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MEASUREMENTS of some DIELECTRIC and ELECTROLYTIC PROPERTIES of PYREX BRAND GLASS.

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A THESIS PREPARED FOR SUBMISSION TO THE BOARD OF
THE FACULTY OF SCIENCE IN THE UNIVERSITY OF DURHAM,
FOR ADMISSION TO THE DEGREE OF MASTER OF SCIENCE.

The experimental work was carried out in the Research Laboratories of James A. Jobling & Co.Ltd., and the author is indebted to the Directors of this company for their permission to incorporate these experiments in this thesis.

INTRODUCTION.

In spite of recent advances, the present state of our knowledge of the physical nature of the structure of glass lags behind the parallel investigations into the structure of other states of matter.

The measurements of the electrical properties of Pyrex brand glass incorporated in this thesis were carried out in the belief that the study of such properties will increase still further our knowledge of the glassy state and the theoretical arguments expressed are basically in harmony with the prevalent ideas of the structure of glass.

With more particular reference to the latter part of this work where attention is given to the dielectric properties of the glass under examination, it is felt that glass represents an ideal medium for further study of dielectric anomalies in matter. A rigorous investigation of the variation of dielectric properties with composition, temperature and other physical conditions is likely to lead to considerable advances in dielectric theory and also to add to the data on which to build a theory of the structure of glass.

P. L. Kirby.

February 1948.

CONTENTS.

PHYSICAL PROPERTIES OF A TYPICAL BOROSILICATE GLASS.

The general tendency towards a scientific outlook which was one of the causes of the industrial revolution had its influence on the art of glassmaking, an industry which dates back to 2000 BC. In spite of considerable expansion, however, it was not until the twentieth century that progress was made in physical and chemical studies of the nature and constitution of glass. Today, theories of the glassy state are being developed by several groups of research workers, most of whom base their theories on the same simple atomic picture.

As in the case of the advances recently made in our knowledge of the solid and liquid states the use of X-rays in the study of the atomic arrangement in glass marked an important step forward. Evidence of X-ray diffraction patterns of a diffuse nature have been obtained in the case of many different glasses and in 1933 Warren[1] presented a definite picture of the structure of silica glass based on X-ray evidence.

Before this time a number of experimenters had suggested that the component atoms in a glass were joined together in molecular aggregates, each such molecule being identified with a definite chemical compound. This theory was supported and attacked with considerable vigour by opposing schools but has had little lasting significance.

After the announcement of results of X-ray diffraction experiments, Zachariasen[2] published an interesting discussion of the atomic arrangements in glass. He suggested that in view of the diffuse X-ray patterns the atoms must form some continuous three dimensional network. Whilst following no large scale periodicity as in the crystalline state the structure is not entirely random in nature as the internuclear distances vary only over a finite range. It is convenient at this point to confine our attention to a substance containing only two kinds of atoms and which exists as a glass and also in various crystalline modifications. This substance is silica (silicon dioxide, SiO_2) and is the major component of the majority of modern glasses. In the amorphous state, fused silica is believed to consist of a network of silicon and oxygen atoms arranged so that each silicon atom is surrounded tetrahedrally by oxygen atoms and each oxygen is attached to two silicons. Silica also exists in three other major allotropic forms, cristobalite, tridymite and quartz. During X-ray investigations[3] it was found that the first sharp peak in the diffraction pattern for cristobalite corresponded to about the centre of the diffuse peak of amorphous silica and at one time it was thought that silica glass may consist of a structure containing large numbers of crystallites of cristobalite. Further work however, had not supported this contention and it is now believed that the smallest unit which constantly repeats itself throughout the structure is the silicon plus four oxygens - this being too small to qualify the structure for the title of a crystal. Fig. 7 shows the difference between the atomic arrangements in cristobalite and silica. (after p 18)

The essential point in this argument is that the difference between silica in the crystalline and amorphous states is that whilst both consist of similar lattice structures of silicon and oxygen atoms the large scale periodicity characteristic of the former is replaced by a random array in the amorphous state. Extending the field to cover glasses containing other oxides, still having silica as the main constituent, the picture is now that of a random network of silicon and oxygen atoms with the additional types fitting into the interstitial vacancies. Or where the number of additional atoms is considerable, they will modify, by their presence, the original background of the silica network and will, of course, considerably alter the physical properties of the structure.

It is thus seen that a comparison has been drawn between the random network of a glass and the completely regular network of a crystal and it remains to be stated what type of crystal is visualised in this comparison. Unfortunately the classification of crystal types has been rigidly performed by chemists who have been anxious (with considerable justification) to simplify the picture and it is usual to classify a crystal into three main categories, ionic crystals, valence crystals and molecular crystals. It was originally thought that the crystalline silica allotropes were of the valence crystal type in which the silicon and oxygen atoms were held together by "co-valent bonds". This is undoubtedly an over simplified picture and the strong polar characteristics of the silicon atom with four electrons in its outer shell and very small atomic radius suggest that the atomic structure of silica is permeated by strong electric fields. In this case one cannot consider that a silicon atom will exert forces only on the four neighbouring oxygen atoms but rather will there be a field of attractive and repulsive forces permeating the entire structure with the individual atoms lying at points of minimum potential.

When another oxide (say sodium monoxide, Na_2O) is added to the network there will, as has been suggested, be considerable modification. There is little doubt that the sodium atoms will be present in an ionised state presumably due to the ease with which the removal of a single electron from such a large atom can be accomplished. Thus it is believed that in general the sodium atoms will be present in a truly ionised condition together with silicon and oxygen atoms which are much more closely bound. As will be shown later, the oxygen atoms can take part in an ionic conduction process and belief is growing that the essential nature of a glassy structure is that of an ionic array.

Turning now to the materials available for examination it is found that amorphous silica, while very representative of the glassy state, is particularly difficult to use. The amorphous allotrope is only stable at temperatures above 1700°C and if held at a lower temperature will tend to revert to a crystalline form. This is particularly true in the temperature range which is of greatest theoretical significance, thus endowing silica with properties which make it an unsatisfactory material for our purpose. The rate of transformation is, of course, greatly decreased at low temperatures due to its increased viscosity and although thermo-dynamically unstable at room temperature, fused silica will not appreciably alter its form even though left for a very long period. Below 1700°C and down to 1470°C cristobalite is the stable allotrope, giving way to tridymite in the 1470 - 870°C range. Below 870°C quartz is the stable form and is the only completely stable silica allotrope at room temperature.

By adding a relatively small amount of other oxides to silica it is possible to decrease the viscosity at high temperatures so that the glass will remain in a stable amorphous form and the temperature below which the glass will devitrify will be greatly decreased.

The chemical resistant properties of pure silica are still retained in the borosilicate type of glass where the silica content is still high. The structure of such a glass presumably differs only in degree to the structure of amorphous silica thus making a borosilicate glass ideally suited to our purpose. A well known glass, a typical borosilicate type, is manufactured in this country under the name of "Pyrex". The composition of Pyrex brand glass is as follows:

Oxide	% weight.
SiO_2	80.76
B_2O_3	12.54
Na_2O	4. 54.
Al_2O_3	1.92
As_2O_3	.24

It will be seen that the main constituents are silica and boric oxide, together with a smaller percentage of sodium monoxide. Due to the relatively loose binding of the sodium ions it will be found that the soda content is of major importance in a discussion of the electrical properties.

The density of this glass is 2.24 gms/cc at room temperature and it is characterised by a relatively low linear coefficient of expansion, 3.2×10^{-6} per°C over the range 0 - 500°C. The liquidus temperature has been found to be 1064°C. Below this temperature cristobalite is found to separate from the glass at a rate which increases with lowering temperature to a maximum at 900°C. On lowering the temperature still further the increasing viscosity of the glass appears to retard the rate of devitrification and at 700°C the rate of separation of the crystalline phase is very small. The subject has been fully investigated and is reported in Nature by Cox and Kirby.[4]

Until recently it was believed that there existed a transition temperature connected with the variation of certain physical properties of a glass with temperature. There was indeed a definite inflexion point on the graph relating temperature to specific physical properties. Littleton[5] showed however, that if before measurements at any given temperature were made, the glass was held for a sufficient period at that temperature, then the final results gave no suggestion of any transition point. The previous results were due to the fact that this necessary "stabilisation period" is much greater at low temperatures, and if a series of measurements are carried out at various temperatures then an apparent transition will occur at a temperature where the stabilisation period is of the order of the time of measurement in the experiment.

The suggestion that on altering the temperature of a glass a finite period of time must elapse before the glass takes on the physical properties appropriate to the new temperature, is now finding general acceptance. This stabilisation period, which must be intimately connected with the internal viscosity of the atomic structure is an inverse function of temperature. Thus on cooling a sample of glass, even though the rate of cooling through the annealing range is very slow thus preventing the setting up of mechanical strain, because of the absence of temperature gradients, some of the high temperature properties will be "frozen in", and it would require an immense period of time to stabilise glass at normal temperatures. According to the temperature at which samplesof glass have been stabilised it is possible to obtain otherwise similar samples at room temperature having widely different physical propetties. The hypothesis of stabilisation is equivalent to supposing that the structure of glass can, after a suitable period, attain a metastable state characteristic of a particular temperature and ~~is~~ still truly amorphous.

THE CONDUCTION PROCESSES IN GLASS.

Early experiments on electrical conduction in glass enable us to build up a picture of the actual nature of the processes occurring. Experimenters during the last century discovered that it was relatively easy to pass an electric current through glass provided the temperature of the latter is raised to several hundred degrees centigrade. It was found that the nature of the electrodes had considerable effect on the results obtained, and there is ample evidence of various types of polarisation occurring when the applied field is unidirectional. The classical work of Warburg and Tegetmeier[6] at the end of the last century consisted of the passing of an electric current through the walls of a glass tube filled with mercury and maintained at a temperature of two or three hundred degrees centigrade. The observed current very soon decreased to a fraction of its original value. When sodium amalgam was used however, no such decrease occurred. Le Blanc and Kerschbaum[7] found that when a poorly conducting layer of glass which appeared at the anode surface was ground off, the glass conducted as well as before, until again this badly conducting layer was formed. From these experiments the assumption is made that the conduction in these cases is due mainly to the migration of the sodium ions in the direction of the applied field, resulting in a decrease in sodium ion concentration in the region of the anode, unless there is a replacement effect from the anode itself.

The sodium can be replaced by any one of a large number of other metals if these are contained in the anode either as an amalgam or in the fused state. We then find the metallic ion diffusing through the glass in the wake of the sodium ions, the phenomenon varying according to the size of the metallic ion. Lithium, for example, with small atomic volume replaces sodium with no apparent effect on the mechanical structure of the glass. Larger ions, however, are found to cause cracking and the appearance of gas bubbles along the lines of the cracks if the glass is subsequently heated. Other metals permeating the glass from the anode cause a coloration characteristic of the colour of the metal when in a colloidal state.

The qualitative picture of the conduction process occuring in any glass of which sodium is a constituent, is that the silicon and oxygen ions form a random lattice background against which the sodium ions move from one interstitial vacancy to another in the direction of the applied field. It is generally believed that forces acting upon an ion, tending to hold it to a given point in the lattice structure, are much weaker in the case of a sodium ion than for the silicon, boron or oxygen ions. This is ascribed to the larger ionic radius of sodium which, if the centre of the ion is regarded as being the point at which all the charge is concentrated, will cause a greater separation between the centres of, say, a sodium + an oxygen ion than between a silicon and an oxygen ion.

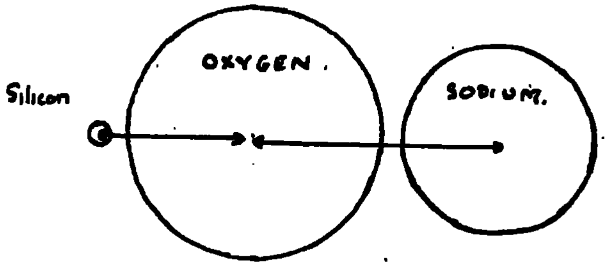


Fig. 1.

There are several experimental facts, however, which suggest that the above picture is over-simplified. For example, if a D.C. potential is applied across electrodes of platinum and a current is passed through the intervening glass then, this current will be observed to decrease over a short period of time and yet the final value so obtained will remain appreciably constant over a much longer period. This final value represents an appreciable current and is not consistent with the view that the anodic layer of glass is being continually stripped of sodium ions . In view of the passive nature of the electrodes we might assume that sodium ions are drifting back into the region of the anode by a process of thermal diffusion, but the current is a measure of the net movement of charge from anode to cathode. Then if we decide that the part played by electronic conduction is small (and this is most probable as there is complete absence of any Hall effect), we are bound to conclude that there is a thermal movement of both positive and negative ions into the anode regions. That is to say, sodium and oxygen atoms diffuse towards the anode in electrically neutral aggregates whilst positive sodium ions travel away from the anode in the direction of the field. This is equivalent to supposing that while sodium ions move towards the cathode, negative (oxygen) ions move towards the anode during the passing of a current through the glass.

This has been investigated in the case of Pyrex glass and it is found that liberation of oxygen at the anode does occur and a large amount of gassing will take place at the anode if a unidirectional current is passed through the glass. In this case both sodium and oxygen ions are important agents in the conduction process. Where the anode is capable of replacing sodium ions into the glass the oxygen ions are notrequired to give up their charge and revert to gaseous molecules, but will remain in the glassy state in combination with the new sodium ions from the anode.

It was hoped to investigate the change in physical properties in the anode layers, with diminished sodium ion content, with particular reference to devitrification. The gassing, however, completely masks any other effect and makes examination of this area rather difficult.

A second experiment was carried out using "replaceable" electrodes of a form of silver paint such that the silver migrated into the glass from the anode thus preventing, to a large extent, the formation of a high resistance layer.

ELECTRICAL CONDUCTION IN PYREX USING "SILVER" ELECTRODES.

