate with varying H_2O -content of the reacting gas is shown by the fact that in the case of attack on glass with HCl no such variation was found and the reaction rates for both dry and wet HCl gas were found

identical. The reason why Douglas and Isard did not get any reaction with dry $\text{SO}_2\text{-O}_2$ gas at moderate temperatures is that in this case the primary water layer is depleted in the initial stages of the reaction. Such a problem is not faced when attack on glass with dry HCl gas is considered.

C. Removal of X-ions from Primary Water Layer

It has already been pointed out that the rate of attack by a particular reagent is determined by the rate of diffusion of X-ions out of the glass, unless the rate of removal of X-ions from the primary water layer or the rate of supply of H-ions for counterdiffusion is slower than the rate of diffusion of X-ions out of the glass, in which case the slowest rate becomes the controlling rate. If the X-ions which have diffused out of the glass are not removed from the primary water layer, there would be a build-up of X-ion concentration in this layer and the diffusion of X-ions out of the glass would stop. This fact was shown by the result of A4 reported in Table I.

1. Attack with Pure Water: The case of attack with pure water is a replica of the case of X-ion diffusion from glass to the H_2O layer. Since a large quantity of water is present, the advancing X-ion does not reach a discontinuous boundary for quite a while. In the case of the presence of stagnant water on the surface of the glass, the diffusion stops when the concentration of X-ions in the water reaches the same uniform value as its concentration in the glass at that instant. However, since the presence of X-ions in water produces XOH, if a strong alkaline solution is formed, the mechanism of the reaction might change due to the alkali affecting the Si-ions. Figure 2 illustrates schematically the mechanism of the attack on glass by bulk pure water. In the case, on the other hand, in which the water is flowing past the surface of the H_2O layer on the glass, there is always fresh water coming in contact with the H_2O layer, and thus the diffusion can stop only when all the diffusible X has diffused out. It would, of course, never be possible to

reduce the X-ion content of the glass to zero, because those X-ions which are part of the doublets, triplets, etc., in the structure are rather permanently associated with their neighbors and would not easily diffuse out.

2. Attack with Neutral Salt Solutions: The mechanism in this case is the same as with pure water except that the water in the solution has a lesser capacity for taking up the X-ions in solution than does pure water. If a saturated solution of the salt is used, there would be only a small amount of diffusion of X-ions from the glass into the solution, depending on the partial solubility of XOH and the salt in water.

3. Attack with Acid Solutions: If the attacking reagent is a water solution of an acid, the removal of the X-ions from the external boundary of the H₂O layer of the glass takes place by two mechanisms. The first mechanism would be the same as in the case of pure water, i.e., the diffusion of the X-ions into the solution. The second mechanism is characteristic of acids; the X-ions would be entrapped by the acid radicals of the acid. The X-ions by this mechanism are precipitated as a salt by associating with the acid radical. Such a mechanism is schematically illustrated in Figure 3.

4. Attack with Water Vapor: Attack of glass with water vapor is of great practical interest, because there always is some water vapor in the atmosphere. So, there is always some attack on glass stored in the atmosphere. Since XOH formed by reaction of X-ions and the primary layer is hygroscopic, more H₂O from the atmosphere is absorbed and thus the reaction can continue. If the concentration of the XOH on the glass surface becomes quite high, we may get attack involving the Si-ions.

5. Attack with Acid Vapor: In the case of the attack of glass by acid vapors, the removal of X-ions from the external boundary of the H₂O layer on the glass is by chemical reaction. The X is precipitated by the acid radical as a salt. Thus, the diffusion of X-ions out of the glass can continue.

Figure 4 schematically illustrates the mechanism of the attack of glass by acid vapors.

D. Temperature as an External Factor

The temperature acts as an external factor inasmuch as it affects the various other external factors.

III. CONCLUSIONS

A mechanism for water- and acid-attack on high-silica glasses is proposed. The proposed mechanism would apply to all cases of chemical attack on glass where the attack progresses essentially by diffusion of ions. The role of various factors, external to the glass, on the chemical attack is considered.

The proposed mechanism postulates the necessity of a "Primary Water Layer" on the surface of the glass for the chemical attack to take place. The necessity of this Primary Water Layer is experimentally demonstrated. It is pointed out that this layer does exist on a glass surface during normal conditions of chemical attack. In the absence of this layer no attack takes place. It may be possible to utilize this fact to improve the chemical durability of a glass without changing its compositions.

In addition to the Primary Water Layer the other important external factors controlling chemical attack on glass are recognized to be: supply of positive ions for counterdiffusion, removal of X-ions from the Primary Water Layer, and the temperature. In the presence of the Primary Water Layer on the surface of a glass, if there is a capacity in the attacking reagent to remove the X-ions from the primary water layer as fast as, or faster than, the rate of their diffusion into the layer from the glass, and to supply H-ions at the same rate, or faster than the rate, at which the X-ions diffuse

out of the glass, the rate of attack will be controlled by the rate of diffusion of X-ions in the glass. If any of the said rates are slower than the rate of diffusion of the X-ions out of the glass, the slowest rate would become the controlling one and would be the determining factor in the rate of attack on the glass by the particular reagent under the particular conditions.

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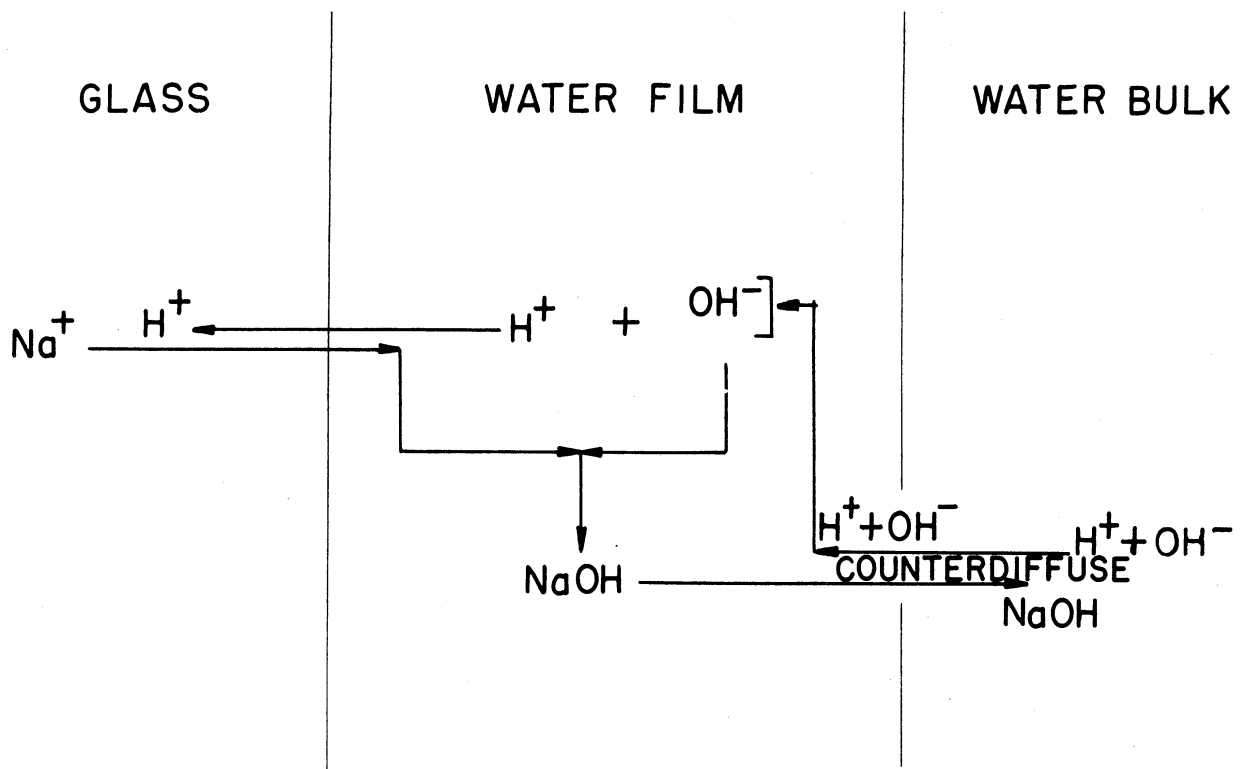


