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THE DIELECTRIC RELAXATION OF GLASS AND THE PSEUDO-CAPACITY OF METAL-TO-GLASS INTERFACES, MEASURED AT EXTREMELY LOW FREQUENCIES

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Summary

The dispersion of the dielectric constant of a glass in the L.F. region has been investigated. The main relaxation time may be explained as the reciprocal transition probability of Na^+ ions jumping between adjacent interstices. Extremely high electrode capacities have been detected, which are frequency and temperature dependent. These are in qualitative agreement with a simple formula derived for the dynamic values of double-layer capacities.

Résumé

On a étudié la dispersion du pouvoir inducteur du verre dans le domain des basses fréquences. Les temps de relaxation ont été discutés en considérant la probabilité d'une transition d'un ion Na^+, ion qui saute entre des interstices adjacents. On a observé des valeurs extrêmement élevées pour la capacité de l'électrode. Ces valeurs dépendent de la fréquence et de la température et ils se sont montrées qualitativement en concordance avec une formule simple pour la valeur dynamique de la capacité d'une couche double.

Zusammenfassung

Es wurde die Relaxation der Dielektrizitätskonstante eines Glases im NF-Bereich untersucht. Die Hauptrelaxationszeit kann erklärt werden als die reziproke Übergangswahrscheinlichkeit von Na^+-Ionen, die zwischen benachbarten Zwischennetzwerkplätzen überspringen. Dabei wurden sehr hohe Elektrodenkapazitäten gefunden, welche frequenz- und temperaturabhängig sind. Diese befinden sich in qualitativer Übereinstimmung mit einer einfachen Formel, die für die dynamischen Werte von Doppelschicht-Kapazitäten abgeleitet wurde.

1. Introduction

Much experimental work has been done on the dielectric losses of glasses at various temperatures and frequencies. It is now assumed that three sources of dielectric loss may be distinguished.

Firstly: the vibrational losses which are due to the damping of the vibrations of all ions. These losses will tend to a maximum at the resonance frequency which will be of the order of 10^{12} c/s and which will be rather independent of temperature *).

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*) In ref. 1) an example may be found of a loss vs frequency curve with a resonance peak at 3.10^9 c/s which, however, is a rather low value caused by the structure of the special glass investigated.

Secondly: the deformation losses which are of the relaxation rather than the resonance type. The occurrence of these losses is typical for the rather loose glass structure in which parts of the network may undergo deformations caused by the electric field. The relaxation time is rather short and will strongly depend upon the temperature. In a number of cases the maximum of these losses for a given temperature has been found experimentally [2]).

The *third contribution* to the losses is due to *the mobility of the individual ions* and in particular of the network modifiers, provided they are small enough to "move" through the glass. It is well known that this mobility gives rise to electric conductivity and dielectric relaxation as well. It may seem difficult to indicate experimentally the two essentially different kinds of displacement involved, for the displacements of mobile ions are very small, even if D.C. voltage is applied for long periods, providing the temperature is not too elevated *). But from the dispersion of the dielectric constant we may still get some insight into the relaxation of at least part of the mobile ions.

It is known that the losses of this third group, if measured at room temperature and at audio frequencies, are far more important than those of the first and second types. They increase at decreasing frequencies and at the same time the dielectric constant increases [3]) [4]). As far as the authors know, A.C. measurements of these quantities at frequencies lower than, say, 50 c/s have never been published. Such measurements could, however, be of some interest. In this paper A.C. measurements of ε down to 0·1 c/s will be presented.

Related to the relaxation just mentioned there appears to be *another remarkable after-effect* shown by glass condensers and characterized by exceedingly long relaxation times. As is well known the Leyden jar, after being connected with a battery and being charged, still consumes a considerable "*absorption current*" persisting for several minutes or longer. From our measurements at very low frequencies it has become obvious that this effect may be represented in terms of a pseudo-capacity at the surface of the glass condenser. This quantity has been derived from the experiments and will be discussed in section 5.

2. Experimental procedure; determination of capacitance and resistance, details of specimens

The measurements have been taken with the aid of the bridge constructed and described by Köhler and Koops [5]). The essential circuit is shown in

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*) If during one minute 10^2 V/cm is applied to a glass with a resistivity as low as $\varrho = 10^8\ \Omega$ cm, only 4 monovalent ions per 1000 Å^2 will have passed.

fig. 1. The sample X is compared with a shunt of a resistor R_{24} and a capacitor C_{24}. The resistors R_{13} and R_{23} are in general both $10^4\ \Omega$, sometimes $10^4\ \Omega$ and $10^3\ \Omega$ respectively.

The phase angles and time constants of these elements are certainly small enough to ensure reliable results for the impedance X. The specimens have been provided with an earthed guard ring. When the bridge and the Wagner earth connections have been balanced the impedance X can be calculated from the readings.

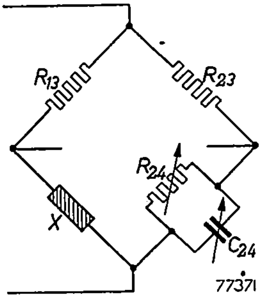

Fig. 1. Main circuit of measuring bridge.