Apparatus: A small cube of fireclay was made with two nichrome wires embedded in the clay. The block was dried at 150°C and then fired at 1000°C in an electric furnace. The wires are arranged so as to support a short length of glass rod about 1 cm. in diameter and 3 cms. long. After cutting the rod to the required length the two end faces were liberally coated with liquid burnish silver. This material consists of a suspension of fine particles of silver in a volatile liquid. If the coated rod is now held in a bunsen flame the volatile component evaporates leaving a layer of good conducting silver covering the ends of the rod. The glass can now be placed in between the nichrome wires as shown in Fig. 2.

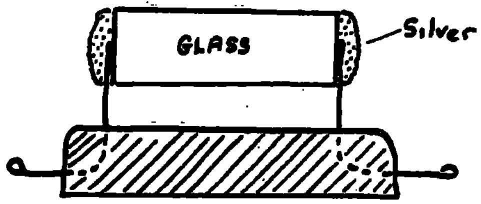


Fig. 2.

Method: This electrode assembly was placed in an electric furnace and the temperature raised to 600°C at which temperature a controller maintained the furnace throughout the experiment. A power-pack giving 450 volts D.C. was connected to the electrodes by way of a milliammeter. On switching on, a current of the order of .015 amps was obtained and it was anticipated that polarisation would soon occur causing a gradual decrease in this current. There was no such decrease, only a slight fluctuation due to variation in the temperature of the furnace, causing variation in the resistance of the glass. It should be noted that it was not possible to run the furnace at a higher temperature as the lowered resistivity of the glass would have allowed a larger current to flow, which in itself would increase the glass temperature resulting in still greater current flow. At 600°C it was possible to obtain equilibrium between the rate of heat input to the glass and the loss of heat to the surroundings in the furnace.

After running for about 20 minutes a slight decrease in the mean value of the current was noticed and this decrease continued until after a period of 3 hours the apparatus was removed from the furnace. It was found that the silver at the anode had almost entirely diffused into the glass (the decrease in effective electrode area accounting for the observed decrease in conductivity), and there was a band of glass which was of a very dark red colour (almost opaque) extending to a depth of 2 or 3 mms. from the anode. This area of glass, the boundary of which is very sharply defined, is coloured with colloidal silver which has migrated into the glass in place of the sodium ions moving towards the cathode. This accounts for the lack of any polarisation in the experiment. By taking into account the quantitative measurements made in this experiment some interesting results can be obtained.

Determination of Ionic Mobility of Sodium ions in Pyrex glass.

A theoretical value for the ionic mobility of the sodium ion can be calculated as follows:

Let n = number of soda ions per unit volume in the glass.

e = charge on each ion.

μ = mobility of the ions.

σ = conductivity of the glass.

These quantities are related by the expression:

$$\sigma = ne\mu. \qquad \text{or } \mu = \frac{\sigma}{n.e}$$

At the temperature at which the experiment was carried out (600°C) the resistivity of Pyrex is $10^{4.17}$ ohm cms. Thus the conductivity will be $10^{-4.17}$ or 6.76×10^{-5} $\text{ohm}^{-1}\ \text{cm}^{-1}$.

The charge "e" on each ion will be assumed to be 4.8×10^{-10} esu or 1.6×10^{-19} coulombs.

The value of "n" is obtained from the density of the glass (2.24 gms/cc) and the percentage weight of sodium oxide present (4.5%). Then the weight of sodium present in 1 cc is

$$2.24 \times \frac{46}{62} \times \frac{4.5}{100} = .079 \text{ gms.}$$

and if Avogadro's number, the number of atoms per gm-molecule is 6×10^{23}, then the number of sodium ions per unit volume is given by

$$n = \frac{.079}{23} \times 6 \times 10^{23} = 1.949 \times 10^{21}$$

Where's (1)

Thus from (1) the calculated mobility is given by

$$= \frac{6.76 \times 10^{-5}}{1.949 \times 10^{21} \times 1.6 \times 10^{-19}}$$

$$= 2.165 \times 10^{-7} \text{ cm/sec/unit voltage gradient.}$$

From the observed depth to which the silver had penetrated (viz. 3 mm in 3 hours) the observed mobility can be calculated. The voltage gradient in the experiment was 150 volts/cm, although during the course of the experiment the voltage will have varied slightly and this must be taken as a maximum value.

$$\text{therefore} \quad = \frac{\text{speed of migration}}{\text{potential gradient}} = \frac{0.1}{3600} \times \frac{1}{150}$$

$$= 1.85 \times 10^{-7} \text{ cm/sec/unit voltage gradient.}$$

Conclusion.

The difference between the observed and calculated values is not excessive in view of the possible voltage fluctuation. The experiment can then be said to give evidence in favour of an ionic conduction process as has been suggested.

The glass rod into part of which the silver had diffused was examined to note any change in physical condition. Under the microscope no change was visible apart from the deep red colour imparted to the glass. In the polariscope the glass at the boundary was in a state of compression. This will have been caused by the differential expansion of the Pyrex and "silvered" Pyrex on cooling from 600°C. In this case the presence of the silver must have increased the coefficient of expansion of the glass.

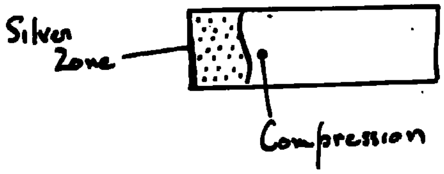


Fig. 3.

EXPERIMENTAL VERIFICATION OF THE ELECTROLYTIC CONDUCTION OF SODIUM IONS THROUGH GLASS.

Introduction.

The following experiment has been described in several text-books as a standard illustration of the conducting properties of a soft soda-lime glass. Usually, however, the experimental details are omitted and the experiment remains on a qualitative basis. It will be shown that with apparatus of a simple nature sodium ions can be transported through the walls of an electric lamp bulb and that the weight of metallic sodium deposited during this process of electrolytic conduction accurately conforms to Faraday's Law.

Apparatus and Method.

The apparatus consists of an iron bath containing a fused salt (in this case a mixture of sodium nitrate and sodium nitrite) into which is placed the lower end of the glass envelope of an ordinary electric lamp. The lamp is connected to the A.C. mains, one of the leads to the filament also being joined to the negative terminal of a high voltage D.C. source, the positive terminal of which is connected to the iron bath. Thus, provided the necessary carrying agents are present, a circuit is completed from the iron bath (anode) through the electrolyte, the glass envelope and the enclosed gas to the filament (cathode). The theory which this experiment is designed to support suggests that in both the electrolyte and the glass the current is due entirely to the migration of sodium ions, whilst within the glass envelope the current flows due to the outward movement of electrons, emitted from the heated filament, under the influence of the electric field.

A small burner of the Meker type is mounted below the iron bath to maintain the mixture of the two salts at about 250°C (this temperature is not critical, and may vary from 150°C to over 300°C the resistance decreasing slightly

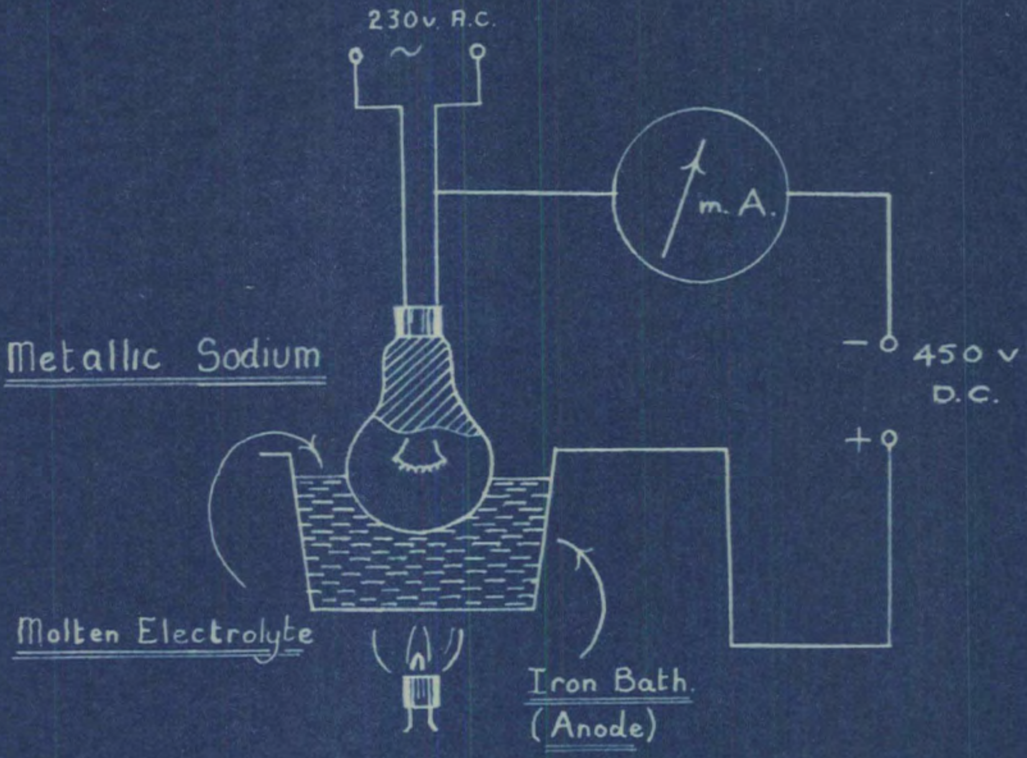


FIG. 4 ELECTROLYSIS OF Sodium Through The Wall Of An Electric Lamp.

with increase in temperature). A eutectic mixture of the nitrate and nitrite of sodium is used in order to keep the melting point low (in this case, 140°C).

It is obviously necessary to ensure that the D.C. source is isolated from the mains supply, and for this experiment a simple power pack was used, utilising a centre-tapped transformer, double wave rectifier and smoothing circuit. The voltage was approximately 450 volts on open circuit, decreasing by about 20 volts at 30 milliamps. The meter used to measure the current was an Avo (model 7) operating on the 100 milliamps range.

The resistance of the circuit depended on the size of the electric lamp and the depth to which it was immersed in the electrolyte. It was eventually found advisable to use a small lamp (rated at 40 watts) and submerge the tip of the bulb no more than one inch below the surface of the molten salts. The sodium salts are first melted and the bulb is then slowly lowered to the above depth, care being taken to keep the thermal stresses on the glass envelope as low as possible. If assembled in this manner the total anode-cathode resistance is found to be of the order of 15,000 ohms, varying according to the temperature and size of the bath, and the type of lamp used.

Verification of Faraday's Law.

As the experiment consists of a process of electrolytic conduction involving a deposition of a metal not, in this case, on the cathode, but on the inner walls of the electric lamp envelope, it was decided to investigate whether Faraday's Laws of electrolysis were upheld. This involved careful weighing of the electric lamp both before and after the electrolysis, and careful measurement of the quantity of electricity flowing. From the chemical equivalent weight of sodium it is estimated that the electrochemical equivalent is approximately

.0002 grms/coulomb. Thus if a current of 30mA. flows for 3600 seconds the weight of sodium deposited will be:

$$30 \times 10^{-3} \times 3600 \times .0002 = 0.0226 \text{ gms.}$$

This amount can be weighed accurately to .0001 gm. on an analytical balance, but allowing for the handling of the bulb during the experiment, the estimated error in weighing is taken as .0005 gm. (half a milligramme).

On placing the weighed bulb into position in the electrolyte and switching on the A.C. and D.C. supplies the current flowing was found to be 31.5 mA. This figure was found to vary throughout the experiment (due to variation in temperature of the electrolyte and the glass) and readings were taken every five minutes. The maximum current recorded was 34.2 mA. and the average 33.0 mA. The estimated maximum error is 0.5 mA. This current was passed for 1 hour allowing a possible error of 10 seconds in measuring this period.

Calculation of Results.

Original weight of bulb = 38.4826 gms.
Final " " " = 38.5108 gms.
Increase = 0.0282 gms.
Average current = 33.0 milliamps.
Time = 3600 seconds.

$$\text{E.c.e. of sodium} = \frac{.0282}{3600 \times 33.0 \times 10^{-3}}$$

$$= .0002373 \text{ gms/coulomb.}$$

The calculated maximum error for this quantity is ± 0.000008 gms/coulomb, and thus the result of the experiment can be stated to be:-

E.C.E. of Sodium = .000237 ± .000008 gms/coulomb.

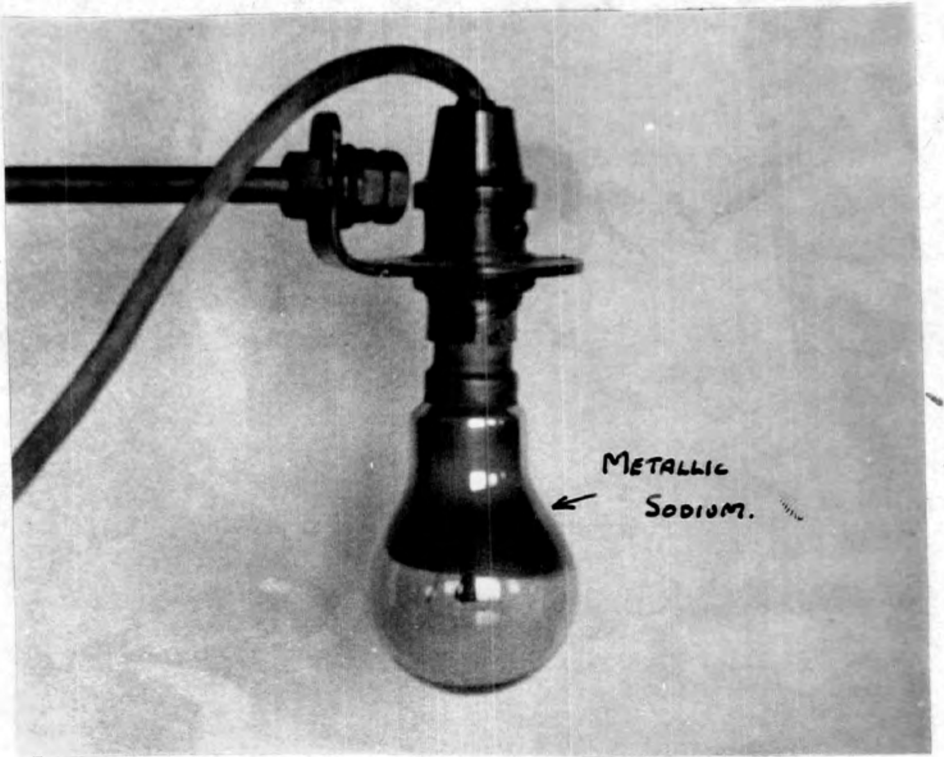


Fig. 5.