FIGURE 2
LIQUID WATER REACTION

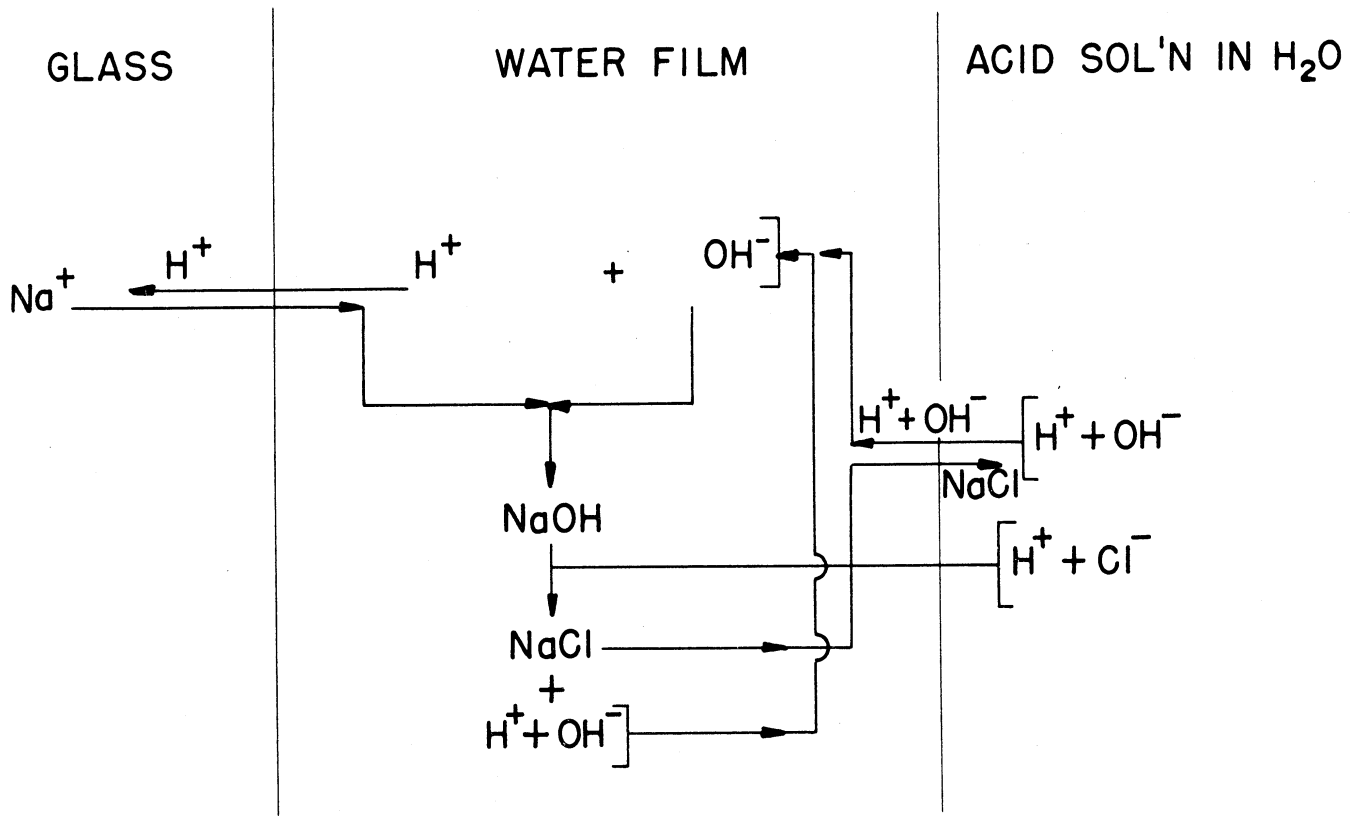


FIGURE 3
ACID SOLUTION REACTION

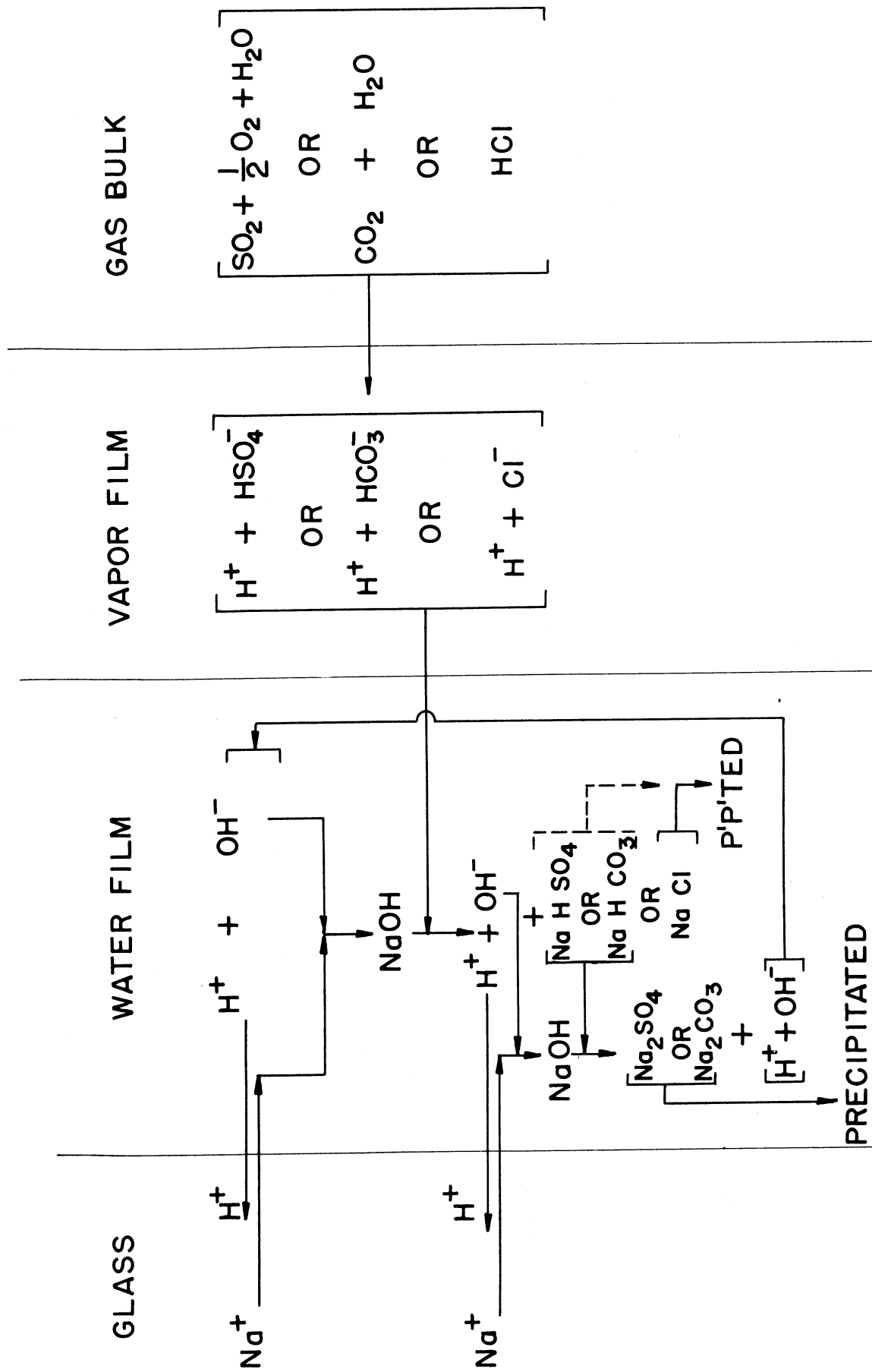


FIGURE 4
ACID VAPOR REACTION

A RE-EVALUATION OF THE CHEMICAL DURABILITY

OF SODA-POTASH-SILICA GLASSES¹

(Presented in the Glass Division at the 58th Annual Meeting
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ABSTRACT

The authors show that the alkali extraction curve for an 18-weight percent alkali oxide glass (balance silica) containing combinations of soda and potash exhibits a maximum and not a minimum as believed previously. This curve also shows that the sodium ions in a pure soda-silica glass are considerably more tenaciously held by the structure than the potassium ions in a pure potash-silica glass, both glasses containing equal weight percent of alkali, a result in direct opposition to the existing belief. It is shown, that the replacement of calcium oxide for part of the silica in the above mentioned alkali-silica glasses changes the results radically. The calcium improves the durability of potash-silica glasses much more than it does that of the soda-silica glasses. The difference in the effect is so pronounced that with 5% (out of the parent 82%) of the silica replaced by calcium oxide, the potassium becomes more tenaciously held than the sodium. Also the introduction of calcium lowers the maximum in the curve, ultimately changing it to a minimum. Thus, it is shown that the interaction of the positive ions in a glass is quite far-reaching.

A RE-EVALUATION OF THE CHEMICAL DURABILITY
OF SODA-POTASH-SILICA GLASSES

1. INTRODUCTION

The first most extensive and systematic study on the chemical durability (alkali-extraction) of glasses as a function of composition was reported by Peddle. The results on the alkali-extraction of soda-potash-lead-silica glasses reported by Peddle (Ref. 5) showed that the plots of alkali-extraction versus the percentage of K_2O or Na_2O exhibited minima at compositions with K_2O/Na_2O ratio of 7:3. He also showed that the minima in the curves at the said K_2O/Na_2O ratio were exhibited independent of the amount of SiO_2 or PbO in the glass. Peddle's results further show that the glasses containing K_2O are more resistant to water leaching than those containing Na_2O . Peddle did not carry out any alkali-extraction studies on soda-potash-silica glasses not containing any lead oxide or alkaline-earth-oxides. On the basis of studies on density and refractive index of soda-potash-silica glasses he made the statement (Ref. 4): "the glasses of the series $100 SiO_2, x K_2O$ and $100 SiO_2, x Na_2O$."

Stevens (Ref. 7) reported similar minima plots of power factor versus K_2O/Na_2O ratio. Moore and DeSilva (Ref. 3) reported these minima in dielectric constant and power factor plots (variation with composition) and a corresponding maximum in the specific resistance plot. Moore and DeSilva also concluded, "the high specific resistance of the glasses containing proportions of potash up to 12% as compared with the all-soda glass shows, however, that the majority of the K^+ ions are much more strongly held than the Na^+ ions." It is reasonable to expect the electrical conductivity and the alkali-extraction of a glass to behave similarly because both the properties are directly dependent on the

diffusion of the alkali ions in the glass. It is pertinent to note that the glasses used by Stevels as well as those by Moore and DeSilva contained appreciable proportions of oxides of the divalent atoms.

The said minima have also been reported by several workers in low temperature viscosity and some other property curves for similar glasses.

The most recent work on this seemingly anomalous behavior of soda-potash glasses was reported by Sen and Tooley (Ref. 6). Their results are quite typical of the conventional thinking on the problem. They reported the minima at a K_2O/Na_2O ratio of 2.6/1.0 (by weight), and, in line with the previous investigators, showed that the potash glass is more resistant than the soda glass. Needless to say that their glasses contained a substantial amount (10% by wt) of CaO . It is interesting to note, however, that their curve, showing the minimum is much flatter than the ones reported by Peddle for soda-potash-silica glasses containing lead oxide.

Figure 1 shows the curves reported by Peddle for alkali-extraction of two series of glasses, namely 20% ($K_2O + Na_2O$), 20% PbO , 60% SiO_2 and 20% ($K_2O + Na_2O$) 30% PbO , 50% SiO_2 . Figure 2 is a reproduction of the curve reported by Sen and Tooley for the series of glasses of the overall composition 18% ($K_2O + Na_2O$), 10% CaO , 72% SiO_2 by weight.