In most of the experiments the bridge has been fed with a signal produced by a three-stage RC-oscillator after Van der Mark and Van der Pol[6]), which is very suitable for very low frequencies. The diagram of the oscillator is shown in fig. 2. The angular frequency ω is found to be

$$\omega = \frac{1}{RC\sqrt{3}},$$

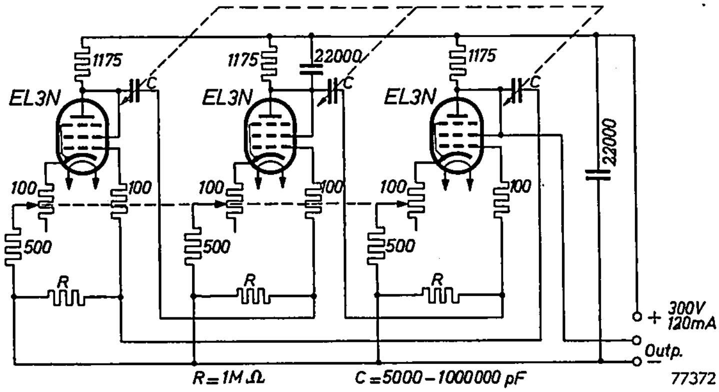

Fig. 2. Circuit of RC-oscillator after Van der Mark and Van der Pol. Values of resistances and capacitances in Ω and pF respectively.

in which R and C are the coupling elements between each of the three stages. R is about 1 MΩ and the C's can be varied in steps from 5000 pF to 1 μF. The frequencies obtained have been measured with the help of a stopwatch or a pulse-counting device. They vary from 0·1 to 20 c/s. Between the oscillator and the input of the bridge a cathode follower and an amplifier have been placed. In this way voltages of 100 or 200 V on the bridge may be obtained without unpleasant retroaction on the oscillator. The detection has been done by means of a standard sensitive galvanometer with a long period. This works satisfactorily even at the highest frequencies of the range mentioned.

Measurements at higher frequencies have been taken with the aid of a standard oscillator for audio frequencies and an amplifier which belong to the normal equipment of the bridge [5]).

Most of the capacitors investigated are cylindrical in shape, the electrodes being metal layers on the inside and the outside. The guard rings used are small strips at both ends of the outside of the cylinders, separated from the main electrodes, as shown in fig. 3. The cylinders have surface areas of the order of 500 cm^2, the thickness of the wall is about 2 mm. Also discs of about 10 cm in diameter and some millimetres in thickness have been measured. They have likewise been provided with guard rings.

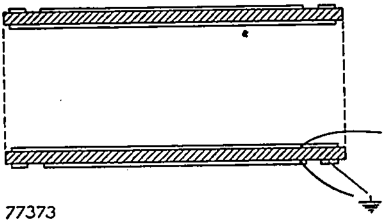

Fig. 3. Intersection of glass cylinder with electrodes.

Some capacitors have been investigated without any preventive measures being taken for the surface conduction at the ends. Our experience has been, however, that in this case no reproducible results are obtainable.

The measurements at higher temperatures have been carried out with the capacitor mounted in a furnace, the temperature of which may be adjusted by hand within one degree centigrade.

Nearly all specimens are of a commercial, well-annealed glass containing 70·6% SiO_2, 1·4% Al_2O_3, 17·5% Na_2O, 9·6% CaO, 0·5% MnO and 0·4% ZnO (mole percentages). This glass will be referred to as A. Some measurements however, have been taken with discs of a glass with a modified composition (B). It contains 70·6% SiO_2, 1·4% Al_2O_3, 27·1% Na_2O, 0·5% MnO and 0·4% ZnO, that is to say, all Ca^{++} ions of glass *A* are replaced by Na^{+} ions, the rest being unchanged.

Various kind of electrodes have been applied, as may be seen in table I.

TABLE I

Nr	Electrodes	Marks in the graphs of figs 4, 5 and 9
I	Silver electrodes obtained by reduction of Ag_2O at 600 °C	•
II	Electrodes of a Bi-Sn-Cd alloy obtained by Schoopp process	+
III	Silver electrodes, obtained by reduction of an aqueous solution of Ag salt at room temperature	○
IV	Gold electrodes obtained by evaporation of Au in vacuum	×

Electrode Nr II has the disadvantage that the specimen cannot be heated higher than about 100 °C. One may probably assume that the gold plating affects the glass to a less degree than do the other processes. Elevation of temperature within the limits of our experiments has not caused irreversible changes in the specimens.

3. General survey of results; search for electrode effects

At room temperature all specimens show a slight increase of capacitance towards lower frequencies and a notable dependency of the resistance upon frequency. As a consequence the power factor runs gradually from about 0·1 at $\omega = 100$ rad sec^{-1} to 1 at $\omega = 1$ rad sec^{-1}. At higher temperatures the increase of capacitance at low frequencies becomes more important whereas the resistivity is almost constant. In fig. 4 a typical example is given. It must be noted that in this graph the apparent dielectric constant ε^* is plotted, a quantity derived from the capacitive component of the measured impedance of the glass condenser and calculated from the dimensions of the sample as if it were the true dielectric constant of the glass. This, however, implies that no extra impedance is present at the electrodes, an assumption which is incorrect. However, the calculated ϱ is reliable, as will appear from fig. 5.

Fig. 5 shows the influence of the electrodes used upon the measurements, in particular upon the apparent dielectric constant, ε^*. The D.C. resistivity is hardly affected by the nature of the plating, but mainly with Ag electrodes of type Nr I some deviations in ε^* occur, the glass being most probably spoiled by diffusion of Ag.