Two views of the electric lamp at the end of the experiment showing the deposit of sodium on the upper parts of the bulb.

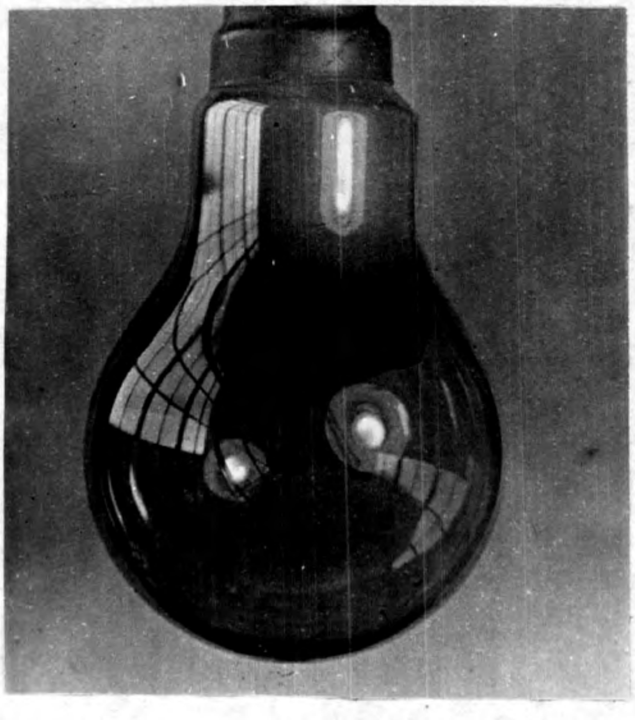


Fig. 6.

Conclusion.

The accompanying photograph shows a 40 watt bulb after the above treatment. It will be noticed that the deposit of metallic sodium is only to be found on the upper parts of the bulb. Evidently the sodium atoms evaporate on reaching the inner surface and are deposited on the cooler parts of the bulb. In spite of this phenomenon there was no pronounced sodium glow in the bulb either during or following the experiment.

The Handbook of Chemistry and Physics gives a value of 0.0002383 gms/coulomb for the e.c.e. of sodium, a value which lies well within the range of the error in the above experiment.

It is thus seen that Faraday's Law applies to the conduction of electricit through glass, setting forward further evidence in support of the theory that electrical conduction puocesses in glass are mainly ionic.

ELECTRICAL CONDUCTION IN RELATION TO THE STRUCTURE OF GLASS.

It is now desirable to try and obtain an explanation of the mechanism of the electrolytic conduction occurring in glass, based on modern hypotheses of the atomic structure of glasses. Recent investigations of certain physical properties of glasses (viscosity, devitrification) and the use of X-ray analysis has greatly increased our knowledge of the atomic arraggement characteristic of the glassy state. Although no unified theory exists most physicists interested in the subject base their ideas on the same simple picture which will be outlined briefly. It is our intention to take this admittedly simplified picture and to apply certain equations obtained from Maxwell-Boltzman statistics and to show that theoretical equations concerning electrical conductivity so obtained, are very closely supported by experimental results.

If we regard silica as the main constituent of the glass (as it is in the case of Pyrex glass) then the majority of atoms in a given volume of glass will be mainly silicon atoms and oxygen atoms. In any of the crystalline forms of silica these atoms are arranged in a symmetrical pattern characteristic of the crystalline state. In the case of amorphous silica it is assumed that although the silicon-oxygen bonds are arranged so that there are four such bonds associated with a silicon atom and two with an oxygen, there is no large-scale repetition or symmetry. This difference between, say, quartz and amorphous silica is shown in Fig. 7. It will be noticed that in a two-dimensional representation the silicon atoms are shown with only three bonds.

To obtain a similar picture in the case of Pyrex we must now add boron atoms and sodium atoms. Both of these are regarded as fitting into the above silicon-oxygen lattice at points where the spacing is sufficiently large,

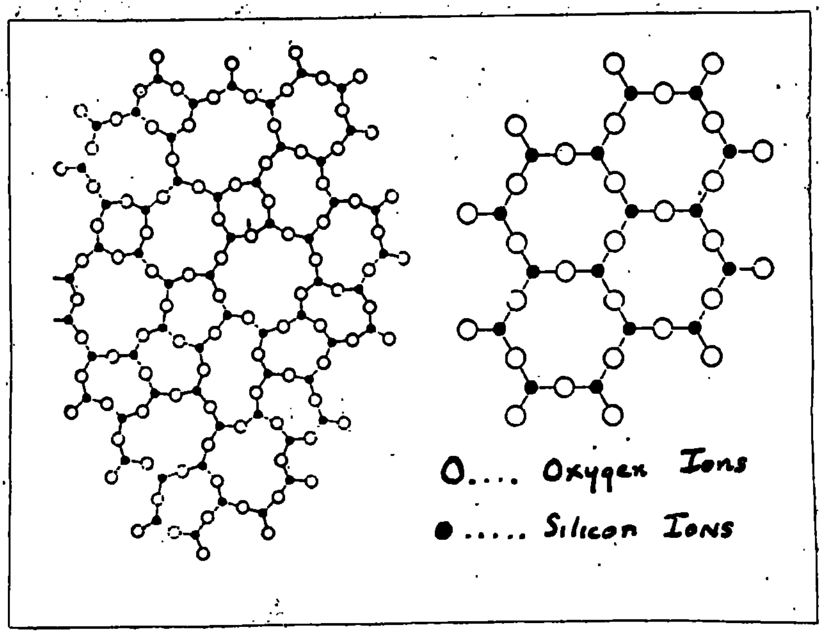


Fig 7.

A two-dimensional representation of silica in the amorphous and crystalline states.

and it is usual to regard the sodium atoms as being held with relatively weak interatomic forces, with the boron atoms next, while the silicon-oxygen bond is the strongest. Not least among the reasons for making this assumption are the facts concerning electrical conductivity mentioned previously. Even though there is only 4% sodium oxide present in Pyrex there is ample evidence that the sodium ions are almost entirely responsible for the transport of electric charges through the glass.

We do not, of course, suggest that any one atom of silica is held by "bonds" to two oxygen atoms, but rather that the whole structure of atoms is permeated by a "field" of attractive and repulsive forces and that any one atom will tend to lie at a point where the field due to all other atoms has minimum potential energy.

Modern theories of molecular structure suggest that the shape of the potential energy function as we approach an atom is of the form shown in fig. 8. The point corresponding to minimum potential represents the equilibrium position of a neighbouring atom. This atom will have a certain vibrational energy and will oscillate about its equilibrium position. When a number of ions are concerned the individual curves combine as in Fig. 10.

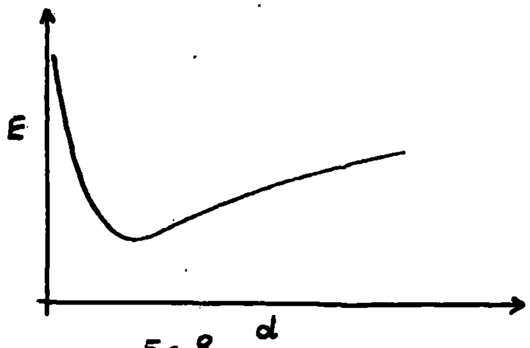


Fig 8.

When we consider a case as in Fig. 9, where a sodium atom occupies a position in a suitable hole in the silica lattice it is held in this position by interatomic forces. In this case the atom will be in an ionised condition

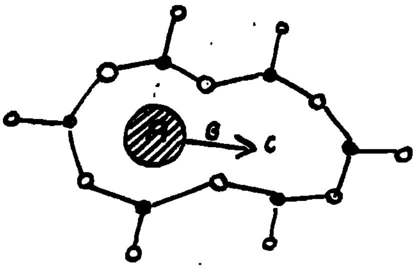


Fig. 9

and thus apart from the lack of symmetry the glass bears considerable similarity to that of an ionic crystal. If we now consider a large number of sodium ions oscillating about similar equilibrium positions throughout the glass we can apply Maxwell-Boltzman statistics to a discussion of the distribution of energy amongst these ions. Boltzman's theorem states that the number of ions whose energy lies between E and E + dE is

$$A e^{-\frac{E}{kT}} . dE$$

where A is a constant depending on the total number of ions in the system. It is then possible to calculate the probability of one ion jumping from one equilibrium position to another neighbouring vacant site. The ion in Fig. 9., in such a case, will move along a path AC and the distribution of potential along the path will be as shown in Fig. 10.

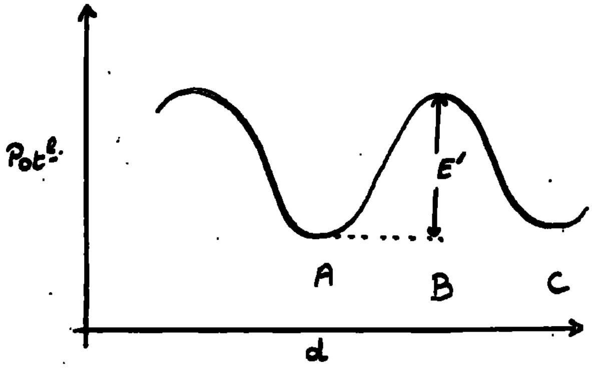


Fig. 10.

So if an ion has sufficient energy (E') it will pass through the saddle point at B. This energy, E', is the activation energy in the case of a uniform (eg. crystal) structure, and in the case of a glass we can say that the average height of the potential barriers in the silicon-oxygen lattice is a measure of the activation energy for the diffusion of sodium ions.

In the case of an ionic crystal it is necessary at this point to define the direction of motion of these diffusing ions with respect to the axes of the crystal. Where the substance is in the glassy state, however, there is equal liklihood of ionic diffusion in any direction. Thus the partition functions for the distribution of energy in the various directions of motion will all be equal.

We will now proceed to calculate an expression for the electrical conductivity in terms of atomic constants.

Consider a Sodium ion situated at a point in the lattice vibrating about its equilibrium position. The probability of it having energy between E and E +dE is

$$A.e^{-\frac{E}{kT}}.dE \quad \text{- - - - - - - - - - - - - - - -} \quad (1).$$

Suppose that the activation energy for the diffusion of this ion is E'(on the average this is the same for all directions in the glass), then the ion must have energy equal to or greater than E' before it can jump to another equilibrium position. From equation (1) the number of ions of energy greater than E is

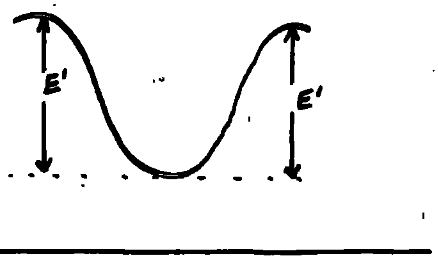


Fig. 11.

$$A\int_{E'}^{\infty} e^{-\frac{E}{kT}}.dE$$

and the fractional number of such ions is

$$\frac{A\int_{E'}^{\infty} e^{-\frac{E}{kT}}.dE.}{A\int_{0}^{\infty} e^{-\frac{E}{kT}}.dE} = \frac{A.(-kT)\left[e^{-\frac{E}{kT}}\right]_{E'}^{\infty}}{A.(-kT)\left[e^{-\frac{E}{kT}}\right]_{0}^{\infty}}$$

$$= e^{-\frac{E'}{kT}}.$$

The probability of one ion jumping to another equilibrium position in unit time is thus $e^{-\frac{E'}{kT}}$.

If an electric field of intensity F is applied to the lattice then the distribution of potential is now of the form shown in Fig. 12. In the direction of the field the barriers are reduced by an amount equal to $F.e.\frac{\delta}{2}$ where e is the ionic charge and $\delta/2$ the distance from the equilibrium position to the saddle point.

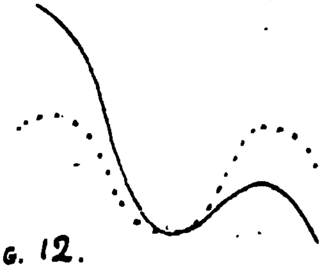


FIG. 12.

The probability of an ion jumping in the direction of the field is thus

$$e^{-\frac{E' - Fe\delta/2}{kT}}$$

and the probability of a jump in a direction against the field

$$e^{-\frac{E' + Fe\delta/2}{kT}}$$

Therefore the total increased probability of a jump in the field direction is

$$e^{-\frac{E'}{kT}}.\left\{e^{\frac{Fe\delta}{2kT}} - e^{-\frac{Fe\delta}{2kT}}\right\} = e^{-\frac{E'}{kT}}.\ 2\sinh\frac{Fe\delta}{2kT} \ldots\ldots (2.)$$

For all normal fields it is found that $Fe\delta \ll kT$ and equation (2) reduces to

$$e^{-\frac{E'}{kT}}.\ \frac{Fe\delta}{kT} \ldots\ldots\ldots\ldots\ldots\ldots (3.)$$

When a sodium ion with charge e does move through a distance δ an electric polarisation of $e\delta$ is obtained. If "n" is the number of sodium ions per unit volume then the current density

$$i = n.e\delta.\ e^{-\frac{E'}{kT}}.\ \frac{Fe\delta}{kT}$$

$$= F.\ \frac{ne^2\delta^2}{kT}.\ e^{-\frac{E'}{kT}}$$

and the conductivity is given by

$$\sigma = \frac{i}{F} = \frac{ne^2\delta^2}{kT}.\ e^{-\frac{E'}{kT}} \quad \text{- - - - - - - - - -} \quad (4.)$$

If we are to regard this expression as a prediction of the variation of electrical conductivity with temperature it is necessary to ascertain the constancy of other terms as the temperature is varied.