The authors were interested in these results because the reported minima point to a preferential (rather than a random) inter-positioning of the Na and K ions, which has been proposed by the authors in some of their earlier work (Ref. 1). However, the structural picture proposed by the authors would have called for a higher resistance to alkali-extraction by the soda-silica than by the potash-silica

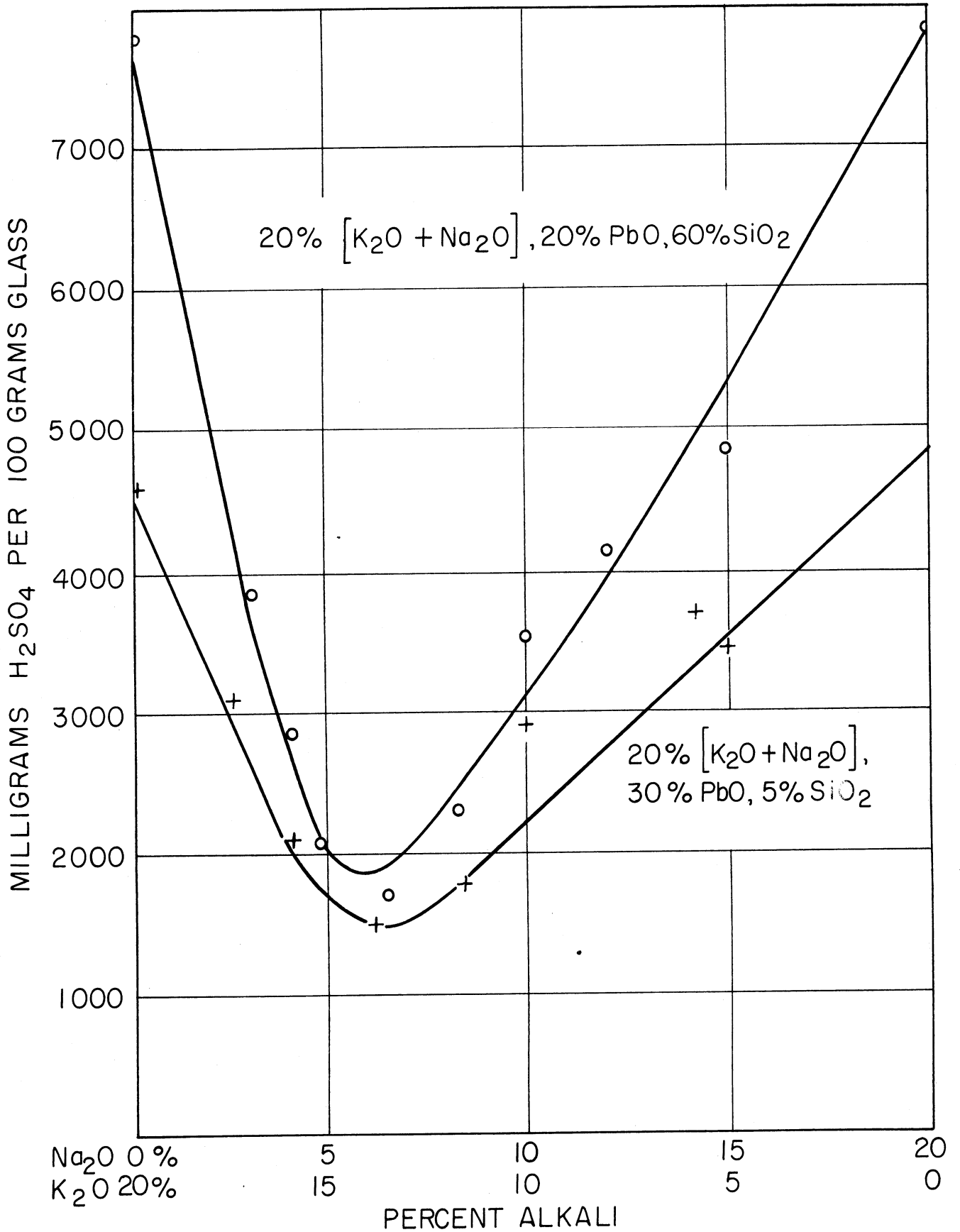


Fig. 1 Solubility of Sodium-Potassium glasses, Lead Oxide and Silica constant, ratio K₂O/Na₂O varying after Peddle

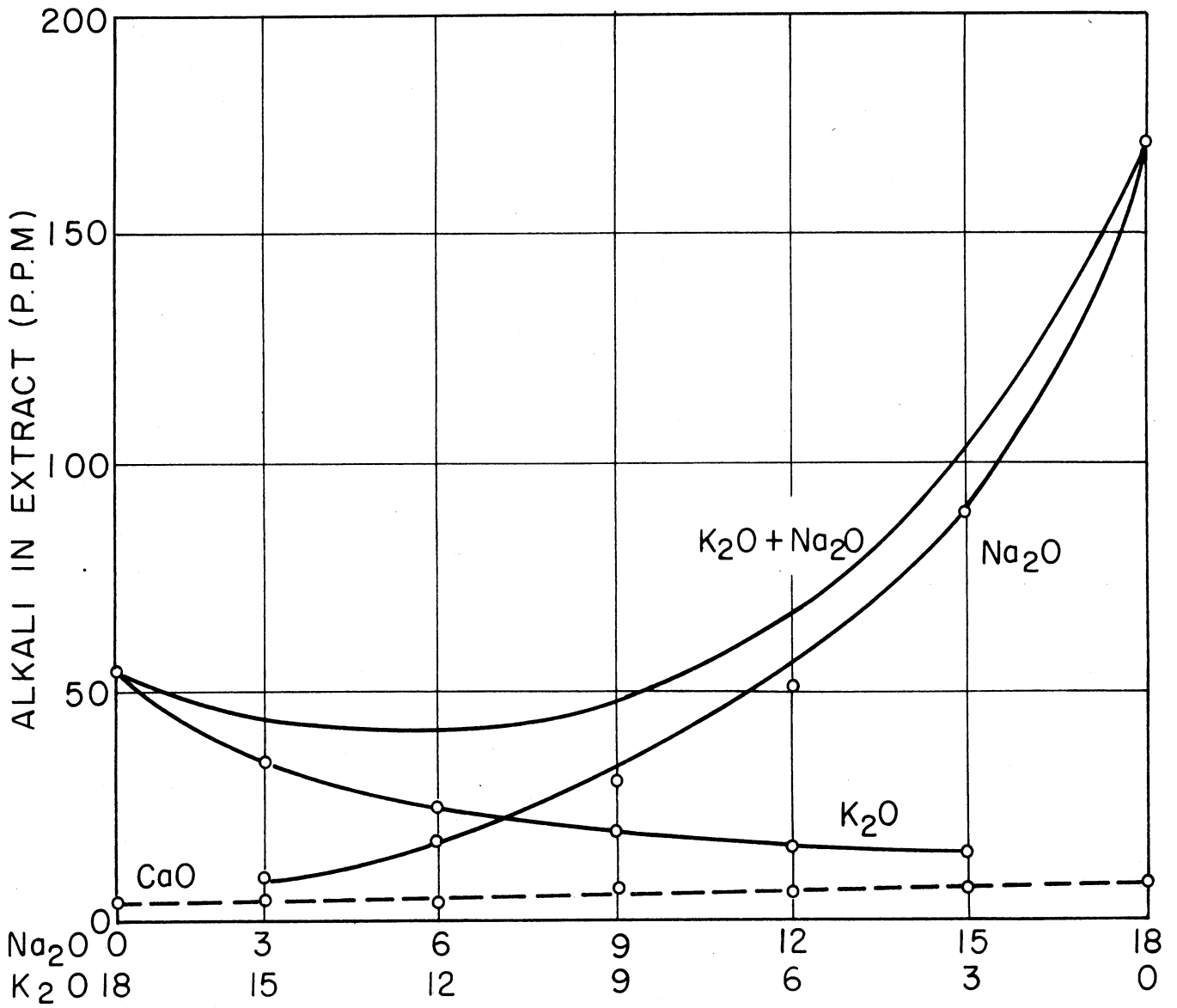


Fig. 2 Alkali extracted (expressed as K_2O and Na_2O as a function of alkali content in glass after Sen and Tooley.

glasses, both containing equal proportions by weight of the alkali oxide; contrary to the reported experimental results. A closer study of these experimental results revealed that the glasses used for all these studies were never pure soda-potash-silica glasses but always contained appreciable proportions of other oxides, especially those of the divalent atoms. Considering the complex nature of the interactions of the positive ions in determining the individual ion diffusion rates expected from the structure proposed by the authors, it was felt that the divalent ions could possibly cause a radical change in the alkali extraction curves for soda-potash-silica glasses. Therefore, it was decided to conduct alkali-extraction experiments on pure soda-potash-silica glasses and to study the effect of the addition of a divalent ion to the pure glasses.

II. EXPERIMENTAL PROCEDURE

Alkali extraction studies were carried on soda-silica, potash-silica, and some soda-potash-silica glasses of the general composition 18% ($K_2O + Na_2O$), 82% SiO_2 by weight and also on glasses of the general composition 18% ($K_2O + Na_2O$), 5% CaO , 77% SiO_2 by weight. The ratios of K_2O/Na_2O investigated for soda-potash combinations were 2.6/1.0 and 1.0/2.6. The authors were particularly interested in the K_2O/Na_2O ratio of 2.6/1.0 since the minimum reported by Sen and Tooley was at this value. It will be noted that the total alkali content of the glasses (18% by weight) used by the authors is the same as that used by Sen and Tooley in their studies. This was purposely done with a view to comparing the two results. Since, in the present study it was the intention only to establish the character of the alkali-extraction curves and not to get their exact shape, it was not considered necessary to study any more K_2O/Na_2O ratios than the two reported.

The method used for the study of the alkali-extraction was the one recently reported by the authors (Ref. 1). For the details of the method a

reference should be made to that paper. The method consists in melting the experimental glass batch in a platinum crucible, drawing a cane of glass from the fired glass, and conducting a dilute hydrochloric acid (in double-distilled water) leaching at 50°C on the freshly-drawn cane. The sodium and potassium ion concentrations in the leach solutions are measured by a Beckman Model-B Flame Spectrophotometer. After measurement of the area of the glass sample and carrying out the appropriate calculations, the rates of diffusion of the sodium and the potassium ions in a particular glass are obtained as "grams of ion x 10⁻⁶ per $\sqrt{\text{min}}$ per sq in." of surface area. Three or four experiments were conducted on each glass and the results reported represent an average of three rate measurements. The total alkali-extraction rate is taken as the sum of the two individual ion diffusion rates.

III. RESULTS AND DISCUSSION

Figure 3 shows the values of K⁺, Na⁺, and (K⁺ + Na⁺)(total alkali) extraction rates at 50°C for the series of glasses of the composition 18% (K₂O + Na₂O), 82% SiO₂ by weight plotted against weight percent of K₂O and Na₂O in the glasses. Figure 4 shows the corresponding results for the series of glasses of the composition 18% (K₂O + Na₂O), 5% CaO, 77% SiO₂ by weights.