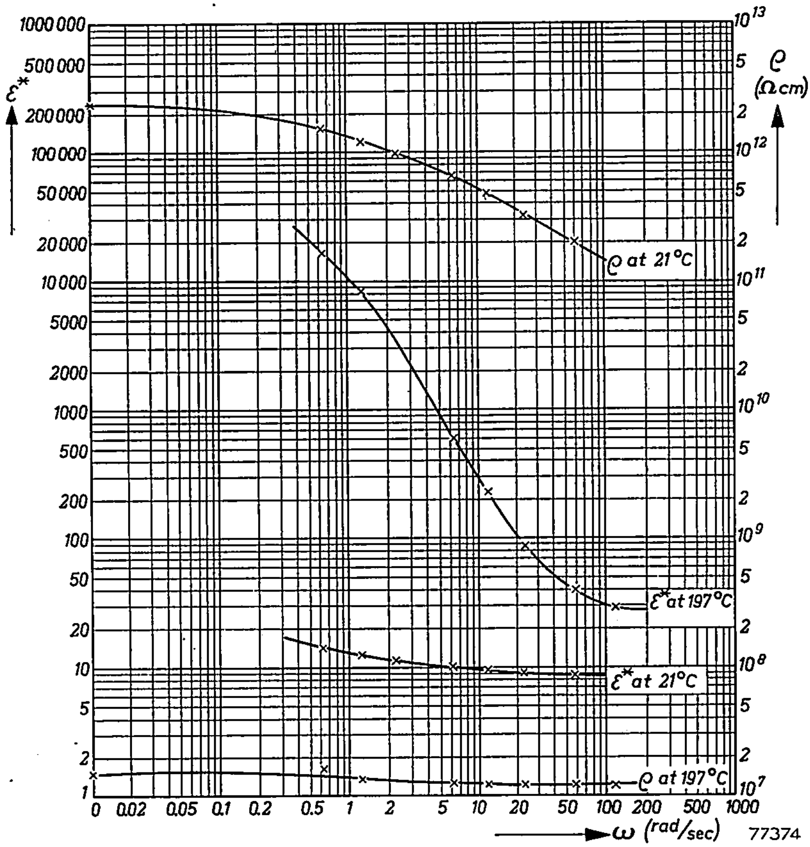

Fig. 4. Apparent dielectric constant (ε^*) and resistivity (ϱ) as a function of circular frequency at two temperatures. The curves refer to a cylindrical condenser of glass *A* with electrodes Nr I. Cf. also table I.

However, it would be an error to conclude that with Au or any other chemically inactive plating no electrode effects are present. This is quite clear from fig. 6 where the capacities of two gold-covered *discs of different thickness but identical preparation* are plotted as a function of frequency (lower part of the figure). The ratio of these values is plotted in the upper part of fig. 6. The dashed straight line at 1·3, running from about $\omega = 10^2$

rad sec^{-1} towards higher frequencies, indicates what might be expected from the dimensions of the samples under the assumption that the capacitance is determined by the dielectric only. A close agreement between the experimental and calculated ratios of C_{thin} and C_{thick} exists in this frequency range. At the lowest frequencies a remarkable deviation occurs. Here the ratio should tend towards a limiting value of 2·3, calculated under the assumption of a high electrode capacitance in a way which will be discussed in section 5. The experimental values do not yet reach this figure.

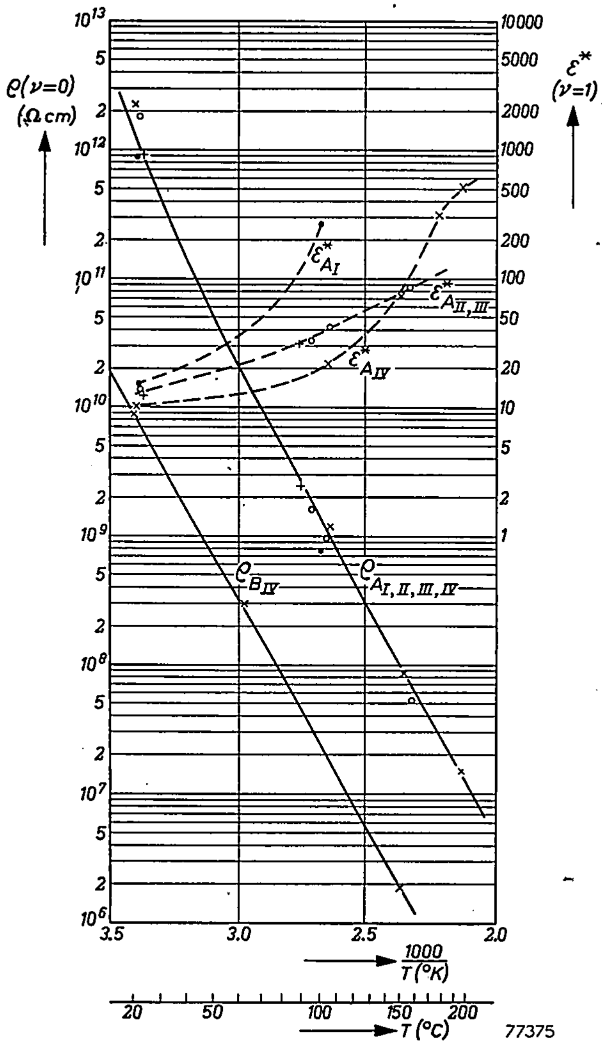

Fig. 5. D.C. resistivity ($\varrho_{\nu=0}$) and apparent dielectric constant at $\nu = 1$ c/s ($\varepsilon^*_{\nu=1}$) as a function of temperature for different specimens. Cf. also table I.

Thus an important conclusion results from this analysis, namely that one must distinguish between bulk and surface properties.