Presumably "δ" the distance between adjacent sodium ion sites will vary in a manner similar to thermal expansion, i.e. $\delta = \delta_0(1 + \alpha T)$. This increase will be relatively small although there is considerable evidence that the thermal expansion of glass increases considerably at temperatures above the usual range of measurement (i.e. above the softening point).

As was shown in an earlier section, there is reason for supposing that only a proportion of the sodium ions take part in conduction at lower temperatures. It has been suggested that n may vary according to

$$n = N e^{-\frac{E'}{kT}}$$ where N is the total number of ions.

In this case our expression (4) will still be of the form

$$\sigma = \frac{A'}{T}.\ e^{-\frac{\theta}{T}} \quad \text{- - - - - - - - - -} \quad (5.)$$

with an alteration to the value of the constants.

It has also been suggested by Jost (in the case of ionic crystals) that the activation energy E' is not constant but contains a linear term aT. If such a term is added to the power of the exponential

$$\sigma = \frac{A'}{T} \cdot e^{-\frac{E' + aT}{kT}}$$

the expression also reduces to the form of equation (5) with a new constant.

$$\sigma = \frac{A'}{T} \cdot e^{-\frac{a}{k}} \cdot e^{-\frac{E'}{kT}}.$$

Then we conclude that equation (5) should give a reasonably accurate picture of conductivity-temperature relationship and go on to compare this theoretical equation with practical results.

EXPERIMENTAL VALUES FOR THE SPECIFIC RESISTANCE OF PYREX CHEMICAL RESISTANT GLASS.

Introduction.

We will interest ourselves in the not inconsiderable temperature range from 0°C to 1200°C. The accepted value for the volume-resistivity of Pyrex at room temperature is 10^{14} ohm-cms and this value will be assumed in this work as the necessary high-voltage equipment was not available to check this figure. It will be noted, however, that this is the true volume resistivity not the surface resistivity, as this latter may be of much lower value at normal temperatures, and is greatly dependent on relative humidity.

The specific resistance of Pyrex has also been measured in the temperature range from 500°C to 800°C (by J.F. Stirling, of these laboratories) and it thus remains to measure the resistivity from 800°C to 1200°C.

An empirical law known by the names of its proposers Rasch and Hinrichsen predicts a straight-line graph between the log. of the resistivity and the reciprocal of the absolute temperature ($\rho \propto e^{\frac{c}{T}}$), but several writers have shown that this usually holds for only small temperature ranges. As an example, figures will be given for a borosilicate glass (measurements made by J.T. Littleton) where it will be seen that there is considerable deviation from this linear relationship at higher temperatures. Pyrex glass also does not accurately follow the law of Rasch and Hinrichsen and it will be shown that the equation (5) deduced from theoretical considerations in the previous section gives much closer agreement with the observed results.

MEASUREMENT OF THE SPECIFIC RESISTANCE OF PYREX CHEMICAL RESISTANT GLASS IN THE REGION 800 - 1200°C.

Apparatus and Method.

Considerable modification of the apparatus used at lower temperatures is required, due mainly to the great reduction in the viscosity of the glass as the temperature rises. The sample of glass must be completely contained in an insulating mould such that its shape does not alter throughout the experiment. It was decided to build a small thick walled fireclay crucible with a thermocouple embedded in the wall and the glass held in a cylindrical shape in the centre. The lower electrode is a sheet of platinum lying through the walls of the crucible and the upper electrode is a heavy block of heat-resisting steel.

The glass sample is placed in the crucible in the form of a short length of glass rod of slightly greater length than the depth of the crucible. The upper electrode is placed in position and the assembly put into the furnace and brought up to 1000°C. At this temperature the weight of the upper electrode forces the glass to take up the exact shape of the crucible, any excess glass being squeezed out between the steel and the fireclay.

As shown in Fig. 13 this results in the glass being of slightly different shape to the interior of the crucible and the correction is applied as follows:

If the resistance of the section A be P ohms and that of B, Q ohms then the measured resistance between the electrodes is P + Q. If ρ is the specific resistance

then $Q = \frac{\rho L}{\pi R^2}$ and $P = \frac{\rho l}{\pi r^2}$

$$\text{therefore } P + Q = \left(\frac{\rho L}{\pi R^2} + \frac{\rho l}{\pi r^2}\right)$$

$$\text{therefore } \rho = \frac{P + Q}{\frac{L}{\pi R^2} + \frac{l}{\pi r^2}}$$

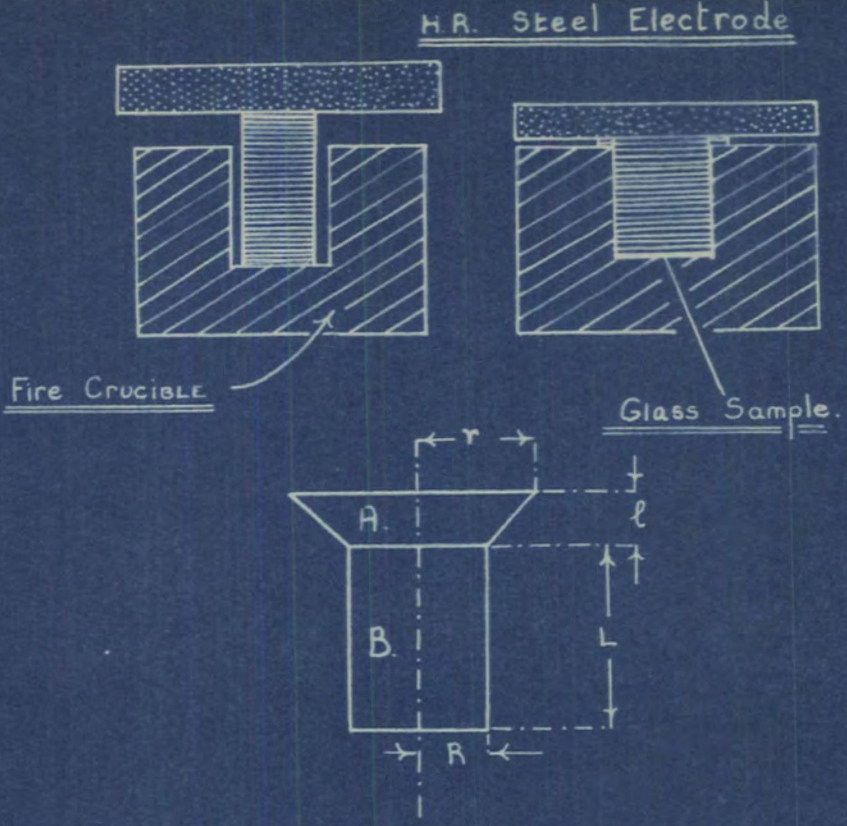


Fig. 13 SHAPE (EXAGGERATED) OF GLASS DURING EXPERIMENT

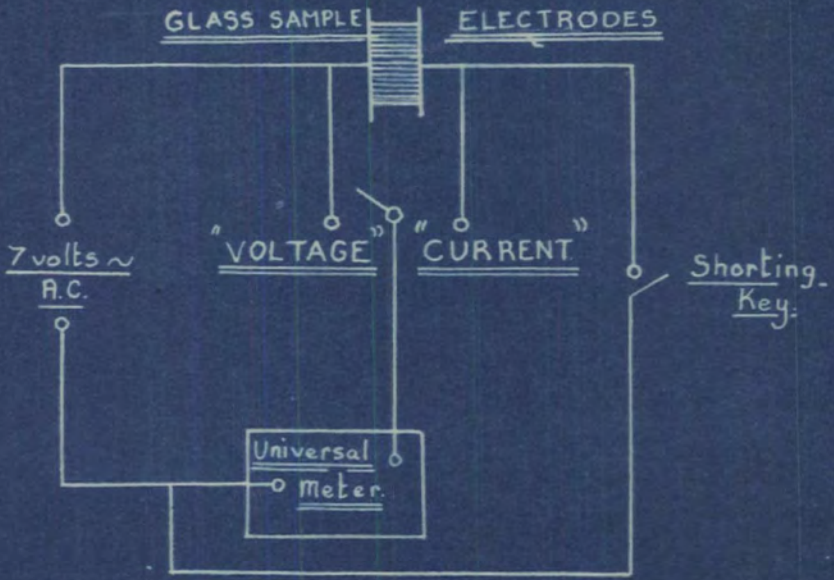


Fig. 14 CIRCUIT FOR MEASURING RESISTIVITY AT HIGH TEMPERATURES

After the completion of the experiment the upper electrode was removed and $\frac{L}{\pi R^2}$ was found to be 1.91 whilst $\frac{l'}{\pi r^2}$ was 0.03.

Thus $= \frac{P + Q}{1.94}$ and from the measured values of P + Q, the resistivity was determined at various temperatures.

The apparatus is contained in a Globar furnace where the heating occurs mainly by radiation from the elements lining the furnace roof. The thermocouple was embedded in the crucible very near to the glass sample, and the thick walls of the crucible together with the heavy steel electrode provided sufficient lagging so that the temperature of the sample could be slowly altered by varying the ambient temperature of the furnace, which depended on the current passing through the Globar elements. This latter was regulated by means of an external rheostat, the maximum current being about 15 amps.

Experimental Procedure.

A circuit was set up as shown in Fig. 14 so that both the applied voltage and the resulting current could be measured on a Universal Avo-meter. The source was a 7 volt transformer operating from the mains and there were slight voltage fluctuations throughout the experiment. To overcome this the voltage was read immediately before switching over to take a current reading.

All voltage measurements were taken with the transformer "on load", i.e. with the shorting switch closed. With the A.C. source operating at 50 cycles per second there was no evidence of any polarisation phenomenon occuring.

The apparatus was finally adjusted and enclosed in the furnace whose temperature was raised to 1050°C in approximately 90 minutes. This temperature was maintained for 10 minutes and a voltage current reading taken. The temperature was then lowered at a rate of not more than 20°C per minute to 1000°C, a series of voltage current readings being obtained. As the glass was now entering into the temperature zone where devitrification occurs the cooling rate was increased decreased to 10°C per minute down to 800°C and then the glass was rapidly heated up to 1000° again. Readings of both voltage and current were now taken as the furnace temperature rose up to 1200°C.

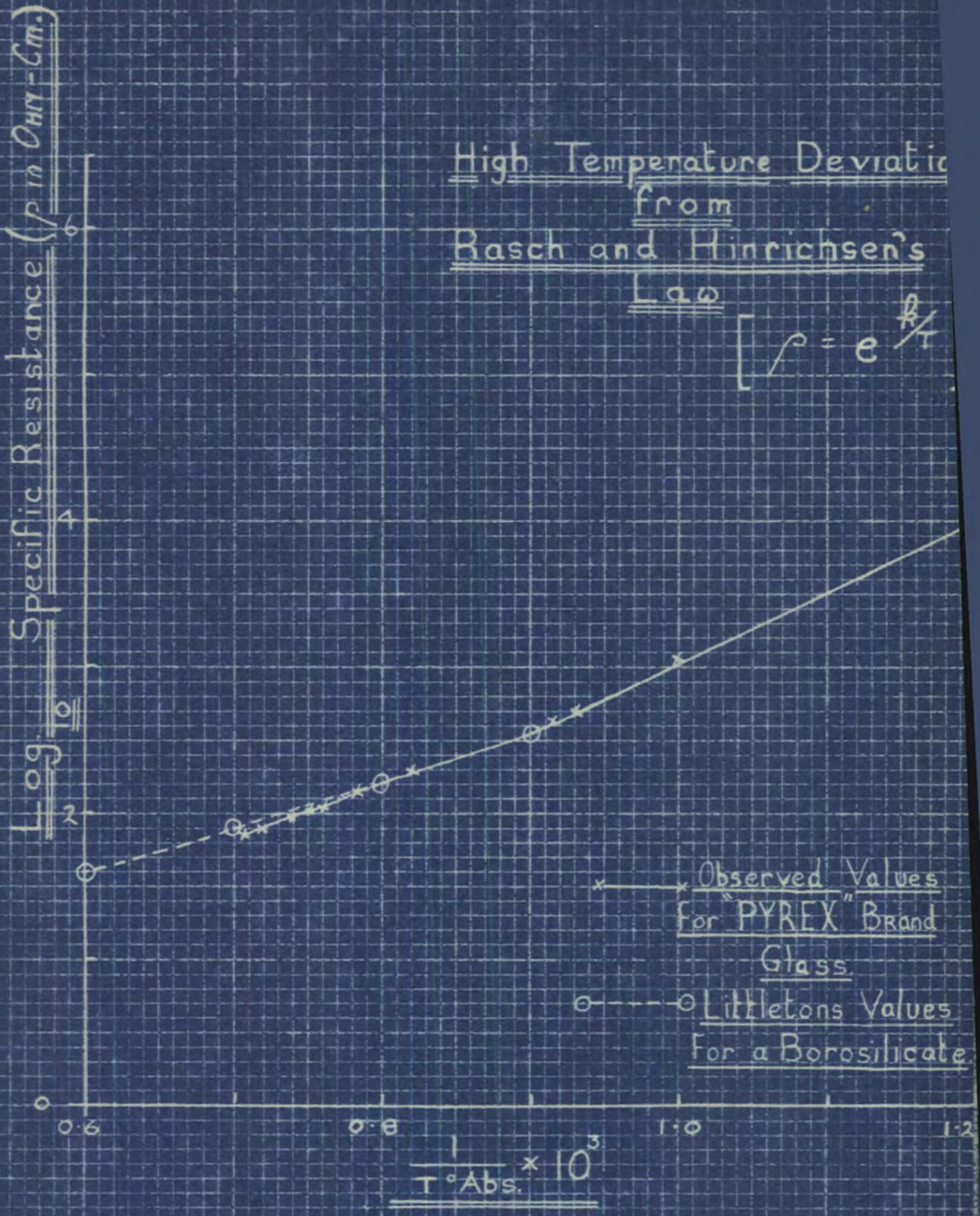
The furnace was allowed to cool overnight and the apparatus was then removed for examination. The upper electrode was removed and the dimensions of the sample were measured - this involved measuring the main cylinder of glass and also the "overflow" caused by the weight of the upper electrode. From these measurements a value of the specific resistance of Pyrex brand glass was obtained at all temperatures between 800°C and 1200°C.