An examination of Fig. 3 shows that a K₂O-SiO₂ glass is less resistant to alkali-extraction than a Na₂O-SiO₂ glass, the ratio of extraction for the two glasses being roughly 4:1. The figure also shows that the total alkali-extraction curve (also the individual ion-extraction curves) has a maximum for a glass composition representing a K₂O/Na₂O ratio of approximately 2.6/1.0 by weight.* Both these facts are contrary to the established notions about soda-potash-silica glasses based on experiments on glasses containing additional oxides. This is

*The exact value of the K₂O/Na₂O ratio at which the maximum occurs in the alkali-extraction curve cannot be established from the authors data since it is not sufficiently exhaustive for that purpose.

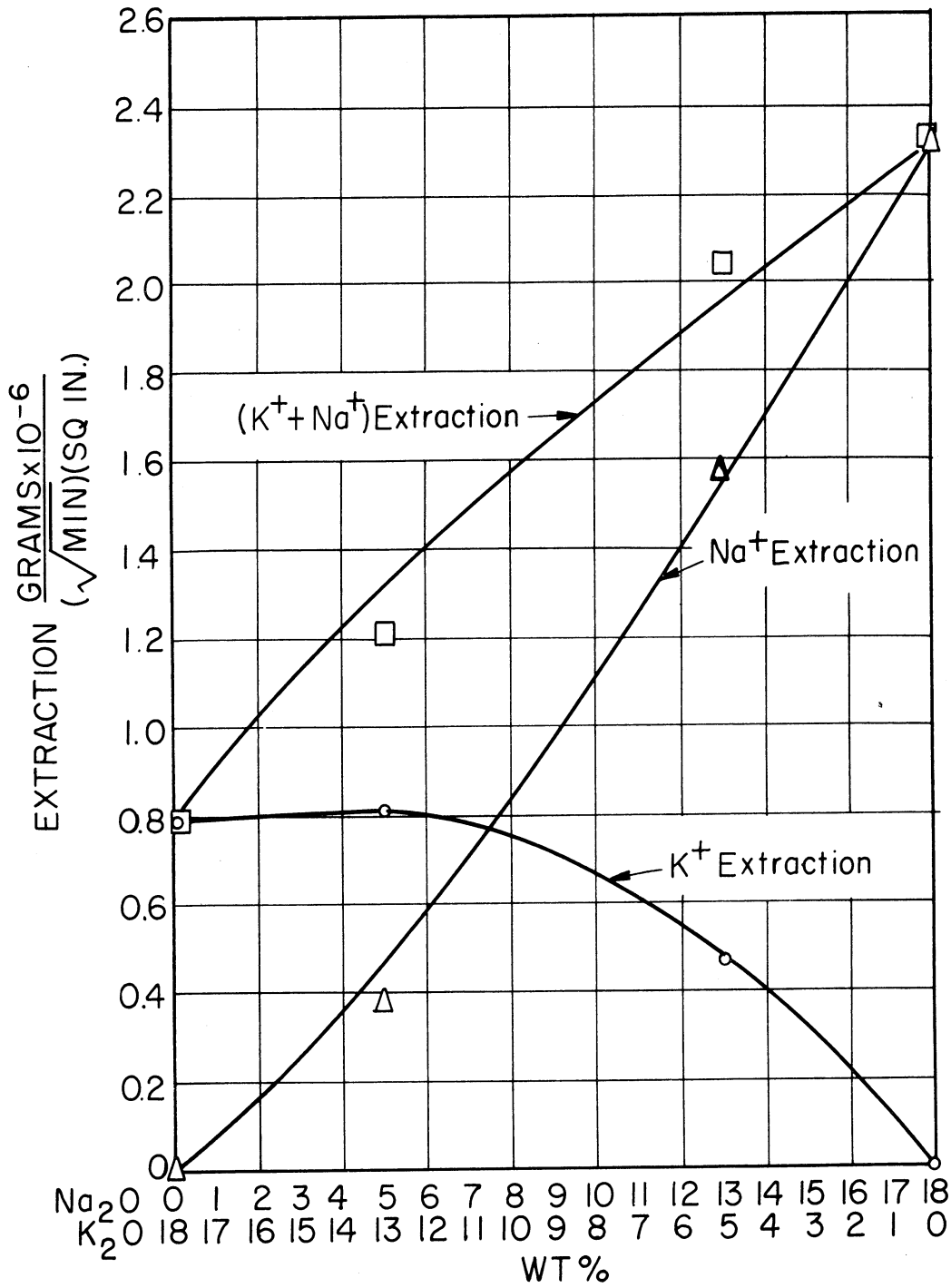
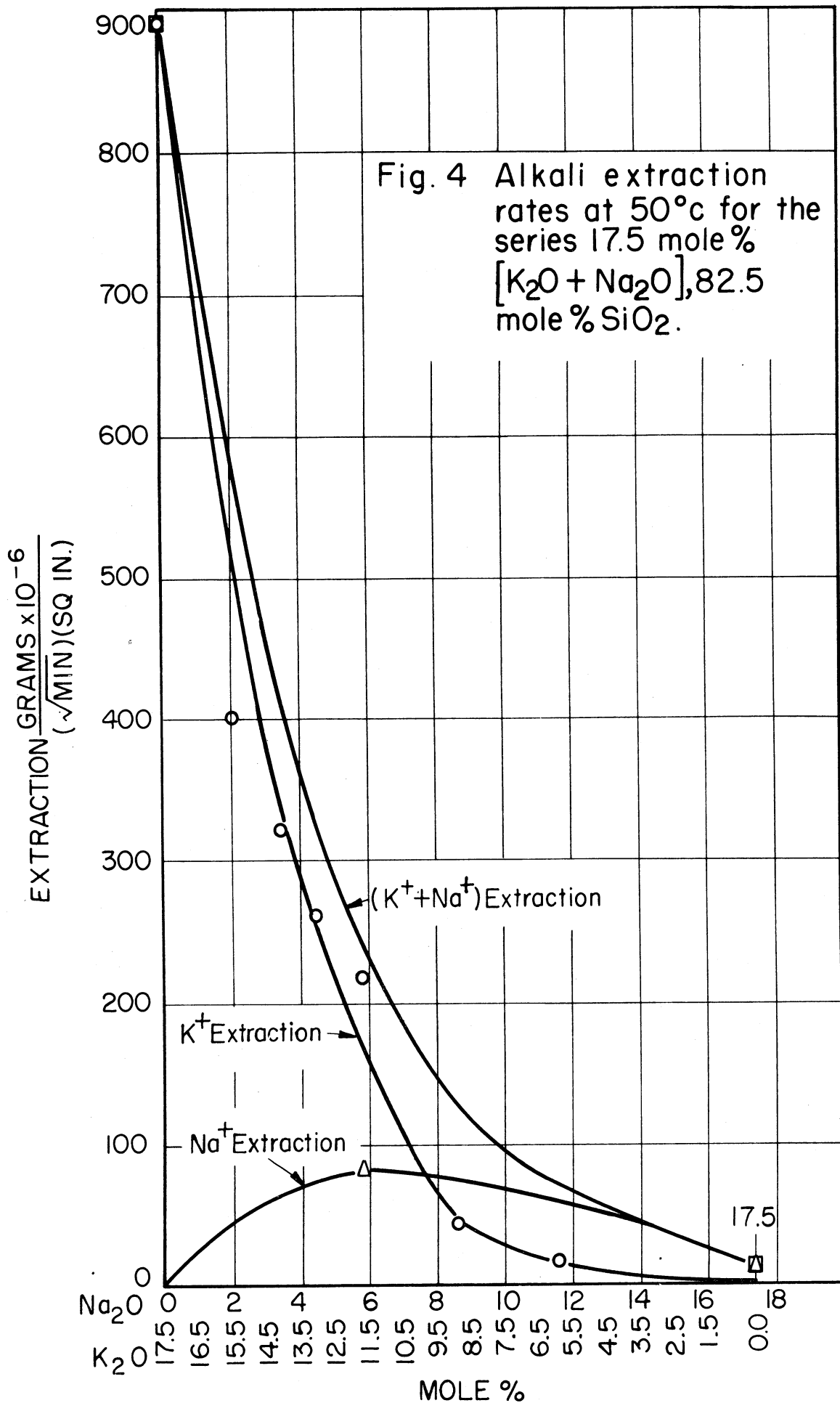


Fig. 3 Alkali extraction rates at 50°c for the series 18% (K₂O+Na₂O), 5% CaO, 77%SiO₂ by weight.



clearly shown by comparing Fig. 3 with Figs. 1 and 2. On the basis of the data shown in Fig. 3, it can be safely concluded that the sodium ions in a pure K_2O-SiO_2 glass are considerably less tenaciously held in the glass structure than the sodium ions in a pure Na_2O-SiO_2 glass, both the glasses containing equal proportions of the alkali by weight. The maximum in the alkali extraction curve signifies that $K_2O-Na_2O-SiO_2$ glasses are less resistant to alkali-extraction than either a K_2O-SiO_2 glass or a Na_2O-SiO_2 glass, for equal weight proportions of total alkali.

Comparison of Fig. 4 with Fig. 3 shows the changes in the individual ion-extractions as well as in the total alkali-extraction by substituting five out of the parent 82% SiO_2 with CaO . It is seen that the effect of the introduction of CaO in the glasses is quite drastic. When 5% by weight of CaO is present in the glass the potash glass is about three times more resistant than the soda glass, showing that the calcium improves the durability of potash-silica glasses much more than it does that of the soda-silica glasses. None of the curves in Fig. 4 show a maximum. The total alkali-extraction curve is quite flat and in fact is close to a straight line. Since the introduction of 5% CaO in the soda-potash-silica glasses eliminated the maximum in the alkali-extraction curve giving a flat curve, it is quite reasonable to believe that an additional 5% of CaO (at the cost of reduction in SiO_2) would cause a minimum in the alkali-extraction curve as reported by Sen and Tooley (shown in Fig. 3). Apparently, as is shown by Peddle's results, the effect of the addition of lead oxide is even more drastic than that of calcium oxide addition.

IV. CONCLUSIONS

It is shown that the potassium ions in a K_2O-SiO_2 glass are considerably less tenaciously held in the structure than are the sodium ions in a

$\text{Na}_2\text{O-SiO}_2$ glass, both glasses containing 18 wt% of the alkali. Further, it is shown that a combination of soda and potash gives a less chemically durable glass than a glass containing either soda or potash alone. It is pointed out that the existent notions about the durability of $\text{K}_2\text{O-Na}_2\text{O-SiO}_2$ glasses, which are quite contrary to the authors results, are due to an un-noticed assumption according to which the improvement in durability of soda and potash with the addition of calcium is considered equal. This assumption has been proved in this paper to be completely fallacious. In fact it is positively established by the authors' results that calcium improves the durability of potash-silica glasses much more than it does that of the soda-silica glasses.