In fig. 6, furthermore, is plotted ε, the true dielectric constant of glass A at 150 °C as a function of the circular frequency. Fortunately at this relatively high temperature in a certain range of frequencies (not low enough to make the electrode effects appearing) a saturation value of ε is manifested. Although one can never be quite sure in this respect we would recognize it as the static value, which in this case is about 28. We see ε drop to a much lower value in a range of three or four decades in the frequency, at the end of which the dispersion of ε seems to have essentially finished. In the case under consideration a value of 11 is reached at $\nu = 10^5$ c/s. The $\varepsilon(\omega)$ curve is flatter than would result from a single Debye formula. A characteristic or half-value frequency ω_c may be noted, which is here about 6.10^3 radians second^{-1}.

Similar results have been gained with some other specimens of glass A and the static ε appears to be always about 25. The half-value frequency ω_c is found to be strongly temperature dependent. It must be remarked that in the frequency range used only above 100 °C can the static ε-value of glass A be indicated with reasonable accuracy (see e.g. ε at 21 °C in

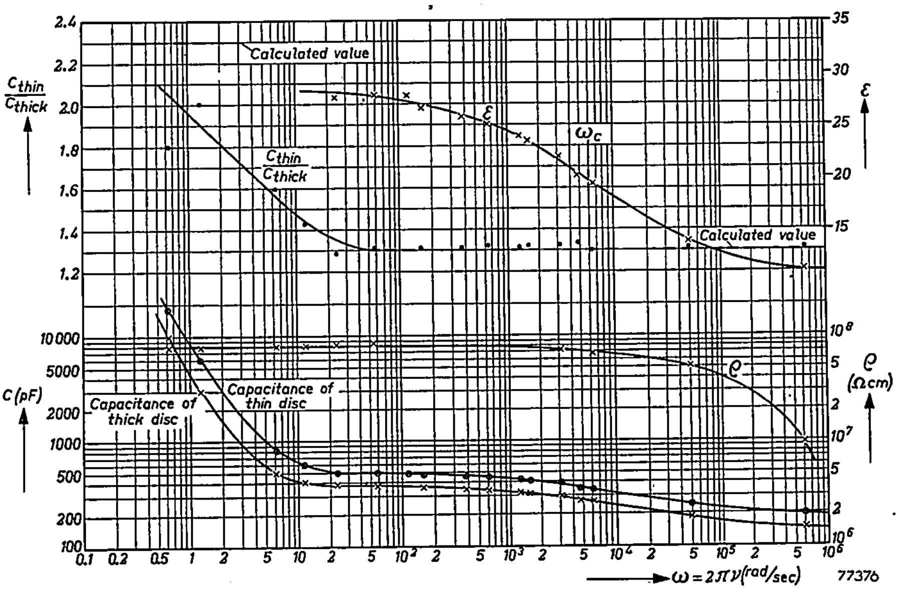

Fig. 6. Capacities of thin and thick discs of glass A at 150 °C. Also the derived true ε values are plotted and, moreover, the resistivity. From an analysis of the ratio of C_{thin} and C_{thick} surface effects have been recognized. The discs had surface areas of 31 cm^2 and 44 cm^2 and thicknesses of 1·53 mm and 2·80 mm respectively.

fig. 4). On the other hand it would not be wise to heat the glass condenser above 200 °C in view of possible chemical reactions with the electrodes.

With condensers of glass B it appears that reliable measurements of the capacitance are very difficult to perform as a consequence of its considerably higher conductance. At 60 °C and 20 °C some results have been obtained, but surface and bulk effects are far too mixed at these temperatures. Measurements of the resistivity cause no trouble at all.

In the next section particularly the true dielectric constant will be considered in greater detail, together with the resistivity.

In section 5 the pseudo-capacities at the electrodes, which have been derived from the measurements, will be discussed.

4. True dielectric constant and resistivity

The temperature dependency of the D.C. resistivity ϱ may be represented by a fairly straight line in the log ϱ vs $1/T$ plot (cf. fig. 5), as has likewise been found by numerous other investigators.

Expressing the results with the aid of

$$\varrho = \varrho_\infty \exp \frac{E}{kT} \quad (\varrho_\infty = \text{constant},\ E = \text{activation energy}), \qquad (1)$$

we find for glass A $\varrho_\infty = 10^{-1}$ Ωcm and $E = 0{\cdot}75$ eV. For glass B $\varrho_\infty = 2.10^{-3}$ Ωcm, whereas its activation energy E is equally 0·75 eV, a value that has been found for a number of glasses of different compositions [7]).

We now consider the glass structure somewhat more closely and in particular the mobility of the network modifiers, especially of the Na^+ ions. These ions are situated in interstices of the open network, formed by an irregular arrangement of tetrahedra of oxygen ions. The presence of each Na^+ ion in the glass requires the presence of a non-bridging oxygen ion, which must be regarded as a weak spot in the network. It marks, in fact, a place where a Na^+ ion may rather easily pass from one interstice to another (see fig. 7). To a first approximation one can say that each non-bridging ion is in between two interstices which form two equilibrium positions (1 and 2 respectively) for the Na^+ ion under consideration. If the Na content of the glass is not too high these "units" are far enough apart for an individual treatment to be allowed. But in reality this picture is too simple. The glasses under consideration contain a large number of Na^+ or other network-modifying ions. From the chemical composition it may be calculated that practically all interstices should be occupied and that on the average in both glasses there are 3·28 bridging and 0·72 non-bridging oxygen ions per tetrahedron, so that the network is rather loose, in fact much more loose than fig. 7 suggests. As a consequence at least a fraction of the Na^+