Conclusion.

The results obtained are shown on the graph in Fig. 16, and it will be noticed that they bear great similarity to those obtained by Littleton for an unspecified borosilicate glass. This latter must then be chemically similar to the glass used. Fig. 17 gives the specific resistance at all temperatures up to 1200°C and Fig. 18 shows that the linear relationship proposed by Rasch and Hinrichsen is closely followed at low temperatures.

Fig. 19 shows the excellent agreement between the observed values and the values calculated from the equation derived in the previous section. This agreement holds good from room temperatures up to nearly 1200°C.

Occasionally workers in this field have found that a discontinuity occurs in the log ρ against $\frac{1}{T}$ graph at some temperature which was arbitrarily described as a "transition" temperature. However it is now generally accepted



High Temperature Deviatio
from
Rasch and Hinrichsen's
Law
[ρ = e^k/T
Log10 Specific Resistance (ρ in Ohm-Cm.)
6
4
2
0
0·6
0·8
1·0
1·2
1/T°Abs. × 10^3
Observed Values For "PYREX" Brand Glass.
Littletons Values For a Borosilicate.

Fig. 16

that if the temperature of any glass is changed suddenly a period of time must elapse before the properties of the glass take on the values appropriate to the new temperature, and this stabilisation period is a reciprocal function of temperature. This phenomenon results in the appearance of fairly sharp chang in direction of the graph of properties, such as electrical resistivity, against temperature. Such a transformation point has been shown to be due to the variation of stabilisation period and depends on the rate of heating and cooling of the glass. Littleton has shown that if the heating rate is gradually decreased, the discontinuity in the curve disappears until eventually a curve truly representative of the properties of the glass is obtained. It is found that there is a real curvature present over any wide range of temperatures and the law of Rasch and Hinrichsen is applicable only to small changes of temperature.

THE DIELECTRIC PROPERTIES OF PYREX.

It is generally appreciated that the study of the electrical conduction processes in glass is of relatively recent advent whilst for the greater part of the eighteenth and nineteenth centuries glass was considered a typical insulator with good insulating properties. Early electrostatic apparatus made considerable use of glass as an insulating medium but the Leyden jar (discovered in 1745) was the first apparatus to make direct use of the high dielectric strength and dielectric constant of glass.

It was during experiments on the charge and discharge of Leyden jars that Franklin (in 1748) first discovered any "anomalous" properties of dielectrics such as glass, but it was not until the time of Hopkinson (c.1880) that any systematic study was made of this phenomenon. Recently a very thorough investigation of the occurrence of absorption in the charging of condensers with a glass as the dielectric medium, and the appearance of residual charge, was made by Guyer.[8] Recent research shows that dielectrics can be classified into two main types, those where the anomalous charging current is reversible and those where at least part of this charging current is not apparent on discharge. Glasses are generally of the first type, the current flowing during charge (after the first large Maxwellian displacement current has died down) being made up of two components, the true D.C. conduction current and the absorption current. On discharge there is only the absorption current which decays in a manner similar to the decay for the charging current. The difference between the charging and discharging currents at any time should thus be a constant and equal to the conductivity current.

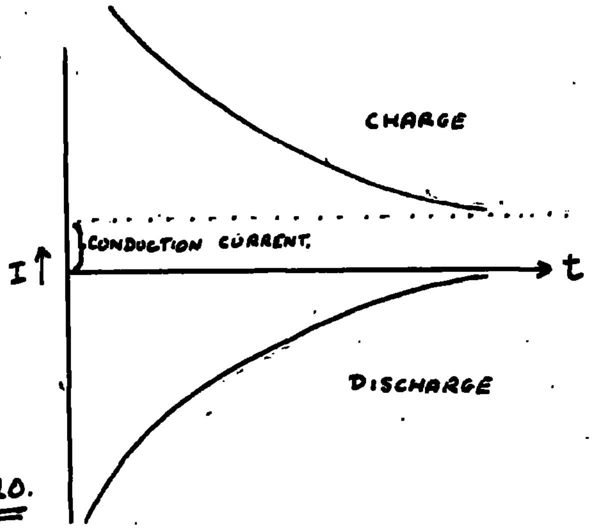


Fig. 20.

Other dielectrics are found to have an irreversible component in the charging current which does not appear during discharge.

Turning our attentions to the case where an alternating potential is applied to the glass condenser we find that the anomalous charging current gives rise to an alteration of phase angle between the applied field and the total current in the condenser. As will be seen later these anomalous properties give rise to an inphase component of current which causes power loss within the material. The appearance of this "Siemans heat" was first noted by Siemans in 1864 in ordinary electrical condensers. Since this time many workers have attempted to explain the phenomena of dielectric absorption (c.f. Whitehead - lectures on "Dielectric Theory and Insulation"), and in most cases have linked it intimately with the anomalous properties discovered on applying D.C. potentials to a dielectric, i.e. residual charge, etc.

In some cases such explanations have been based on the behaviour of atoms or even electrons within the atom whilst the earlier theories were based on Maxwell's original picture - the "double-layer" dielectric. In accordance with the treatment of conduction earlier in this work we will hope to show that all the main properties (anomalous and otherwise) can be explained by using a similar atomic picture of glass to that used previously.

Fundamental Equations.

Before any attempt is made to obtain a theoretical explanation of the known facts concerning dielectrics it is necessary to indicate thefundamental equations on which the following work will be based.

The original Maxwell theory was based upon four equations which are applicable to an uncharged isotropic medium and which inter-relate the electric and magnetic field vectors, with the electric and magnetic polarisation intensities and the electric current.

In a dielectric medium the Maxwellian displacement D is given by the sum of the electric field and the field due to the polarisation, or separation of charge, within the dielectric.

$D = E + 4\pi P$ where P is the polarisation set up in the materials.

The first electromagnetic equation is: $\mathrm{div}\, D = 0$.

Another equation involves the vector J, the current per unit area. It is usual to define two constants, the conductivity σ, and the polarisability α, of the medium, which are related to the applied field by the equation

$$\begin{aligned} P &= \alpha E. \\ J &= \sigma E. \end{aligned} \qquad \ldots\ldots\ldots\ldots (1).$$

It has been found that these two properties, conductivity and polarisability are not independent of frequency as suggested by the Maxwell theory and it will be one object of the following treatment to explain this variation when the dielectric material under consideration is glass.

For any given physical condition of the dielectric there is another useful tensor defining the ratio between the total electric displacement and the applied field, this is the dielectric constant, k:-

$$D = k.E.$$

This from equation (1)

$$k = 1 + 4\pi\alpha \qquad \ldots\ldots\ldots\ldots (2).$$

In this equation α is the large scale or macroscopic polarisability, and it can be shown that this is not the same as the polarisability of a small cavity (for example, a sphere) withih the material and, of course, it would be the latter which would govern the behaviour of a single atom or ion. It can be shown that the necessary correction (the "local field" correction) is of the form

$$\alpha = \frac{n\alpha_0}{1 - \frac{4\pi}{3}.n\alpha_0}$$

where α_0 is the polarisability of a single ion or atom where there are n ions per unit volume. The derivation of this equation involves the assumption that the "cavity" occupied by an ion is spherical in shape.

A further observation to be made is that in Maxwells equations there are two distinct currents,

$$J\ (= \sigma E) \quad \text{and} \quad \alpha \frac{dE}{dt}.$$

The latter is the polarisation current and is out of phase with the applied field (when the latter is a sinusoidal oscillation) by an angle of 90°. We can eliminate the latter by using a complex conductivity σ_c where:

$$\sigma_c = \sigma + j\omega\alpha.$$

Then the current given by $J = \sigma E$ is the inphase current and is instrumental in causing power loss within the material. The polarisation current, on the other hand is at 90° tothe field and does not contribute to any such energy absorption.

Now we are in a position to examine a circuit such as that in fig. 21 where the current throughout is continuous. In the dielectric there are the

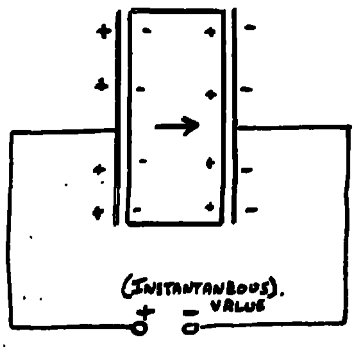


Fig. 21.

two types of current, conduction current and polarisation current. We will see however, that on consideration of the ionic and electronic movements which give rise to such currents it is no longer possible to asign to them causes which differ in any physical respect other than the phase angle between these currents and the applied field. This movement of electric charges within the material involves the setting up of polarisation by the polarisation current, but the total current flowing is a function of the movement of the ionic charge and the resolution of this displacement current into inphase and out of phase components is quite arbitrary.

The displacement current is, of course, at right angles to the actual displacement vector

$$i_D \propto \frac{dD}{dt}$$

and in a general case this displacement vector will not be inphase with the field E.

It is convenient to use an Argand diagram to denote the phase of the various vectors concerned. In the case of a condenser with capacity C and zero conductivity an applied voltage E (the rms value of $E_0 .\cos wt$) causes a current I to flow through the condenser where I is the rms value of $I_0 .\cos (wt + \frac{\pi}{2})$. The current vector leads the voltage vector by an angle $\frac{\pi}{2}$. The magnitude of the current is given by

$$|I| = E\omega C.$$

or by using the vector notation and the "j" operator we denote the phase difference of 90° by saying $I = jEwC$.

However, in all known dielectrics the resultant current leads the voltage by an angle ϕ, where

$$\phi < \frac{\pi}{2}.$$

This current can be resolved into an inphase and out of phase component, the latter will be the ideal charging current and the former the conduction current. It is invariably found that the inphase component of current is greater than would be accounted for by normal D.C. conductivity, and this excess which (being an inphase current) will contribute to further power loss within the material, is called the dielectric loss current. There seems to be little doubt that this dielectric loss is the same phenomena as the anomalous charging current previously discussed in connection with dielectric absorption. This absorption current gives rise to an increase in both components as shown in Fig. 22.

I_c = charging current.
I_D = dielectric loss current.
I_R = D.C. conductivity current.
I_A = Absorption current.

The presence of I_A causes an increase of CB in the inphase and AC in the out of phase currents.

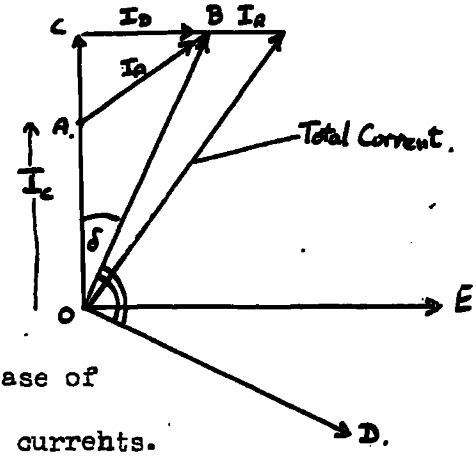


Fig. 22.

Glass as a Dielectric.

Returning now to our atomic structure of glass which we consider to consist of an irregular lattice structure of silicon and oxygen ions. In the case of Pyrex glass there are also a number of boron ions, small and incompressible and also a smaller number of much larger (but more compressible) sodium ions which lie in pockets of the lattice. At normal temperatures all the ions possess given amounts of thermal energy as expressed by laws of the kinetic theory, but the liklihood of any ion moving away from its equilibrium position and penetrating the surrounding potential barrier is relatively small. We have seen that on the application of an electric field to such a lattice the sodium ions are more likely to jump barriers and cause a current to flow than any of the other ions, and we can assume that the resultant forces tending to hold an ion to its equilibrium position are smaller in the case of the sodium ions. When we now come to consider the possible causes of the anomalous dielectric properties which are possessed by most glasses at room temperature we could not assume that the sodium ions will again play the major role were it not for the known fact that "low-alkali glasses" are notably less susceptible to dielectric loss than glasses with an appreciable sodium content. Pyrex brand glass has a very low conductivity at room temperature but the dielectric loss is much greater than in the case of some insulators. If we regard the volume conductivity as negligible, then only a negligibly small number of ions will actually jump from their interstitial positions. The currents associated with the dielectric properties of the glass must then be due to the movement of charged ions within the lattice. As the sodium ions are in general more loosely bound and will hence be likely to move further than other ions under the application of a uniform electric field, it is probably that the dielectric displacement current is made up mainly of sodium ion movement. However, as no ion actually breaks free from the bonds holding it to its equilibrium position it is not vitally necessary to stipulate which ions are concerned.

It is necessary at this point to recognise three parameters intimately connected with the movement of ions within the lattice. Each ion besides being endowed with charge "e" also has a mass "m", and thus on application of an electric field displays inertia. The ion is also acted upon by a number of forces the effect of which is to keep the ion oscillating about the same equilibrium position. When the ion undergoes displacement in an electric field we will assume the retaining force tending to hold the ion to its equilibrium position to do so according to Hooke's Law. Suppose the force per unit displacement is "f", we are now in a position to define the equation of motion of the ion under an applied alternating field. It will be found that the expression is similar to that obtained by Lorentz for the motion of electrons displaced by an electric field from their normal position - and by using such a picture Lorentz was able to explain the phenomena of absorption and dispersion in insulators. In this latter treatment it is found necessary to stipulate an arbitrary "frictional term", a function of the velocity of the moving electron.