It would be hard to explain the results reported in this paper on soda-potash-silica glasses solely on the basis of a geometric packing due to difference in sizes of the two ions, namely K^+ and Na^+ , as has been done by some workers to explain the minimum reported in the literature. This is especially so, since it has now been established that the minimum reported in the literature is due to the effect of the addition of calcium. In the opinion of the authors the concept of doublets, triplets, etc. advanced by them in some of their earlier work can adequately explain the results. The theoretical explanation of the results on this basis is dealt with in an ensuing paper by the authors. It may be mentioned here that to gain structural information and to determine the relative stability of the various alkali ions glasses containing equal mole percent rather than equal weight percent alkali should be compared.

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STRUCTURAL ROLE OF THE MODIFYING OXIDES IN HIGH-SILICA GLASSES¹

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ABSTRACT

It is pointed out that the explanation of the structural role of the modifying oxide (specially alkali and alkaline earth) cations in silica glasses advanced by the proponents of the "Random Network Theory" for the structure of glass is not adequate. On the basis of data reported in the literature and some experimental work by the authors, it is shown that these cations have a preferential rather than a random orientation in the glass structure. These cations are believed to play a very definite and useful role in the glass structure and not just fill the holes in an otherwise normal silicon-oxygen network. A probable structural role for these cations, based on differences in the oxygen environment of the available holes, is proposed. Various characteristics of glass, which are controlled mainly by these cations, are explained on the basis of the proposed structure.

STRUCTURAL ROLE OF THE MODIFYING OXIDES IN HIGH-SILICA GLASSES

I. INTRODUCTION

The structure of glass has long been a subject of controversy. Some of the earliest views on the subject presented in the literature were by Randall and co-workers (Ref. 9) on the basis of X-ray diffraction patterns. According to these workers vitreous silica consists of cristobolite crystallites. This view was later discredited by Zachariasen (Ref. 17), and by Warren (Refs. 13, 14). The crystallite theory for the structure of glass, though still supported by some workers---Hägg (Ref. 4), Valenkov and Poray-Koshitz (Ref. 12) ---is now almost out of vogue.

In 1932 Zachariasen (Ref. 17) postulated his, now famous, "Random Network" theory for the structure of glass. This theory was later supported by the X-ray diffraction work of Warren (Refs. 13, 14) and others (Refs. 1, 2, 15, 16). According to the Random Network Theory the atoms in glass are considered as being linked together by forces essentially the same as in crystals. Over large ranges of temperature the atoms are believed to oscillate about definite equilibrium positions. As in crystals, extended three-dimensional networks are supposed to be formed. The principal difference between a crystal network and a glass network, according to this theory, is the presence of symmetry and periodicity in the former and the absence of periodicity and symmetry in the latter.

The network in vitreous silica, according to the Zachariasen-Warren concept of the structure of glass, is built up of oxygen tetrahedra which surround the silicon. 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.

Up to this point the authors agree with the Random Network Theory of Zachariasen and Warren. However, the explanation of the structural role of the modifying oxide (specially alkali and alkaline earth) cations in silica glasses advanced by the proponents of the Random Network Theory is considered by the authors to be inadequate.

In a silicate glass containing alkali or alkaline earth, the Random Network theory considers the added cations to exist as "randomly situated in the holes of the silicon-oxygen network" (Warren, Ref. 14). In the words of Zachariasen in his original paper "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."

From a study of the characteristics of glass which are affected mainly by the modifying oxide cations, the authors are convinced that these cations have a preferential rather than a random orientation in the glass structure. The authors further believe that these cations play a very definite and useful role in the glass structure and do not simply fill the holes in an otherwise normal silicon-oxygen network. In this paper, the authors have set down the reasons for the beliefs held by them, and further, they have proposed a probable structural role for these cations.

II. COMPOSITION LIMITS

The present study is restricted to high silica glasses containing alkali oxides and alkaline earth oxides as the modifying oxides. This limitation was imposed because it was felt that to properly understand the structural

role of the modifying oxide cations one must start with fairly simple glasses. Especially, considerable data is available on glasses containing these oxides, and therefore the study was restricted to these two categories of oxides. In the text, the alkali oxides are referred to as X_2O (X being Li, Na, K, Rb, or Cs) and the alkaline earth oxides as YO (Y being Be, Mg, Ca, Sr, and Ba). This restriction is, however, temporary, and it is planned to extend the ideas presented in this paper to other classes of commonly used oxides. The behavior in the case of the modifying oxides that are not considered here would not be expected to be radically different from that of the alkali- and alkaline-earth-oxides. The restriction as to the high silica content is imposed because several of the properties of glass are known to reverse as the modifying oxide content is increased much beyond about 20 percent. It is suspected that the basic tetrahedral Si-O coordination may be changed---possibly to a six-fold coordination (Ref. 11)---as the modifying oxide content is increased beyond a critical concentration. To avoid this complication, only the silica-rich end of the phase diagram is considered here. However, this does not constitute too much of a limitation, since most of the commercially important silica glasses lie on this end of the phase diagram.

III. THE ARGUMENT FOR A NON RANDOM ORIENTATION OF MODIFYING OXIDE CATIONS

Several German workers have, from time to time, proposed the existence of chemical compounds or complexes in modifying oxide-silica glasses. Hartleif's work (Ref. 5) on K_2O-SiO_2 glasses is to some extent typical of this school of thought. On differencing radial distribution curves obtained from X-ray diffraction data on K_2O-SiO_2 glasses and SiO_2 glass, Hartleif pointed out maxima in the difference curves which could be attributed to a K-K distance. From his results, which indicated that the K-ions cannot be assumed to be uniformly and randomly distributed in the silica structure, Hartleif

concluded that in a K_2O-SiO_2 glass two structural parts---one an almost undistorted silica glass structure part and the other a K_2O -rich part---existing near one another must be assumed. In essence, Hartleif made an attempt to reconcile the Random Network Theory for the structure of glass and the ideas about the existence of chemical compounds or complexes in glass advanced by earlier German workers who were opposed to the Random Networks Theory.

Whether one accepts Hartleif's conclusion or not, the indication of definite K-K distances from his results cannot be ignored. Lukesh (Ref. 6) indicated the existence of similar Na-Na distances by differencing the radial distribution curves for Na_2O-SiO_2 glass and SiO_2 glass reported by Warren and Bischoe (Ref. 15). He also indicated the existence of definite Na-Na and K-K distances in soda-boric oxide and potash-boric oxide glasses respectively. All these results seem to point to a non-random orientation of the modifying oxide cations.

Aside from the study of X-ray diffraction patterns, the structural role of the modifying oxide cations in glass is indicated by some of the characteristics of glass which are controlled mainly by these cations. It is fairly well known that the electrical conductivity of X_2O-SiO_2 and $X_2O-YO-SiO_2$ glasses is ionic in nature and is caused mainly by the movements of the alkali oxide cations in the glass structure. The mechanism of water- and acid-attack on modifying oxide-silica glasses containing alkali oxides is also known to be ionic in nature (the attack reaction is believed to proceed by a counter-diffusion of the alkali cations from the glass and the hydrogen ions from the attacking agent). Thus, either the electrical conductivity of a glass, or the rate of alkali extraction from it can give a measure of the ease of migration of the alkali ions in the glass structure. A study of this ease of migration of the alkali ions in glass with respect to its composition can afford an insight into the structural role of these ions.

On an examination of the plots of electrical conductivity and chemical durability of X_2O-SiO_2 and $X_2O-YO-SiO_2$ glasses vs. the glass composition reported in the literature, one cannot escape several peculiarities in these plots. For example, soda-potash-silica glasses (containing an additional oxide) exhibit minima in their alkali extraction vs. composition curves (Refs. 8, 10) and maxima in the specific resistance vs. composition curves (Ref. 7). Further, the alkali extraction vs. YO content curves of $X_2O-YO-SiO_2$ glasses reported in the literature (Ref. 3) exhibit sharp changes in slope around the X:Y ratio of 2. These composition dependent abnormalities seem to point to a non-random orientation of the X and Y ions in the glass.

The supporters of the random orientation views have tried to explain some of these characteristics on the basis of a geometric packing due to the difference in sizes of the various ions. The authors, however, do not consider this explanation to be adequate. Most of these arguments are based on the erroneous inference that for the same valence charge smaller ions migrate with greater ease than do the larger ones. This inference is made from the experimental fact that for $X_2O-YO-SiO_2$ glasses containing equal proportions (by weight) of the various alkali oxides, the ease of migration of the X ions is inversely proportional to the size of the X ions. It must be pointed out that all the experimental work reported in the literature on which the above-mentioned inference is based was conducted on $X_2O-YO-SiO_2$ glasses and not on pure X_2O-SiO_2 glasses. It is well known that the introduction of Y ions in an X_2O-SiO_2 glass reduces the ease of migration of the X ions to a considerable degree. To base any inferences regarding the relative ease of migration of the various X ions in X_2O-SiO_2 glasses on experimental data obtained on $X_2O-YO-SiO_2$ glasses is tantamount to assuming that the effect of the introduction of YO in X_2O-SiO_2 glasses on the ease of migration of the various X ions is equal. In the authors' opinion this assumption is

completely baseless. The results of some experimental work by the authors on the effect of the addition of YO to various X_2O-SiO_2 glasses on the extraction of the various X-ions in standard alkali-extraction tests support the authors' opinion regarding this assumption. These experimental results (reported in a later paper) indicate that the introduction of YO in X_2O-SiO_2 glasses affects the ease of migration of the various X ions in pure X_2O-SiO_2 glasses to different degrees. Specifically, the authors' results show that the rate of extraction of potassium ions from a K_2O-SiO_2 glass is reduced much more by a replacement of part of the SiO_2 with CaO than is the rate of extraction of sodium ions from a Na_2O-SiO_2 glass by an equivalent substitution of SiO_2 with CaO. The results further show that in pure X_2O-SiO_2 glasses the order for the ease of migration of the various alkali ions is $K > Na > Li$ rather than $Li > Na > K$ as previously believed. Hence an explanation of the peculiar composition-dependent characteristics of glass can no longer be explained on the basis of a single geometric packing due to differences in the sizes of the various ions.