ions can move over greater distances. We may characterize the migration of the Na^+ ions by a diffusion constant D. This constant is related to d, the distance between two neighbouring interstices, and A, the transfer probability for a Na^+ ion jumping from the one interstice to the other, by the following somewhat simplified expression

$$D = d^2 A \,. \tag{2}$$

From the Einstein relation

$$\varrho = \frac{kT}{Ne^2 D}, \tag{3}$$

where N is the number of mobile ions per unit volume and e their electric charge, we find for the resistivity of the glass

$$\varrho = \frac{kT}{Ne^2 d^2 A}. \tag{4}$$

For A holds

$$A = \nu_0 \exp - \frac{E}{kT}, \tag{5}$$

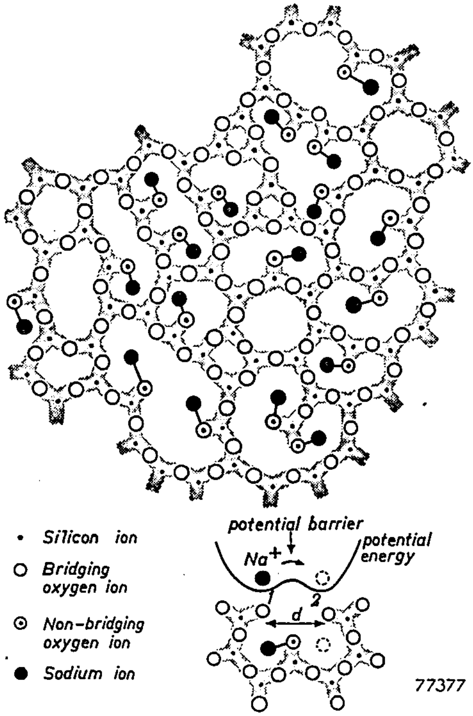

Fig. 7. Two-dimensional model of a glass containing Na^+ ions in moderate concentration. A typical set of interstices is shown in the lower part of the figure.

where E is an activation energy equal to the potential barrier between the interstitial positions. ν_0 is a quantity which is of the order of magnitude of the vibration frequency of the ions in the matrix, say 10^{12} or 10^{13} sec^{-1}. Inserting (5) into (4) we get

$$\varrho = \frac{kT}{Ne^2d^2\nu_0} \exp \frac{E}{kT}. \tag{6}$$

This or similar expressions may be derived in different ways of course [cf. for instance the formula for the conductivity in [7])].

(6) may be identified with the experimental formula (1). Strictly speaking there is an inconsistency in the pre-exponential factor in (6) being temperature dependent whereas ϱ_∞ in (1) is not. But in comparison with the strongly temperature-dependent exponential factor this may be ignored and for T may be taken an average value of the temperature, say 400 °K.

The glasses investigated contain a considerable number of Na^+ ions. For glass A $N = 9.10^{21}$ cm^{-3} and for glass B $N = 1{\cdot}4.10^{22}$ cm^{-3}. From crystallographic considerations d is known to be about 5 Å. If we take $\nu_0 = 3.10^{12}$ sec^{-1} (6) gives a ϱ agreeing with the experimentally found value of ϱ_∞ in the case of glass B, which is the glass containing only Na as a network modifier.

Obviously in glass A things are different. Here, although an equally loose network is present, the Na^+ ions are limited in their mobility or perhaps even imprisoned by the immobile network modifiers, especially by Ca^{++} ions. From the experimental value of ϱ_∞ for this glass it must be concluded that only a few per cents of the Na^+ ions contribute to the true D.C. conduction.

We now apply the model introduced to the discussion of the dielectric properties.

The $\varepsilon(\omega)$ curves (fig. 6) show the existence of a *relaxation process in glass*, and in explaining any relaxation phenomenon one has to deal with either a macroscopic or a molecular (microscopic) theory.

The *macroscopic theories* are based on an inhomogeneity model of the substance. Maxwell, and later Wagner, has given a now classical treatment of the effect of certain inhomogeneities on the dielectric constant and the power factor. The result is a pair of dispersion formulae of what is now known as the Debye type. In these theories the relaxation times which govern the relaxation processes are actually RC-constants, depending upon the resistivities and the dielectric constants and in general also on the shape of the constituent substances. For instance in the Maxwell model of an insulator (dielectric constant ε) containing non-interacting conductive spheres (of resistivity ϱ and dielectric constant ε), which occupy a small volume fraction q of the dielectric, the dielectric constant of the substance has increased by an amount

$$\left(\frac{3q}{1+\omega^2\tau^2} - j\,\frac{3q\omega\tau}{1+\omega^2\tau^2}\right)\varepsilon\,. \tag{7}$$

This excess value of ε can be understood[8]) by considering the spheres as very strongly polarized systems if an electric field is present. These dipoles are established, however, by a flow of electric currents, which at higher frequencies decrease. The relaxation constant τ is here independent of the radii of the spheres:

$$\tau = 2{\cdot}7.10^{-3}\,\varepsilon\varrho \quad (\tau \text{ in sec})\,, \tag{8}$$

where ϱ is the resistivity of the spheres in Ω cm [8]). In the case of well-conducting spheres distributed in a less conducting medium similar formulae will apply.