There is no doubt that at optical frequencies this type of electronic polarisation will occur and the Lorentz theory gives an adequate explanation of anomalous properties without resort to quantum mechanics. However, we must now decide what other types of polarisation can possible occur in the glassy state at frequencies below the optical range.

Pyrex chemical glass transmits rays of wavelength up to 2.8μ, where there is an absorption band. There is further transmission up to 3.3μ, but from this wavelength throughout the entire infra-red spectrum there is complete absorption. It is generally assumed that in thisregion the incident electromagnetic radiation is setting up forced vibrations of certain ions with respect to the ionic lattice, and the fact that all wavelengths greater than 3.3μ are absorbed indicates that the structure of glass is far more complex than, say, certain crystals which have transmission bands in the far infra-red.

Turning now to the longer electromagnetic radiations of "radio" frequency, we find that most glasses are considered fairly typical dielectrics at normal temperatures. Any absorption bands must be due either to ions or ionic aggregates of much greater mass or much smaller force constant than those giving rise to infra-red absorption. We will see shortly that an absorption peak occurs at frequency ω_0, where

$$\omega_0 = \sqrt{\frac{f}{m}}$$

where m is the mass and f the force constant of the ion concerned. It will be remembered that of all the constituents of Pyrex glass, the sodium ions are more loosely bound than any other. Thus the force per unit displacement will be less for the sodium ions, and it may be that the displacement of these ions is the major causes of dielectric absorption in the radio frequency spectrum.

It is now necessary to look for further possible types of polarisation which could occur in a glassy structure. This is of particular importance in view of the fact that there is reason to believe that the relaxation frequency, ω_0, for one particular type of polarisation lies at the very lowest electrical frequency, of the order of only a few cycles per second. That this could be due to ionic displacement is hardly credible as the force constant would have to be so very much less than in the case of those ions causing absorption at infra-red frequencies.

The occurence of dispersion caused by molecular dipoles has been studied by Debye and the following argument shows that there is something akin to a dipole in the random network of ions in a glass. Let us consider one particular sodium ion A carrying unit positive charge, this ion is held at

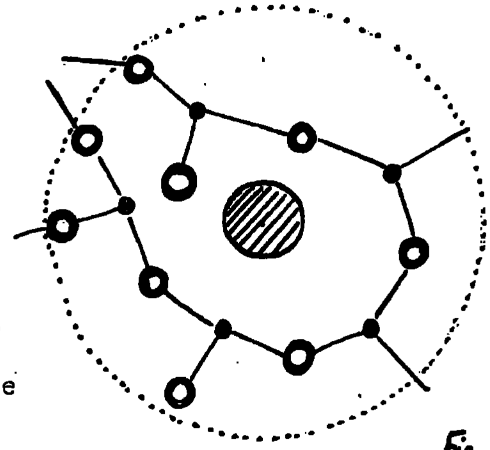


Fig. 23.

its equilibrium position by the forces of repulsion and attraction of neighbouring ions. If we regard the dotted circle in Fig. 23 as representing the "sphere of influence" of ion A then all the other ions in this circle are responsible for the above forces acting on A. These other ions will be in the main either silicon ions (Si^{++++}) or oxygen ions (O^{--}). In order that the complete random lattice be electrostatically neutral there must be two oxygen ions for every silicon, and "half" an oxygen ion for every sodium ion. Thus in the circle in Fig. 23 there will be oxygen atoms to neutralise the silicon ions plus sufficient to neutralise the sodium ion A. It is suggested that the distribution of the negative ions concerned will not necessarily be symmetrical within this unit although it is neutral electrically. Thus this ionic cluster will have a finite dipole moment. The total electric moment over the entire volume of glass is zero, but on the application of a field of intensity E, an ionic cluster whose dipole moment is M will experience a couple C, given by $C = EM \sin \theta$. when lying at an angle θ to the field.

In an alternating field this dipole will oscillate, the amplitude depending on the applied frequency and the physical properties of the cluster. It seems probable that the natural frequency of vibration would be considerably less than that of a single ion owing to the greater inertia of the complete cluster. Thus at frequencies much lower than in the case of ionic polarisation it is possible to pass through a transition region where a type of polarisation (dipole) ceases to occur.

Having enumerated the possible causes of electrical polarisation we can now discuss the effect of these phenomena on the dielectric properties, with particular reference to frequency variation. It will be remembered that the Maxwell theory gives no account of the variation of dielectric constant with frequency. At frequencies in the radio band any electronic displacements will occur instantaneously and there will be only negligible phase difference between the applied field and the movement of the electrons. For the present we will only consider the type of ionic or dipole movements previously mentioned. When referring to the mass of an ion and the restoring force constant "f" it will be born in mind that these quantities can refer equally to linear ionic displacements and to angular rotation of an equivalent dipole. In the latter case "f" is defined as the restoring torque per unit displacement and "m" is the moment of inertia.

Derivation of Dielectric Constant in steady field.

If an applied field E displaces an ion (charge e) by an amount x. then $E_e = fx$.

The polarisation P associated with this displacement is Nex where N is the number of ions per unit volume.

From the equation $D = E + 4\pi P$

we have $D = E + 4\pi Nex. = E + \frac{4\pi NEe^2}{f} = E\left(1 + \frac{4\pi Ne^2}{f}\right)$

and dielectric constant $k = 1 + \frac{4\pi Ne^2}{f}$

When the applied field at alternating $E = E_0 \cos \omega t.$ the polarisation may or may not be set up depending on the frequency w.

On deriving the equation of motion of a glassy ion in an alternating field it will be seen that the phenomena is one of forced vibration. At very low frequencies, well below the natural frequency of vibration given by

$$\omega_0 = \sqrt{\frac{f}{m}}$$

the ion will move with the field, there will be no appreciable lagging and the polarisation will attain its full value.

If the applied frequency is increased to ω_0, we would expect the amplitude of the oscillations to increase and theoretically would attain an infinite value. Quite obviously the maximum attainable amplitude for any ion is limited by the presence of neighbouring ions. In his theory of absorption Lorentz was also faced with this problem in so far as it affected the motion of electrons, and he arbitrarily added a frictional term proportional to the velocity, to the equation of motion. A lucid account of the development of this theory is given by Seitz (Modern Theory of Solids) but this work involves only the macroscopic polarisability without the local field correction. On the other hand H.A. Wilson (Modern Physics) derives an expression giving the true polarisability of a charged particle constrained under Hooke's law forces in an alternating field. The dielectric constant is given by

$$k = 1 + \frac{Ne^2}{f - \frac{Ne^2}{3} - m\omega^2}$$

This involves no "frictional term" and at resonance, $f = mw^2$ and the formula no longer holds.

A more correct picture of the amplitude limiting conditions is probably obtained by assuming that the ion moves in S.H.M., through its equilibrium position but as it reaches the extremity of its motion the force constant "f" increases considerably. The ions will not oscillate in S.H.M., and the solution of the equation of motion when "f" is made a function of the displacement "x", becomes complicated.

Recently, other workers, have attempted to substantiate the "frictional term" in the Lorentz theory of electronic displacement and have shown that a lower limit to this term can be obtained by assuming that the friction on the oscillating electron is caused by radiation damping. The value of this term can be obtained from classical theory although it is usually found that the damping caused by radiation at optical frequencies is masked by the much greater damping caused by collisions.

In our case where we are interested in the periodic displacement of charged particles of at least atomic dimensions the damping of the forced vibration can be assigned almost entirely to collisions with other ions. When such a collision occurs then an interchange of energy will take place, and on the whole the particles which are the major cause of the ionic polarisation will have greater energy than the surrounding (more closely bound) ions, in the lattice, and thus will tend to give up energy to the lattice ions. In particular if the sodium ion, or some ionic cluster centered around a sodium ion, is vibrating in an alternating electric field its energy of vibration will be greater than the corresponding energies for the silicon and oxygen ions. Thus there will be a continual loss of energy on the part of the sodium ions when collisions with the other lattice ions occur. This argument justifies the idea of a damping action and if we make the assumption that the motion of an ion in an applied alternating field is simple harmonic, then the following equation represents the motion of the ion. The frictional force is included and made proportional to the velocity.

$$m\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + fx = -eE_0e^{j\omega t}$$

and the solution is
$$x = \frac{-eE_0 e^{j\omega t}}{f - m\omega^2 + j\omega\gamma}$$

The current per unit area is found

$$I = -Ne\frac{dx}{dt} = \frac{Ne.\ j\omega e E_0 e^{j\omega t}}{f - m\omega^2 + j\omega\gamma} = \frac{Ne^2.\ j\omega E_0 e^{j\omega t}.}{e^{j\phi}\sqrt{(f-m\omega^2)^2 + \omega^2\gamma^2}}$$

$$= Ne^2.\ \frac{\omega E_0 e^{j\omega t}.\ e^{-j(\phi+\frac{\pi}{2})}.}{\sqrt{(f-m\omega^2)^2 + \omega^2\gamma^2}} \qquad \text{where } \tan\phi = \frac{\omega\gamma}{f - m\omega^2}$$

and the complex conductivity σ_c is dervied from

$$\sigma_c = \frac{I}{E_0 e^{j\omega t}} \qquad \therefore\ \sigma_c = \frac{Ne^2.\ \omega.\ e^{-j(\phi+\frac{\pi}{2})}.}{\sqrt{(f-m\omega^2)^2 + \omega^2\gamma^2}}$$

The true conductivity and polarisability can be obtained from this

$$\sigma_c = \sigma + j\omega\alpha.$$

$$\therefore\ \sigma = \frac{Ne^2.\omega.\sin\phi.}{\sqrt{(f-m\omega^2)^2+\omega^2\gamma^2}} \quad \ldots\ldots\ldots\ldots (4.)$$

$$\text{and} \quad \alpha = \frac{Ne^2.\cos\phi}{\sqrt{(f-m\omega^2)^2+\omega^2\gamma^2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5).$$

The angle ϕ represents the phase angle between the applied field and the resulting ionic motion.

The variation of σ, α and ϕ are shown in Fig. 24, ω_0 is the natural freqnency of vibration of the ion and is given by

$$\omega_0 = \sqrt{\frac{f}{m}}$$

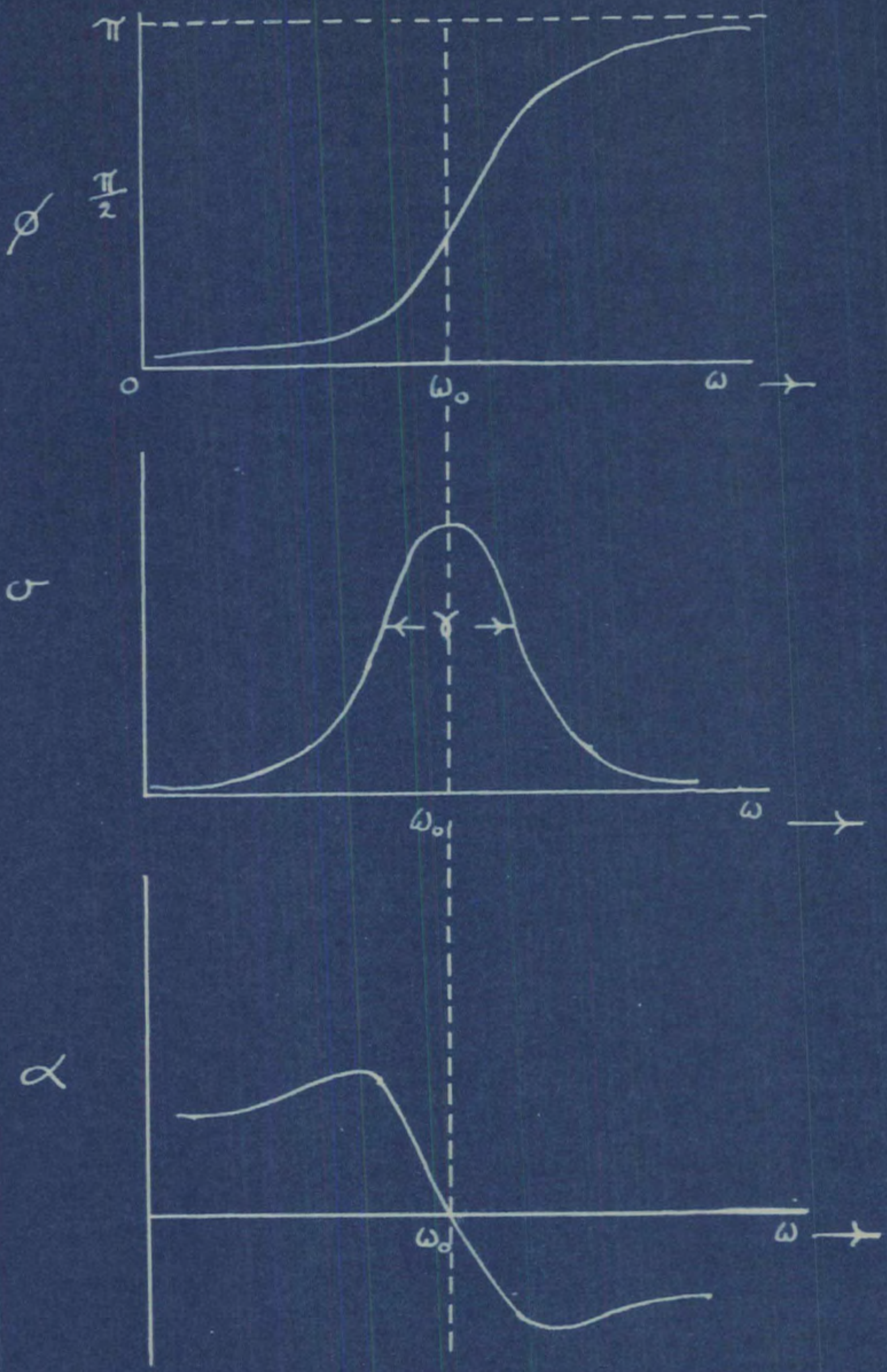


Fig. 24 Variation of Phase Angle φ, Conductivity σ and Polarisability α with Frequency, Due to Ionic Displacement

The dielectric constant k is found to decrease with increasing frequency and is unity when $\omega = \omega_0$

The physical interpretation of these results is in accord with certain experimental data although there is very little data available concerning the dielectric properties of Pyrex glass over sufficiently complete frequency and temperature ranges.