Considering the above arguments the authors are convinced of the inadequacy of the views of the proponents of the Random Network Theory regarding the structural role of the modifying oxide cations. A preferential orientation of these cations seems much more plausible than a random and uniform distribution in an otherwise normal Si-O network.

IV. THE PROPOSED STRUCTURE

In pure vitreous silica there are two oxygen atoms per silicon atom. According to the Random Network Theory the basic unit of the random structure is the Si-O tetrahedron. Thus the silicon atoms are, on an average, four-coordinated with oxygen atoms, and the oxygen atoms are, on an average, two-coordinated with silicon atoms. Thus, on an average, each oxygen in such a structure has valence associations with two silicon atoms. This type of oxygens have been referred to in the literature as "double-bonded" oxygens.

The authors, however, are not quite happy with this terminology since valence associations are not rigid and permanent and the use of the words "bonds" and "links" has created considerable misunderstanding in the literature. The authors, therefore, would like to call such oxygens as "doubly associated" oxygens. Figure 1 is a two-dimensional schematic representation of the structure of vitreous silica as originally given by Zachariasen. Being a two-dimensional representation, only three of the four oxygens of each Si-O tetrahedron is shown. All the oxygens are doubly associated. The tetrahedra associate with one another through a shared doubly associated oxygen atom.

Let us consider a pair of adjoining tetrahedra from the structure represented in Figure 1. Figure 2a shows such a pair taken at random from the structure of Figure 1. It should be pointed out that there is nothing special about the two tetrahedra in Figure 2a. All pairs of adjoining tetrahedra would look similar except for the angle of location of the two tetrahedra in a pair with respect to each other which according to the Random Network Theory varies considerably. Now let us imagine the introduction of a single oxygen ion in the vitreous silica structure under consideration. By its very nature, the incoming oxygen would associate with a silicon. It can associate with any one of the silicons in the vitreous silica structure. When this incoming oxygen ion establishes its association with one of the silicons, it deprives one oxygen, already existing in the structure and partly associated with the silicon in question, of its association with the silicon. Thus on the introduction of a foreign oxygen into the vitreous silica structure we get two oxygens (one of these the incoming one, and the other, one of the already present doubly associated oxygens) having valence associations with only one silicon each. Such oxygens can be termed "singly associated".

Figure 2b shows the two tetrahedra of Figure 2a in the presence of a foreign

oxygen ion (cross-hatched), illustrating the formation of two singly associated oxygens. It must be stressed that two adjacent singly associated oxygens as shown in Figure 2b would be obtained irrespective of which silicon does the new oxygen associate with. In other words, it may be said that singly associated oxygens occur in the structure in pairs.

It should be noted that the two singly associated oxygens, being close neighbors, would exert repulsive forces on each other. Thus, the introduction of oxygens in an Si-O network would weaken the structure due to the repulsive forces between the two members of every pair of singly associated oxygens. It is very important to appreciate this weakening role of the added oxygen ions in order to understand the structural role of the modifying oxide cations in a glass. If it were possible, by some means, to introduce oxygen ions (not accompanied by any cations) there would be a definite weakening of the glass structure---which would become manifest by a lowering of the liquidus point and corresponding changes in the other properties of the glass---for a particular proportion of the oxygens introduced. In practice however, the oxygen ions are always accompanied by associated cations (the two are introduced as the modifying oxides). The cations accompanying the oxygen ions, being opposite in charge to the negative oxygens, tend to overcome a part of the weakening effect of the oxygens. The various cations, being of different sizes and having different charges, naturally have varying degrees of capability for overcoming the weakening effect of the oxygens. This can easily explain the differences in lowering of the liquidus point of vitreous silica on the addition of comparable amounts of the different modifying oxides.

If a considerable number of oxygen ions is introduced into a vitreous silica structure, the resulting pairs of singly associated oxygens would normally be expected to be statistically distributed. There would be a definite statistical probability for two such pairs to exist in proximity to each other.

Similarly, there would be a definite, though lesser, degree of probability for the existence of rows of three or more pairs of singly associated oxygens. Figure 3 shows a two-dimensional representation of the structure of vitreous silica containing several foreign oxygen ions illustrating a few lone pairs, two pairs in proximity, and a row of three pairs of singly associated oxygens. It is believed by the authors that the degree of probability of a particular number of pairs of singly associated oxygens existing in proximity is affected, to some extent, by the nature and amount of the cations accompanying the foreign oxygens.

Let us now consider the hypothetical introduction of alkali and alkaline earth cations (X and Y respectively), if not accompanied by any oxygen ions, into a vitreous silica structure. Being positive these ions would naturally tend to associate with the oxygens in the structure. An examination of the structure represented in Figure 1 would show that the best location for these cations will be the "holes" in the structure surrounded by doubly associated oxygens. The distribution of these cations will be random in this case. Figure 4 shows such a hypothetical structure in two dimensions showing four X ions in the holes created by the doubly associated oxygens of the vitreous silica structure.

As has been pointed out before, in practice the X and Y ions are always accompanied by oxygen ions in the form of oxides. This is necessary due to electrical neutrality considerations. We have seen how the oxygens and X- and Y-ions will be expected to locate in the vitreous silica structure if added separately and by themselves. Let us now consider the practical case when the oxygen ions are accompanied by X and/or Y ions.

It has already been shown that the introduction of each new oxygen results in the creation of a pair of singly associated oxygens which represents a weak point in the structure owing to the repulsive forces between the

two singly associated oxygens. When the incoming oxygen is accompanied by two X ions, the question arises as to where the two X ions would be located in the structure. There are two possible types of positions that each of these X ions can occupy. Firstly, they can occupy the "holes" surrounded primarily by doubly associated oxygens as would be the case if the X ions were not accompanied by the oxygen ions. The alternative to this is their occupying holes adjacent to the pair of singly associated oxygens and thus have associations with this pair of singly associated oxygens in addition to a number of doubly associated oxygens, as illustrated in Figure 5. This cation arrangement can, for convenience, be referred to as "doublets". This latter arrangement would be the more probable one thermodynamically. First, the presence of the X ions near the oxygen ion with which they came will represent a lesser energy level than their separation from the parent oxygen, and secondly, the presence of the X ions in the vicinity of the pair of singly associated oxygens will, as was pointed out before, overcome part of the repulsive forces between the two singly associated oxygens. Thus the presence of the X ions in the vicinity of the pair of singly associated oxygens as illustrated in Figure 5 will represent a more stable state than their presence in holes surrounded primarily by doubly associated oxygens. However, since glass is not at stable equilibrium, both types of positions would be expected to be occupied in a glass containing considerable number of X or Y cations and oxygen ions. For a fixed composition and thermal history there would be a definite proportion of the cations occupying each type of position. In a glass containing a considerable number of added oxygen ions, as has been shown earlier, there would be a certain degree of probability of the existence of two, three, or more pairs of singly associated oxygens in rows. A hole which includes in its surroundings two pairs of singly associated oxygens would be even more stable location for X

or Y ions than the hole which has only one such pair in its surroundings. A study of Figure 3 will reveal that all the holes that can be possibly occupied by an X or Y ion can be classified into three categories depending upon the oxygen environment of the holes. These categories of holes can be named A, B, and C types and defined as follows:

1. Type "A" holes are those containing only doubly associated oxygens (and no singly associated oxygens) in their environment. This type of a hole would represent the least stable residence for an X or Y ion.

2. Type "B" holes are those containing on an average, one pair of singly associated oxygens in addition to some doubly associated oxygens in their environment. This type of a hole represents a more stable residence than an "A" type hole for an X or Y ion.

3. Type "C" holes are those containing on an average, two or more pairs of singly associated oxygens in addition to some doubly associated oxygens in their environment. Of the three types of holes defined here, this type represents the most stable residence for an X or Y ion.

Figure 6 classifies and labels all the holes in the Si-O structure represented by Figure 3 according to the above classification.

Due to the presence of a larger concentration of the singly associated oxygens in their environment, the "C" type holes would represent a higher negative charge than the other types of holes. The same thing applies to the "B" type holes as compared to the "A" type holes. Thus the order of preference for location in the various holes would vary from "C" to "B" to "A" as the electron charge per unit size of the cation goes down. Thus, in a glass containing both sodium and potassium ions the Na^+ ions would occupy the "C" type holes in preference to the K^+ ions. Similarly in a glass containing both X and Y ions the Y ions will occupy the "C" type holes in preference to

the X ions. The proportion of each type of holes occupied by a certain type of ions in a glass would be determined by their ion characteristics and their proportion in the glass.

Once the fact about the existence of three different types of holes in a vitreous silica structure containing excess oxygen is recognized, it becomes obvious that all the alkali and alkaline earth cations in a glass will not behave alike as would be expected if they were randomly distributed. For example the cations in the "C" type holes will be less mobile than those in the "B" type of holes which in turn will be less mobile than those in the "A" type of holes.

Most of the characteristics of glass which are controlled mainly by the modifying oxide cations, can be explained with the help of the proposed theory, the following points are worth mentioning:

1. The X or Y ions occupying holes adjacent to pairs of singly associated oxygens as shown in Figure 5 would represent definite X-X or X-Y distances presumably detectable by X-ray diffraction. Reports in the literature of the existence of X-X distances in X_2O-SiO_2 glasses have already been mentioned.

2. Due to charge-size considerations of the cations the order of preference for "C" to "B" to "A" type of holes for the various alkali cations will be expected to be $Li > Na > K > Rb > Cs$. This, according to the theory presented here, would indicate that for equimolar pure X_2O-SiO_2 glasses the order of chemical durability will be $Li > Na > K > Rb > Cs$. It has already been mentioned that the authors' experiments on pure Li_2O-SiO_2 , Na_2O-SiO_2 , and K_2O-SiO_2 glasses indicate this order for chemical durability.

3. The sharp changes in slopes of the curves for alkali extraction versus composition reported in the literature for $X_2O-YO-SiO_2$ glasses around

the X:Y ratio of 2:1 can be easily explained on the basis of this theory. It has already been mentioned that the Y ions will be favored over the X ions for occupancy of the "C" type of holes. If the maximum number of pairs of singly associated oxygens occurring in rows is limited to two, the above consideration will provide the cation arrangement for a glass with an X:Y ratio of 2:1 to be as shown schematically in Figure 7. Since in such an arrangement three cations exist in a row, this cation arrangement can, for convenience, be referred to as "triplet". This is a stable arrangement. In glasses with larger X:Y ratios the excess X ions will occupy the "A" type holes. Thus a sharp change in the slopes of alkali extraction curves would be expected around an X:Y ratio of 2:1 because the X:Y ratio for triplets is 2:1. This phenomenon was observed by the authors in mixed alkali glasses also, though the change in slope is less sharp depending on the cation combination. The above reasoning applies to this case as well.