In the *molecular types of theory*, on the other hand, the displacement of charge is considered not to surpass essentially the interatomic distance, the effect of an applied electric field being a polarization instead of a true conduction current. The problem is here to calculate the after-effect in terms of transfer probabilities of the ions. The static value of ε has to be calculated from the polarizability and the molecular dipoles assumed to be present in the substance.

In principle both types of theory seem applicable in our case.

An inhomogeneity model may be justified (a) by considering the probability that statistical fluctuations of composition and therefore of conductivity may occur in adjacent regions in the interior of the glass; (b) by the recently published ideas relating to certain frozen-in structures [9]) equally pointing in this direction; and (c) by keeping in mind that both the network (as far as it has been kept intact) and the large Ca^{++} ions may imprison a certain amount of mobile Na^+ ions. It must be remarked, however, that (7) and (8) cannot be correct in our case because (1) the proper Maxwell model does not yield D.C. conductivity of the glass; (2) if (a) were not an essential objection, the value of q required for agreement with the experiment has still to be much too large to make Wagner's formula (7) hold; (3) the dispersion experimentally found cannot be represented by one relaxation time. If we nevertheless wish to indentify τ in equation (8) with the experimental $1/\omega_c$ value, it lies at hand to insert in (8) the value $\varepsilon \approx 10$ and the ϱ values found for glass B (cf. curve $\varrho_B(T)$ in fig. 5), as glass B (which does not contain Ca^{++} ions) should be similar to the substance of the hypothetic, well-conducting regions of glass A. However, we then do not get agreement at all. Remarkably enough we do get agreement if $\varrho_A(T)$ of glass A is used, which is not very satisfactory.

A molecular theory perhaps is more to the point. In our model some Na^+ ions are bound to stay within isolated, extremely small regions, consisting of a few interstices only (fig. 7). As a matter of fact this model can be obtained from the foregoing by reducing the size of the well-conducting regions to such small dimensions that they become too small to be treated as conductors characterized by well-defined macroscopic quantities.

As the ions in these small systems are able to occupy different positions they behave essentially as permanent dipoles. Their dipole moment, p, could for the model in fig. 7 be calculated as $\frac{1}{2}\, ed$, i.e. about 12 Debye units.

Onsager has derived [10]) that for substances with permanent dipoles under certain conditions

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + \frac{1}{9\varepsilon_0}\,\frac{p^2 N}{kT}\, f(\varepsilon_s, \varepsilon_\infty), \tag{9}$$

where

$$f(\varepsilon_s, \varepsilon_\infty) = \frac{3\varepsilon_s(\varepsilon_\infty + 2)}{(2\varepsilon_s + \varepsilon_\infty)\,(\varepsilon_s + 2)}.$$

Here ε_s is the static dielectric constant, which we want to consider now. ε_∞ is the dielectric constant of the skeleton; $\varepsilon_0 = 8{\cdot}85.10^{-12}$ F/m if Giorgi units are used. Inserting the experimentally found values $\varepsilon_s = 25$ and $\varepsilon_\infty \approx 10$ into (9) we find for the concentration of Na^+ ions contributing to the dielectric constant in glass A

$$N \approx 8.10^{19}\ \mathrm{cm}^{-3},$$

which is only one per cent of the actual amount and of the same order as the amount of free-moving ions derived from the D.C. conductivity of glass A.

The relaxation of the dielectric polarization may likewise be explained with the help of the molecular model. If the transfer probability for a Na^+ ion jumping between the equilibrium positions 1 and 2 in the double-minimum potential of fig. 7 is A, and if the local field in the interstices is assumed to be

$$E_{\mathrm{loc}} = E_0 \exp j\omega t$$

with all dipole axes parallel to the field, common methods for the treatment of relaxation phenomena give for the field-induced deviation (n) from the statistical occupation numbers ($\frac{1}{2}\, N$ in 1 and 2 respectively)

$$2n = \frac{1}{1 + j\omega/2A} \frac{Np}{kT} E_{\text{loc}}. \tag{10}$$

If there were no coupling between n and the local field the quantity $1/2A$ could be recognized as the relaxation time which determines the after-effect of the occupation numbers and as a consequence of the macroscopic dielectric displacement. A coupling does exist, however, and therefore the relaxation time τ in the well-known dispersion formula

$$\varepsilon = \frac{\varepsilon_s + \varepsilon_\infty\, j\omega\tau}{1 + j\omega\tau} \tag{11}$$

might be somewhat greater than $1/2A$ *).

The value of ω_c experimentally found and the quantity A given by equation (5), agree if we take $E = 0{\cdot}75$ eV and $\nu_0 = 3.10^{12}$ sec^{-1}, which are very acceptable values and, in fact, the same as have been used for the discussion of the resistivity (equation (6)). In fig. 8 are shown both the A curve calculated for these values and some experimental ω_c values ($\times$) for glass A.

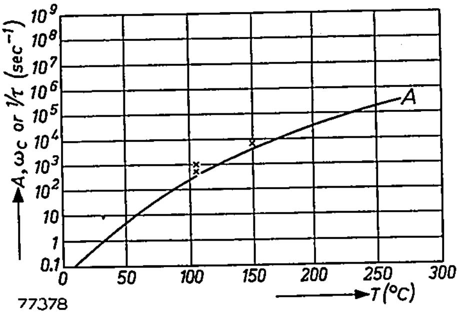

Fig. 8. Theoretical values of jump probability A of Na$^+$ ions in glass (full-drawn curve) and experimentally found values ($\times$) of L.F. relaxation frequency ω_c. Cf. fig. 6.