At low frequencies the polarisation of the material attains its maximum value due to the movement of the ion being practically in phase with the field. The current associated with this displacement lies vectorially at an angle $\frac{\pi}{2}$ to the displacement itself and therefore the current is almost entirely wattless. This is seen from the fact that the in-phase conductivity is zero. The high positive value of the polarisability involves a large value for the dielectric constant.

As the applied frequency is increased the displacement begins to lag behind the field, the phase angle reaching $\frac{\pi}{2}$ when $\omega = \omega_0$. At this point the current due to the displacement is entirely in phase with the field and the losses (given by σ, the conductivity) are a maximum. The polarisability is zero and thus the dielectric constant is unity.

On increasing the frequency still further the phase angle increases and approaches the value π asymptotically. At this stage the amplitude of the forced vibration will be decreasing and the displacement current will be lagging further behind the applied field resulting in decreased power losses. The polarisability is now negative and the dielectric constant approaches a low value.

This variation in dielectric properties refers only to one type of polarisation. In actual fact at high radio frequencies the polarisation due to electron movement will still be complete thus increasing the dielectric constant. Only at optical frequencies will absorption bands be caused by electron phenomena. Thus over an extremely large frequency spectrum the dielectric constant will be expected to vary as in Fig. 25. Absorption maxima will occur at the centre of the changing zones as before.

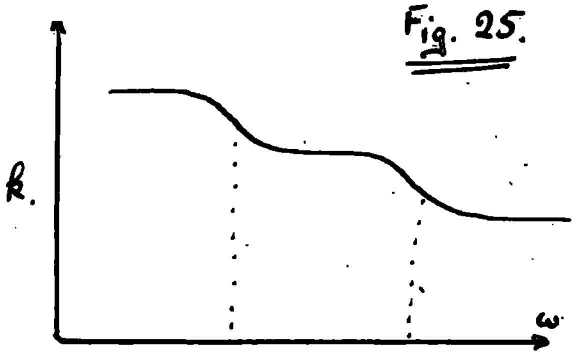
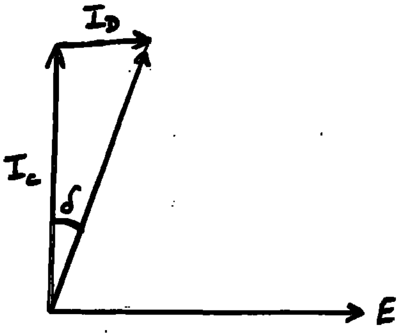


Fig. 25.

The losses are seen to depend upon the quantity σ, the in-phase conductivity. In normal practice the loss occurring in a dielectric is measured by the loss angle of the material "δ". The connection between σ and δ can be derived as follows.

Let the dielectric be placed between the plates of a parallel plate condenser and let us substitute a pure capacity C and pure resistance R.



On applying a voltage V to this circuit

$$I_D = V/R.$$

$$I_c = V\omega C.$$

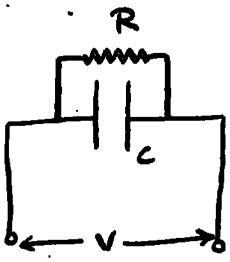


Fig. 26.

therefore $\tan\delta = \frac{I_D}{I_c} = \frac{1}{\omega CR}$

now if σ is the conductivity then $R = \frac{d}{\sigma A}$

where d is the thickness and A the area of this condenser. Also

$C = \frac{kA}{4\pi d}$ where k is the dielectric constant.

Then $\tan\delta = \frac{1}{\omega C R} = \frac{1}{\omega \cdot \frac{kA}{4\pi d} \cdot \frac{d}{\sigma A}}$

$$= \frac{4\pi\sigma}{\omega k} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6.)$$

As w increases from a frequency well below to a frequency above a resonance point the variation of tan δ can be found by combining the variations of w, k and σ given by equations (4) and (5). The general shape of the tan δ - w curve is similar to that for the variation of σ with frequency.

Fig. 27.

The whole series of changes occurring in dielectric properties can be illustrated by referring to the Argand diagram of Fig. 28. As ϕ varies from 0 to π due to frequency variation the vector A B swings round. The amplitude is proportional to the displacement current I. The charging current reaches a value appropriate to k = 1 when $\phi = \frac{\pi}{2}$ and the inphase component is a maximum. This is practically the same frequency as would make tan δ a maximum.

Temperature Variation of Dielectric Properties.

Most of the following discussion will be based on the variation of the force constant "f", with temperature where this term refers to the displacement of the ion or dipole causing the predominate amount of polarisation. This variation can be discussed in terms of the modern theory of solids. The force of interaction between two atoms is usually quoted as being made up of a repulsive and attractive term,

$$F = \frac{a}{r^x} - \frac{b}{r^y}$$

where r is the interatomic distance and a, b, x and y are constants The index in the denominator of the repulsive term,

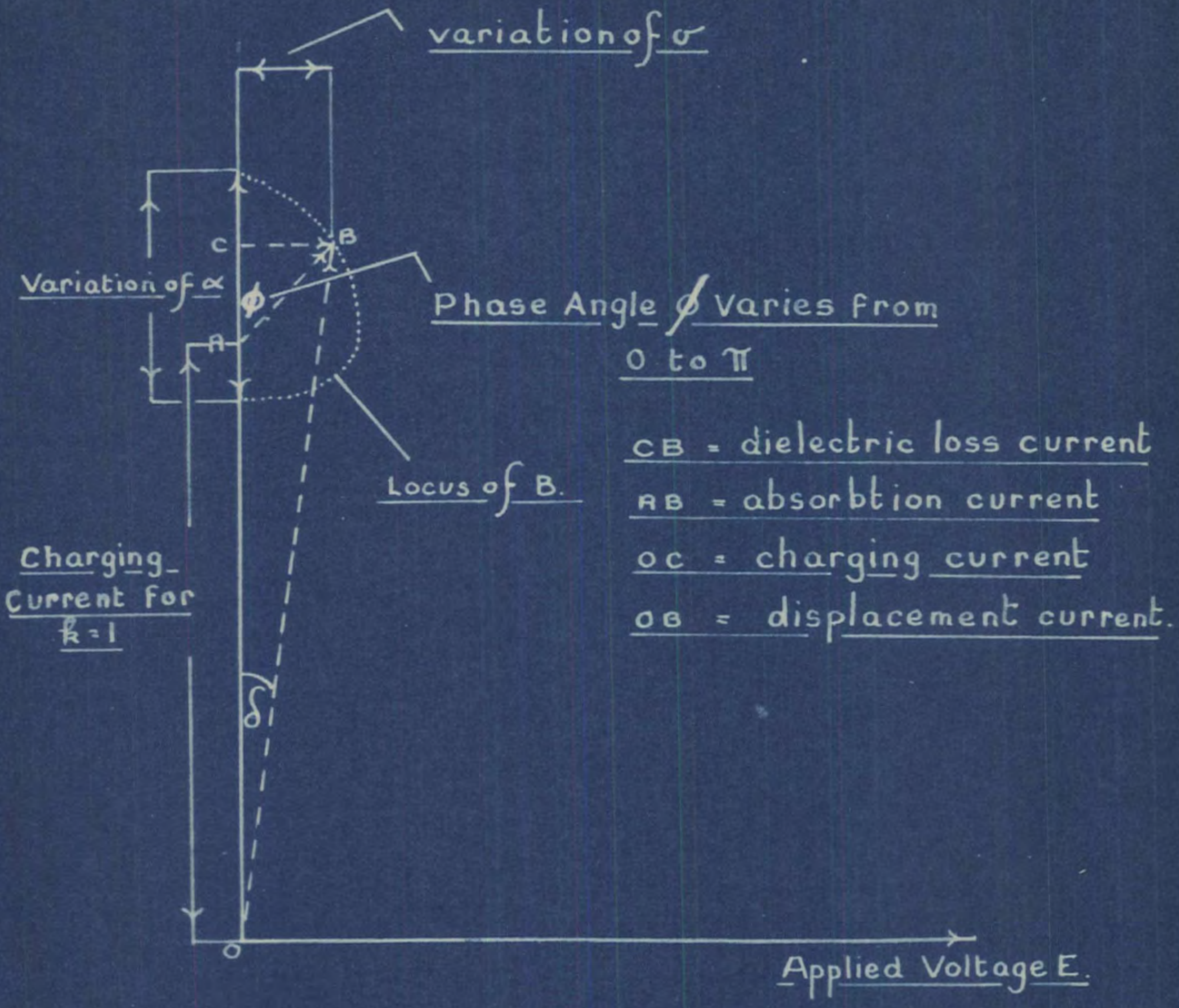


FIG. 28.

Variation of φ, α and σ with frequency showing resultant variation of tan δ.

"y", is greater than the index "x".

It is usual to assume that in the random lattice structure any given ion will oscillate about an equilibrium position in S.H.M., where the force constant is given by the vector sum of the reactions between it and neighbouring ions. Obviously, however, these neighbouring ions cannot be considered to be at rest but will themselves oscillate with amplitudes which are temperature dependent. As the temperature increases then the amplitudes of all the vibrating atoms will increase. Thermal expansion will be accounted for by a small increase between the equilibrium positions. The ion under consideration will now oscillate with greater amplitude due to its increased thermal energy but with the greater degree of approach of neighbouring ions and the resulting greater effectiveness of the "repulsion" terms, the resultant forces acting upon the ion will be increased.

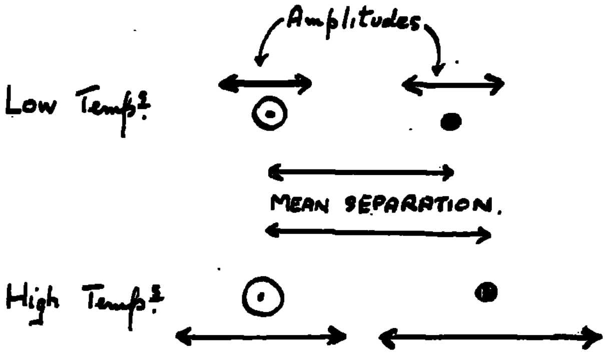


Fig. 28.

As the relaxation frequency is dependent on the term "f" it is to be expected that the former will increase with temperature as in Fig. 29. Thus the change in dielectric constant will occur at higher frequencies for higher temperatures.

This effect is entirely due to variation of relaxation frequency $\omega_0 = \sqrt{\frac{f}{m}}$ where f increases with temperature.

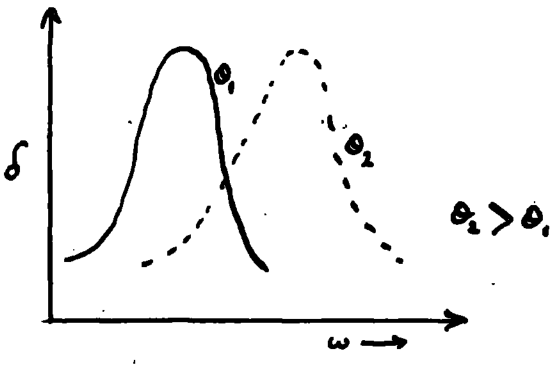


Fig. 29.

However on the low frequency side of the relaxation frequency this variation of force constant has the effect of decreasing the value of the dielectric constant if the temperature is increased due to the appearance of "f" in the D.C. equation

$$k = 1 + \frac{4\pi N e^2}{f}$$

The effect of increasing the temperature is illustrated in Fig. 30, where $\theta_1 < \theta_2 < \theta_3$ and the permittivity - temperature curve is given in Fig. 31. In the succeeding section an account is given of the temperature variation of dielectric constant for Pyrex glass. The shape of the curve obtained is in close agreement with the predicted result, and is shown in Fig.**33**.

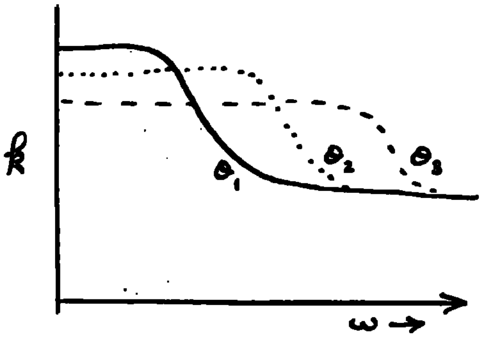


Fig. 30.

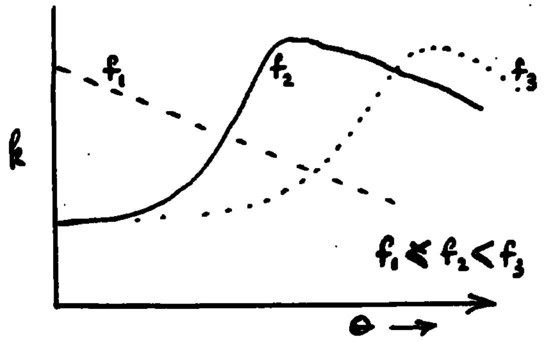


Fig. 31.

VARIATION OF DIELECTRIC CONSTANT OF PYREX BRAND GLASS WITH TEMPERATURE.

Introduction.

The theoretical discussion incorporated in this work requires an experimental investigation of the variation of Specific Inductive capacity of Pyrex with increase in temperature.

The following experiment describes how this was done using a simple four-condenser bridge energised from a low power 1,000 cycle source with the test electrodes enclosed in an electric furnace.

Apparatus.