4. The immiscibility of YO alone in SiO_2 and its miscibility in the presence of X_2O can also be explained on the basis of this theory. It has already been mentioned that Y ions would have a preference for the "C" type of holes. Considering the experimental fact that the Y ions in X_2O -YO- SiO_2 glasses are always very immobile, it may be assumed that "C" type of holes are natural residences for Y ions and that it is necessary for a Y ion to be screened by at least two pairs of singly associated oxygens (as in the case in a "C" type hole) for it to become part of the structure. When only YO is added to SiO_2 , we have only one pair of singly associated oxygens per Y ion added. Thus, the formation of "C" type holes is not possible and it is to be expected that the YO would not be soluble in SiO_2 . However, when a large amount of YO, above a critical amount, is added, the YO dissolves in the SiO_2 . This can be possible either through the formation of low rows of

singly associated oxygens with the help of some X_2O present as an impurity (as illustrated schematically in Figure 8) or by a change in the basic silica structure which is possible (as explained earlier) when a large proportion of the alkali or alkaline earth oxide is present. The YO is miscible in SiO_2 in the presence of X_2O because when both YO and X_2O are present the oxygen ions of X_2O can join in with the oxygen ions of the YO forming a "triplet" type of structure illustrated in Figure 7. For ratios of X:Y less than 2:1 formation of XXX "quadruplets" or larger groupings is possible.

V. CONCLUSIONS

A non-random orientation of the alkali and alkaline earth cations, based on differences in the oxygen environment of the available holes for these ions, is proposed. It is shown that a preferential orientation of these cations as proposed is much more plausible than a random and uniform distribution in an otherwise normal Si-O network. The proposed orientation of the alkali and alkaline earth cations is illustrated in Figure 9 which is a two dimensional representation of the structure of an X_2O -YO- SiO_2 glass showing an X-Y-X triplet, an X-X doublet and a lone X ion. Various characteristics of glass, which are affected mainly by the alkali and alkaline earth cations, are explained on the basis of the proposed structure.

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LEGEND

• SILICON

○ OXYGEN (WITH SILICON)

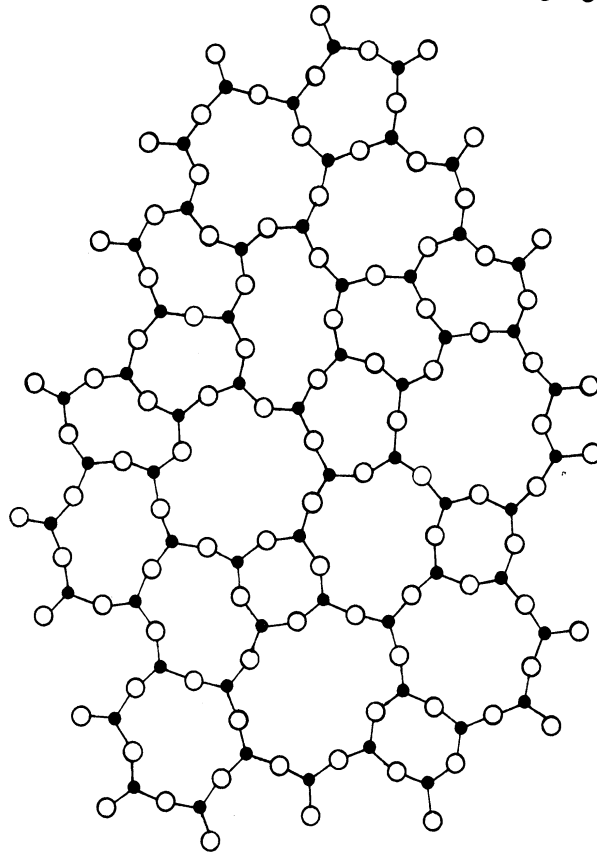


Figure 1

LEGEND

● SILICON

○ OXYGEN (WITH SILICON)

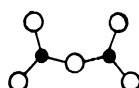


Figure 2a

LEGEND

● SILICON

○ OXYGEN (WITH SILICON)

⊕ ADDED OXYGEN

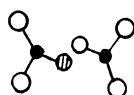
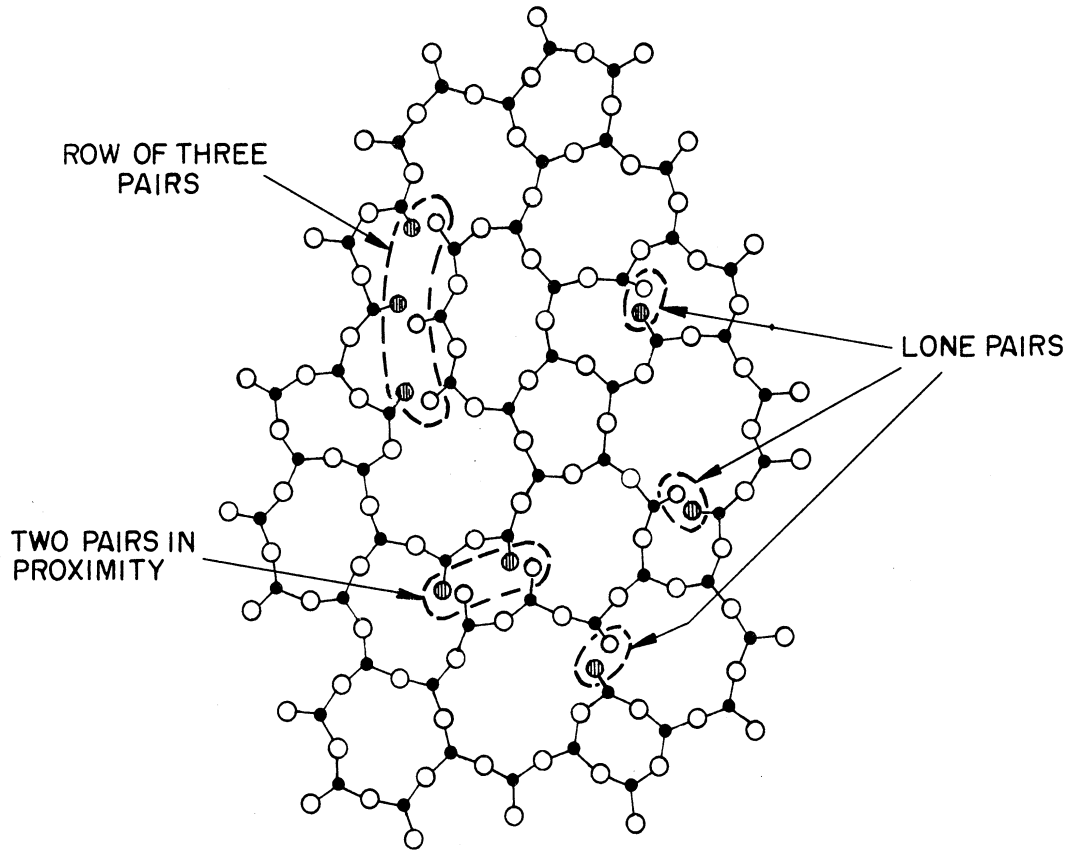


Figure 2b

LEGEND

- SILICON
- OXYGEN (WITH SILICON)
- ⊕ ADDED OXYGEN



LEGEND

◦ SILICON

○ OXYGEN (WITH SILICON)