In an actual glass of course the dispersion of ε is governed not by ω_c alone, but by a distribution of relaxation times. Of this distribution usually only the tail is of importance (cf. the analysis of Gevers and Du Pré [11]). But with our experiments the whole distribution becomes manifest, including its centre. As appears from our reasoning this main

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*) If $f(\varepsilon_s,\varepsilon_\infty)$ in (9) may be neglected (Debye), we have

$$\tau = \frac{\varepsilon_s + 2}{\varepsilon_\infty + 2} \frac{1}{2A},$$

f is 0·55 in our case.

relaxation time and its temperature dependency can be understood from a few simple assumptions which equally explain some features of the conductivity. It is encouraging that also recently published experimental data on the ionic diffusion [12]) [13]) and on the elastic relaxation of glass [14]) [15]) are in accordance with the principles of our analysis.

Finally it must be remarked that, as a rule, relaxation processes are most easily detected by studying the power factor as a function of frequency and temperature. In our case, however, the conductivity of the substance overrules the dielectric loss almost completely in the ultra-low frequency range, the power factor being much greater than 1. Therefore full attention is paid to the dispersion of ε, which is even more directly informative.

5. The pseudo-capacity at the electrodes

We now return to the surface effects, the existence of which has been recognized by examining the capacitances of a thin and a thick disc and in particular their ratio (fig. 6).

Assuming a surface capacitance C_s (with parallel resistance R_s) in series with the bulk capacitance C_b (with parallel resistance R_b) and assuming, furthermore,

$$C_s\,R_s^2 \gg C_b\,R_b^2 \text{ and } R_s \ll R_b$$

one derives with the aid of common A.C. calculus for the apparent parallel capacity C of the system

$$C \approx C_b + \frac{C_s\ (R_s/R_b)^2}{1+\omega^2 C_s^2 R_s^2}, \tag{12}$$

whereas the apparent parallel resistance of the system will not exhibit appreciable dispersion. This feature and (12), predicting the disappearing of surface effects at sufficiently high frequencies, are in accordance with the properties found. If $\omega^2 C_s^2 R_s^2 \gg 1$, then C will tend towards $C_b + 1/\omega^2 C_s R_b^2$. However, C_s and R_s most probably are frequency-dependent quantities for which $\omega R_s C_s = 1$, as will be discussed later. In this case $C = C_b + 1/2\omega^2 C_s R_b^2$, which is essentially the same result. At low frequencies $C_b \ll C$ and the "calculated value" 2·3 in fig. 6 is in fact the ratio of the values $1/C_s R_b^2$ for the thin and the thick disc respectively, as derived from their dimensions.

From measurements with a gold-covered cylinder made of glass *A* (surface area about 400 cm^2) values of C_s have been computed with the aid of (12) under the assumption $\omega^2 C_s^2 R_s^2 \gg 1$. At higher temperatures the surface capacity per cm^2 assumes astonishingly high values which vary almost inversely proportionally to $\sqrt{\omega}$ as may be seen in fig. 9.

These properties make it very improbable that C_s is caused by fixed thin layers of some insulating material under the electrodes. It seems more likely that the current itself modifies a little the composition of these regions.

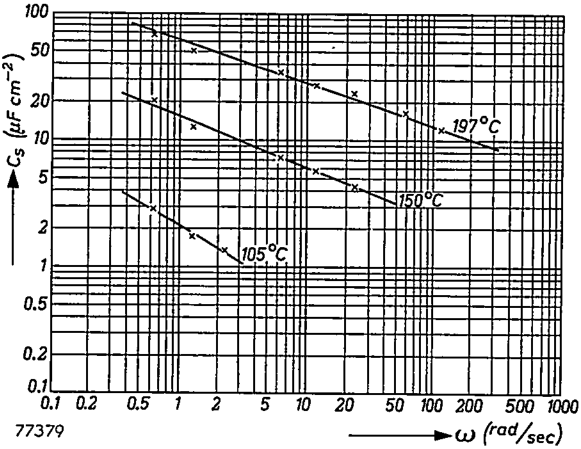

Fig. 9. Surface capacity per cm² of a gold-covered glass condenser derived from measurements at different temperatures and frequencies.

Proposed explanation

We shall assume that the Na$^+$ ions, which are moved by the electric field, cannot leave the specimen at the electrodes as electrons do and, moreover, that any interaction with electrons or ions entering from the electrodes into the glass may be neglected. We then have to deal with modifications of the concentration of Na$^+$ ions near the interface. As a consequence of the excess concentration (n) a diffusion current flows in this region. The total current is therefore

$$S = S_{\text{cond}} + S_{\text{diff}} = \sigma E - eD\,\frac{\partial n}{\partial x}, \tag{13}$$

where x is a coordinate perpendicular to the surface and σ the conductivity.

Furthermore we have

$$\frac{\partial S}{\partial x} = -\,e\,\frac{\partial n}{\partial t} \quad \text{(continuity equation)}, \tag{14}$$

and

$$\frac{\partial E}{\partial x} = \frac{ne}{\varepsilon_0 \varepsilon} \quad \text{(Poisson)}. \tag{15}$$

If σ and D may be treated as constants (small changes in the Na$^+$ concentration), it follows from equations (13), (14), and (15) that

$$\frac{n}{\tau_s} + \frac{\partial n}{\partial t} = D\,\frac{\partial^2 n}{\partial x^2}, \tag{16}$$

where $\tau_s = \varepsilon_0 \varepsilon \varrho$ is the "natural relaxation time" for the establishment of a charge distribution, as follows from the basic equations (14) and (15).