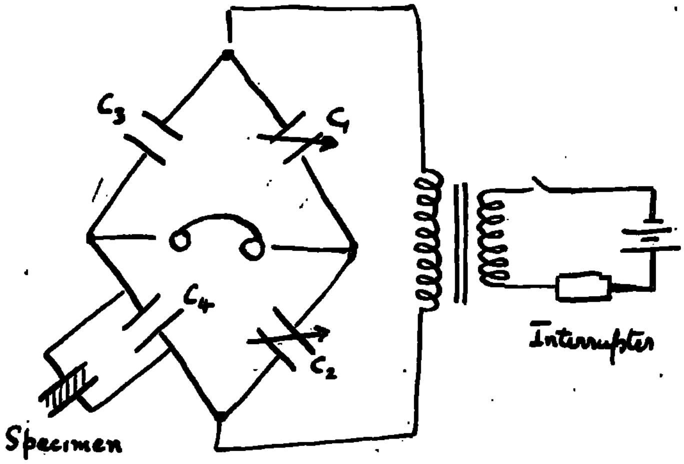


Fig. 32.

The circuit of the bridge is as shown, C_1 and C_2 are mounted on the same spindle so that as C_1 increases, C_2 decreases, while C_3 and C_4 are standards.

The C_1 , C_2 combination is calibrated for use with C_3 and C_4 so that the value of the capacitance of the specimen (in parallel with C_4) can be read directly. The apparatus operated satisfactorily and gave sharp null-points, but it was found that a resistance in parallel with C_4 (even with a value of over 10,000 ohms) caused a flow of current through the detector when the capacities were balanced. This made the null point difficult to obtain and if the magnitude of such a resistance was lowered a point was reached where readings were unobtainable.

As the conductivity of the glass increases rapidly with temperature such a resistive component will be encountered in the experiment when the temperature of the glass is increased and ~~i~~t was found impossible to obtain readings with this apparatus above 500°C.

An attempt was made to balance out this conductivity current by placing a variable resistance across C_2. However, it was found that this balancing operation depended on the capacity ratio of C_2 to C_4 and an unlimited number of balance points could be obtained. Nevertheless without using more complicated apparatus the temperature range from room temperature up to 500°C was investigated.

The leads from either side of C_4 were taken through the refractory door of a small electric furnace to the specimen of Pyrex glass. The latter measured 8 cms. x 7.6 cms. and was .203 cms thick. The opposite surfaces were coated with silver burnish paint which was then baked at 600°C to render it conducting. The leads were then brought into firm mechanical contact with the two silvered surfaces.

Method.

The capacitance of the leads was found to be 6 micro-microfarads and this quatity was subtracted from all subsequent readings. A chromel-alumel thermocouple was arranged to lie near to the electrodes and was connected to a Cambridge recorder giving the temperature in °C to ± 5°C.

Readings of the capacity were taken with increasing and decreasing temperatures up to about 500°C, and the results obtained are shown on the accompanying graph, fig. 33. To calculate the dielectric constant it was necessary to obtain the theoretical vacuum capacity of the electrodes

$$C = \frac{kA}{4\pi d} \qquad \text{where } A = 8 \times 7.6 = 60.8 \text{ sq. cms.}$$

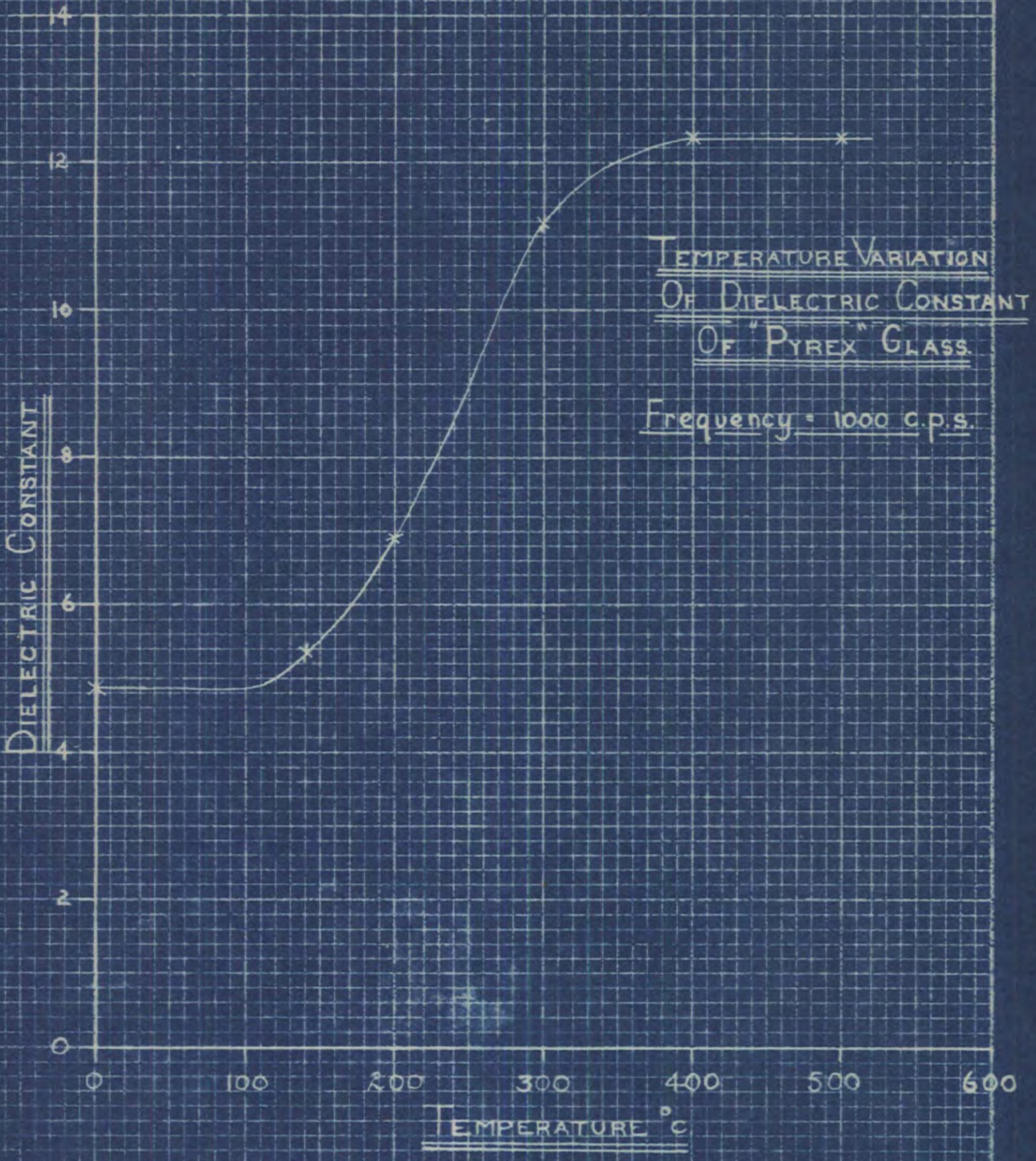
$$d = .203 \text{ cms.}$$

Thus when $k = 1$, $c = \frac{60.8}{4\pi .203} = 23.8$ e.s.u. $= \frac{23.8}{9 \times 10^{11}} = 26.5\,\mu\mu\text{F.}$

Measured value of C at 20°C $= 125\,\mu\mu\text{.F.}$

Therefore $k = \frac{125}{26.5} = \underline{\underline{4.72.}}$

The results of the experiment show an increase in dielectric constant of Pyrex glass from 4.7 to 12 over the temperature range 0°C to 400°C, at a frequency of 1000 c.p.s. It will be seen that such an increase is expected from the preceding theory. From Fig. 31, it would be expected that a lower frequencies the inflection point on the dielectric constant - temperature curve (maximum on the loss angle - temperature curve) will occur at lower temperatures. Thus at room temperature the resonance frequency for this predominant type of polarisation must occur at a frequency well below the above 1000 c.p.s. In this connection is quoted a result obtained by Hopkinson. At a frequency of 7.3 c.p.s. the capacity of a glass condenser was found to be approximately twice what it was at a frequency of 100 c.p.s. Also, the curve in Fig. 34 shows that all the available data records a decrease of power factor with frequency at room temperature for Pyrex glass. This suggests that the relaxation frequency at room temperatures is well below the 50 c.p.s., this latter being the lowest frequency for which data is available.


TEMPERATURE VARIATION OF DIELECTRIC CONSTANT OF "PYREX" GLASS.

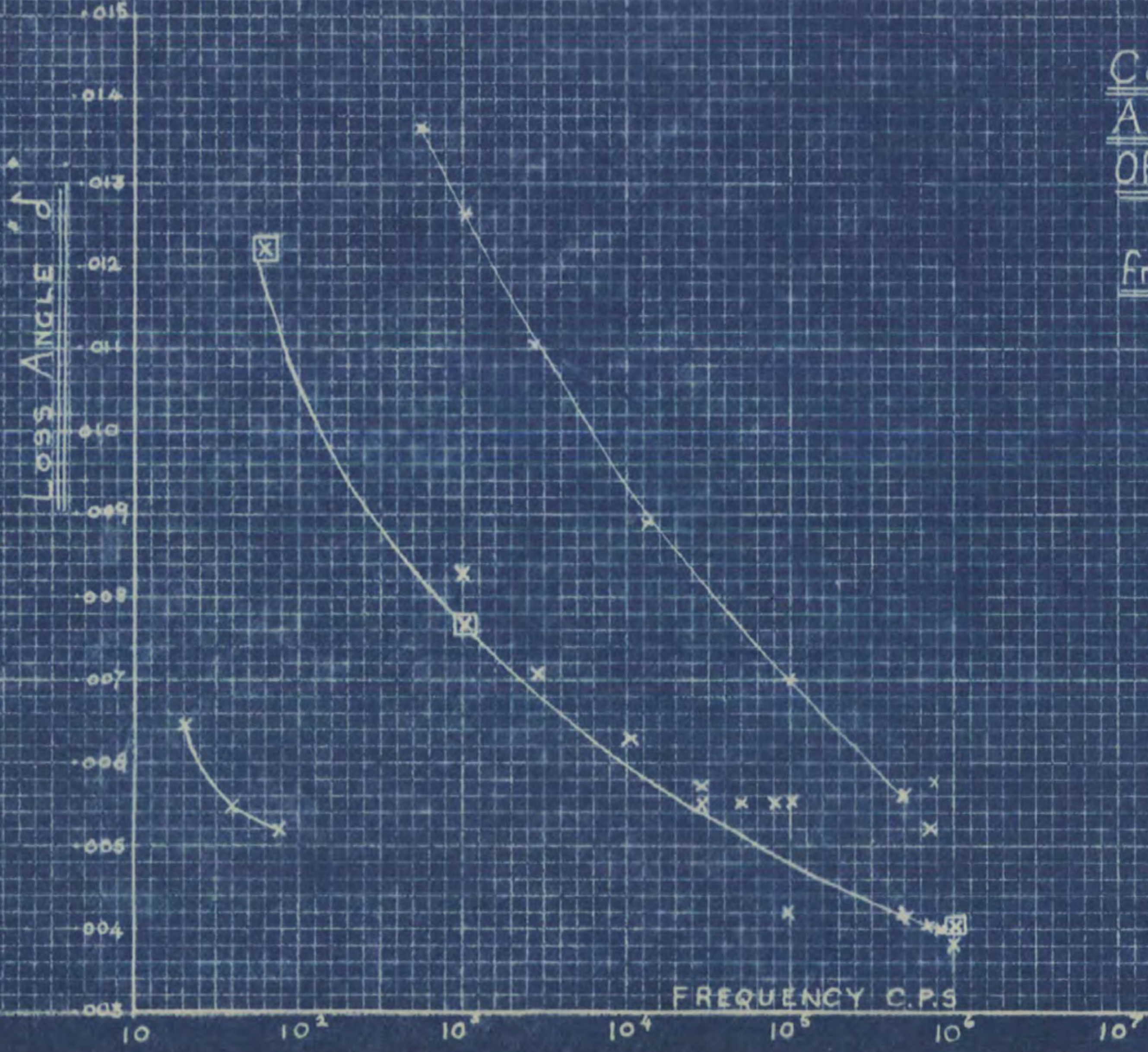
Frequency = 1000 c.p.s.

Fig. 33

CONCLUSION.

Referring again to Fig. 34, it is seen that very considerable discrepancies occur between the results of different workers. In discussing this point, Morey ("Physical Properties of Glass") suggests that the deviation is due to variation of chemical composition, actual dielectric heating causing temperature variation during the experiment, and experimental error in measurements concerning this low-loss glass. However, it is difficult to account for such wide disagreement by any or all of these sources of error, and recourse must be had to the possibility that the glass was in different states when used by the various experimenters. It is now generally believed that when glass is cooled from high temperatures to a lower temperature a finite period of time must elapse before the atomic structure takes on properties appropriate to the new temperature. This stabilisation period is greatly dependent on the viscosity of the glass and will presumably vary in similar manner to the ordinary viscosity. Thus if a sample of glass is stabilised at 600°C by remaining at this temperature for a short periodof time it will require very much longer to stabilise the glass at 400°C. It is more than likely that different pieces of glass which have been annealed and are strain-free from the macroscopic point of view when cooled down to room temperature, may vary according to the state of stabilisation which has been achieved in each sample. A temperature is reached on cooling a glass where certain properties of the atomic lattice are frozen in, and on cooling, the glass will still behave in a manner dependent on the extent to which stabilisation to a relatively low temperature state has been achieved.

Whether this question of previous heat treatment of the glass will account for the observed discrepancies is a matter for careful experiment, but the fact that all dielectric properties are seen to be very closely connected



Collected Data For Loss Angle - Frequency Variation OF PYREX CHEMICAL GLASS

from Morey's "Physicial properties of Glass"

Fig 34

with the structure of glass is good reason for presuming thermal history to be of importance in a discussion of dielectric properties.

Recent investigations using other dielectric materials has shown that relaxation frequencies for important types of polarisation occur at very low frequencies. Future research might well be applied to a study of the dielectric properties of a glass at low power frequencies and would presumably add to existing knowledge in the two fields of dielectric theory and hypotheses of the structure of glass.

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