⊗ X ION

⊗ Y ION

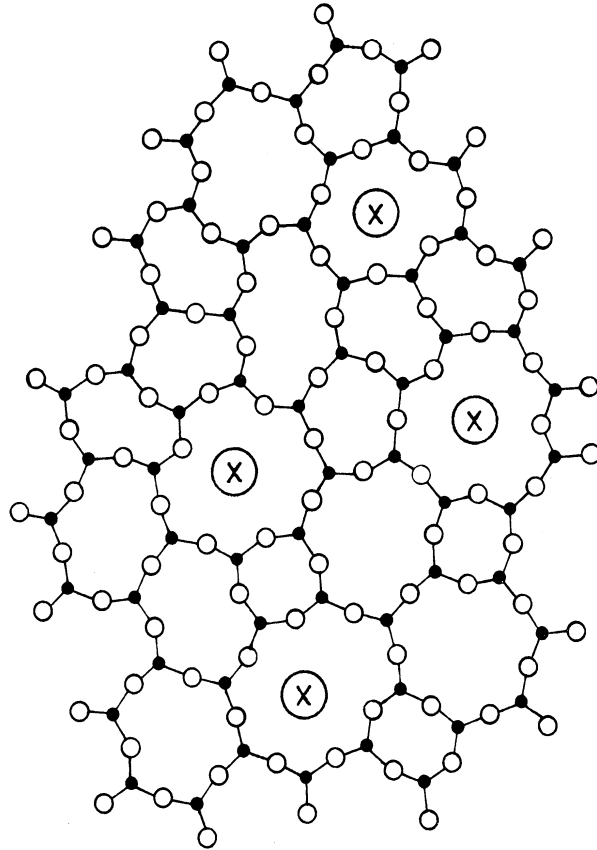


Figure 4

LEGEND

- SILICON
- OXYGEN (WITH SILICON)
- ⊕ ADDED OXYGEN
- ⊗ X ION

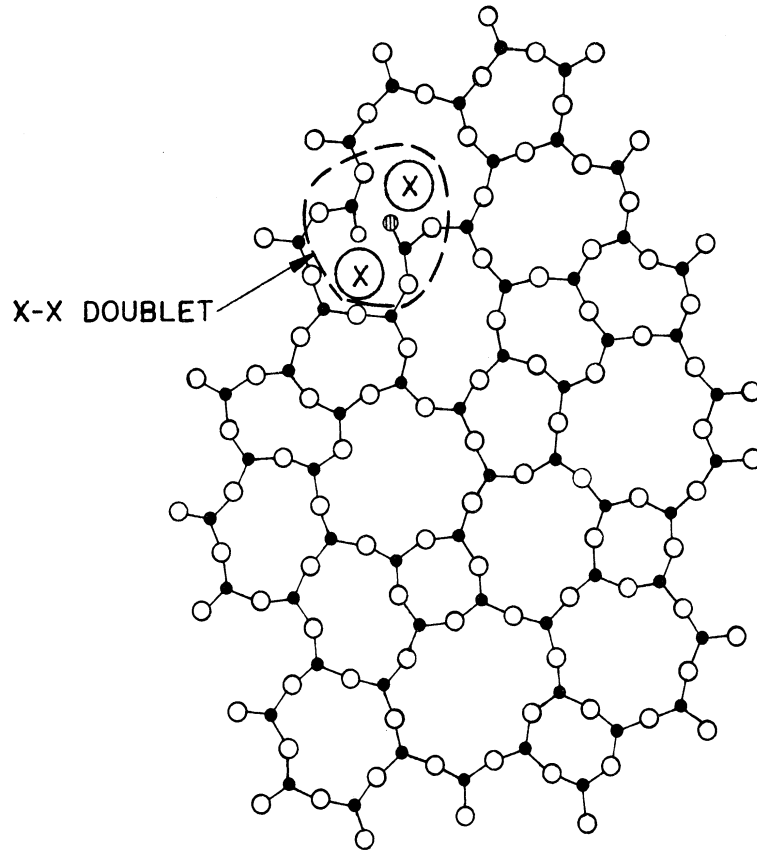


Figure 5

LEGEND

- SILICON
- OXYGEN (WITH SILICON)
- ⊕ ADDED OXYGEN

A,B,orC TYPES OF HOLES

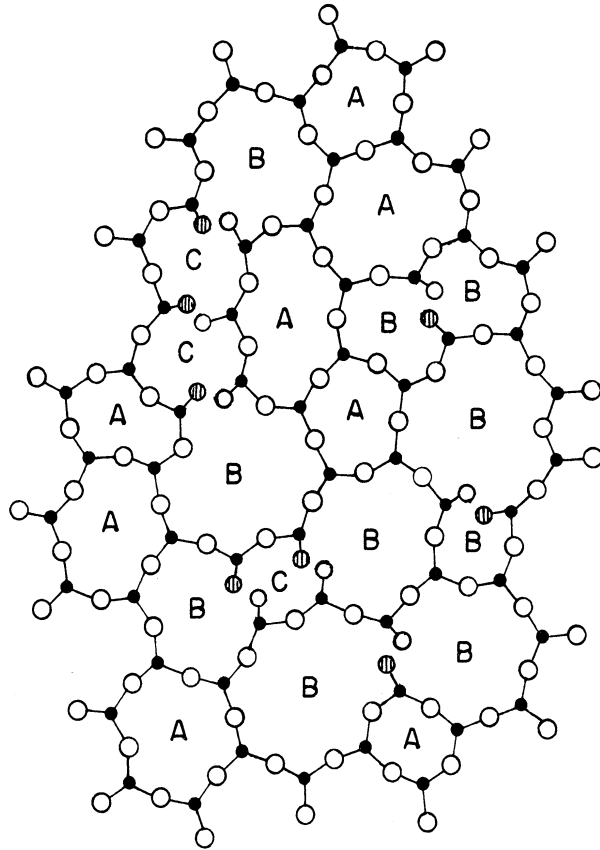


Figure 6

LEGEND

- SILICON
- OXYGEN (WITH SILICON)
- ⊕ ADDED OXYGEN
- ⊗ X ION
- ⊙ Y ION

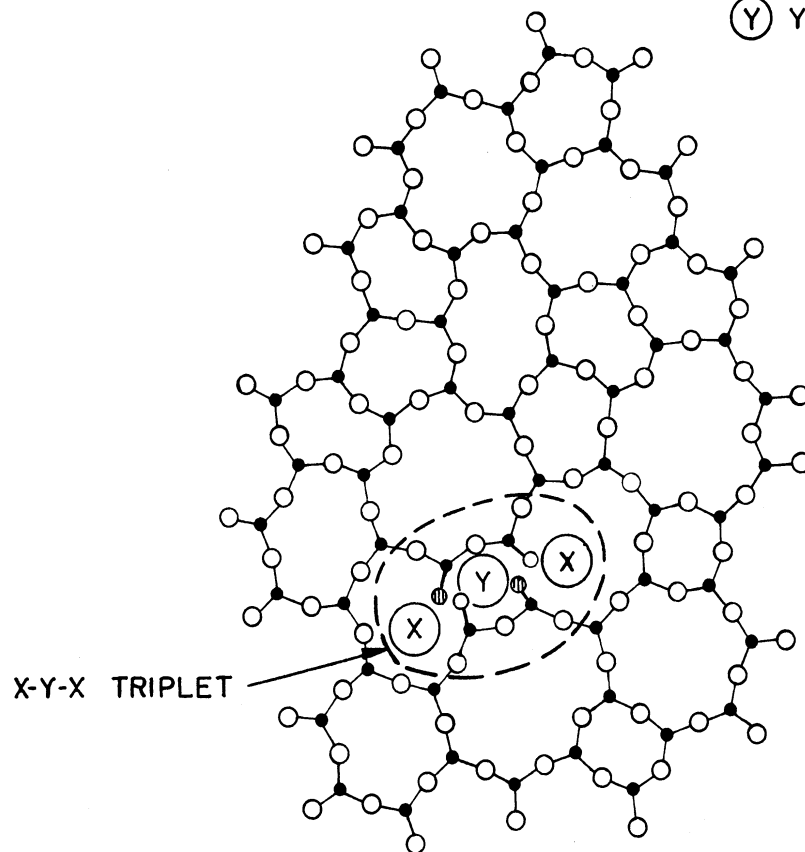


Figure 7

LEGEND

- SILICON
- OXYGEN (WITH SILICON)
- ⊕ ADDED OXYGEN
- ⊗ X ION
- ⊙ Y ION

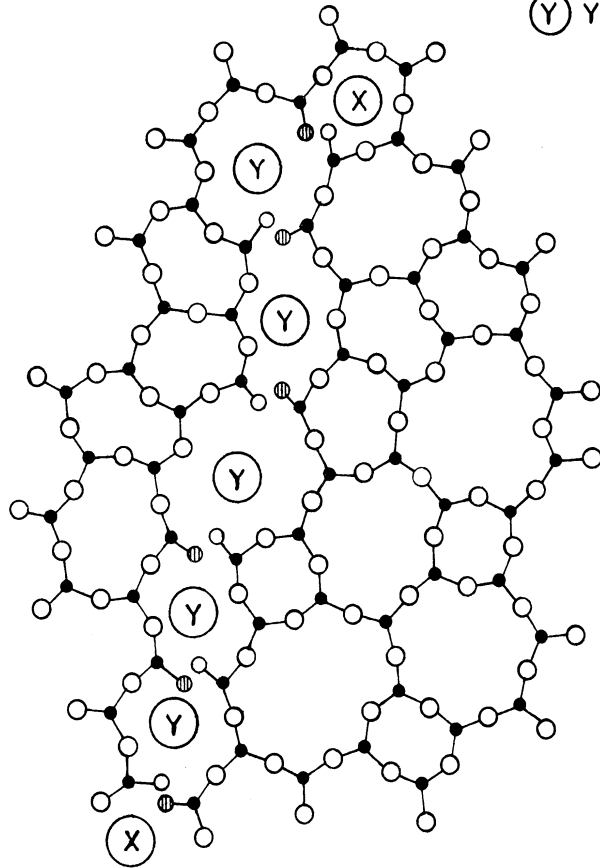


Figure 8

LEGEND

- SILICON
- OXYGEN (WITH SILICON)
- ⊕ ADDED OXYGEN
- ⊗ X ION
- ⊙ Y ION

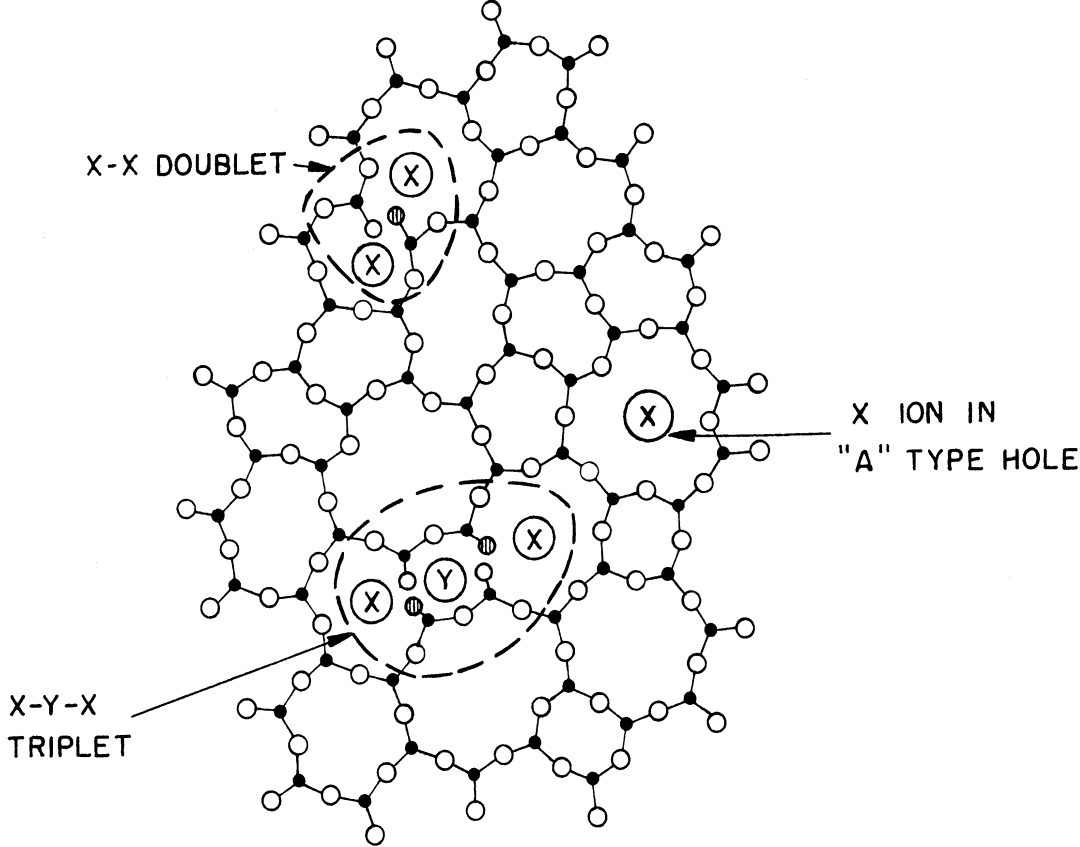


Figure 9