It now depends upon the frequency used in the experiments whether the first or the second term in the left-hand side of (16) predominates.

If $\partial n/\partial t$ may be neglected we deal with what may be called the *pseudo-static case* and the well-known formulae for a static double-layer result:

$$\text{effective thickness of static double-layer} = \delta^{(\mathrm{stat})} = \sqrt{D\tau_s}; \tag{17}$$

$$\text{capacity of static double-layer} = C_s{}^{(\mathrm{stat})} = \frac{1}{\varepsilon_0 \varepsilon \delta^{(\mathrm{stat})}} = \frac{\sigma}{\sqrt{D/\tau_s}}. \tag{18}$$

It may be remarked that these expressions may be rewritten in more common form [16] e.g.

$$C_s{}^{(\mathrm{stat})} = \sqrt{\frac{Ne^2\varepsilon\varepsilon_0}{kT}}$$

in view of Einstein's equation (3). The capacity C_s in (18), unlike the experimentally found values of C_s being frequency independent, we feel that the static formulae do not refer to our experiments.

If, on the other hand, $\partial n/\partial t > n/\tau_s$ (i.e. $\omega > 1/\tau_s$) we deal with the *dynamic case.* Now, contrary to the static case, the influence of the space charge is of minor importance and (16) reduces to the normal equation for diffusion processes

$$\frac{\partial n}{\partial t} = D\,\frac{\partial^2 n}{\partial x^2}. \tag{19}$$

The applied field being little affected by the space charge we have at the interface

$$S = 0, \text{ or } \left(\frac{\partial n}{\partial x}\right)_{x=0} = \frac{\sigma E}{eD} = \frac{\sigma E_0 \sin\omega t}{eD}, \tag{20}$$

which means that at the interface the backward diffusion current and the unperturbed conduction current just balance. From (19) and the known influx $(\partial n/\partial x)_{x=0}$ as a boundary condition (20) we find for n

$$n = \frac{\sigma E_0}{e\sqrt{D\omega}} \exp\left\{-x\sqrt{\frac{\omega}{2D}}\right\} \sin\left\{\omega t - \tfrac{1}{4}\pi - x\sqrt{\frac{\omega}{2D}}\right\}. \tag{21}$$

Mathematically similar problems are met with in the theory of periodic laminar motion of a viscous fluid and in the theory of heat conduction[17]). Integrating (13) and using (21) we get

$$\int_0^\infty S\varrho \mathrm{d}x = \int_0^\infty E_0 \sin \omega t \,\mathrm{d}x - E_0 \sqrt{\frac{D}{\omega}} \sin\left(\omega t - \tfrac{1}{4}\pi\right). \tag{22}$$

From this equation we see that in addition to the normal resistance of the specimen there exists an impedance of the surface layer. It may be represented by a surface resistance R_s and a capacitance C_s in parallel, for which

$$R_s = (\omega C_s)^{-1} = \sqrt{\frac{2D}{\omega}}\,\varrho = \delta\,\varrho, \tag{23}$$

where δ is the dynamical value of the thickness of the double-layer (cf. the exponential in equation (21)). Of course the resulting formula for the capacitance, viz.

$$C_s^{(\mathrm{dyn})} = \frac{\delta}{\sqrt{2\omega D}} \tag{24}$$

is not correct for $\omega \rightarrow 0$. If $\omega < \tau_s^{-1}$, the dynamic value of the thickness of the double-layer (cf. (21) and (23)) would become greater than the static value (17) and we then have the pseudo-static case again. Obviously (18) is the upper limit for the surface capacity.

Earlier treatments of what happens at the interfaces of metal electrodes and ionic conductors (electrolytes) exist [18]) [19]) [20]), and it is well known that a pseudo-capacity may be related with polarization effects at the electrodes. However, the application of these concepts to a substance like glass may be somewhat unexpected. But in the case of our glass, being an ionic conductor with only *one* kind of mobile ions, where gold electrodes have been applied which probably do not interact appreciably with the glass, it may be justified to have given a simple and direct analysis along the lines given.

(24) is the right type of formula in view of our experimental C_s values. A qualitative agreement with respect to the dependency on both frequency and temperature occurs. A quantitative agreement, however, is only obtained if, besides the known D values, σ values are inserted which are about 1 or 2% of the values actually found (fig. 5). It must be remarked also that, strictly speaking, from the actual σ values very small relaxation times τ_s are calculated and that therefore, according to (18), experimentally even a constant value of C_s should have been found in our frequency range, which is not the case. These effects may be explained by assuming

a depletion layer at the surface containing less Na^+ ions. On the other hand, the assumption of one value of the diffusion constant, regardless of the distribution function of jump probabilities involved, may be an oversimplification.

The double-layers are only very thin, as follows from

$$\delta = \sqrt{\frac{D}{\omega}} = d\sqrt{\frac{A}{\omega}},$$

where $d = 5.10^{-8}$ cm and A is given in fig. 8. If, however, $\omega \gtrsim A$ the double-layer would be too thin and the considerations given no longer valid.

It is easily seen that according to (18) a glass condenser should indeed be capable of absorbing very slowly large electric charges at the surfaces. Our A.C. experiments give additional information concerning the nature of this process. Equally the after-effect of the discharge current and also the well-known phenomenon of its reversals, induced by the previous application of suitable reversed voltages, fit into the picture given.

It is an interesting fact that the formation of superficial space charges in glass recently has been recognized as having much influence upon its electric breakdown [21]).

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