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Dielectric constant of absorbed water

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DIELECTRIC CONSTANT
OF
ADSORBED WATER

By
Reiji Funabiki

January 27, 1932
A Thesis
Submitted to the Department of Physics
College of the Pacific

In partial fulfillment
of the
Requirements for the
Degree of Master of Arts

ED:

\[\text{Signature}\]
Head of the Department

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Garrett E. Ross, Librarian
To
Dr. Samuel R. Cook
and
Dr. Samuel S. Kistler

This volume is dedicated
with gratitude and respect.
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Relation of the Dielectric Constant to Chemical and Physical Properties of Substances

That the dielectric constant of a substance is one of its important properties is a fact that has been very commonly taken into consideration by electrical engineers in design of apparatus and transmission lines. The importance of the dielectric constant is equally evident to the chemist working in the field of nonaqueous solutions, and Walden\(^1\) and others have spent a great deal of time and energy in attempting to measure the relationship of the dielectric constant of a solvent to its solvent ability, the degree of ionization of a solute dissolved in it, etc. Indeed it has become very common in chemistry to consider the dielectric constant as one of the fundamental properties of a substance.

The reason for the large influence of dielectric constant is perhaps not evident at first sight. Dielectric constant may be considered as a measure of the electrical energy that can be stored in unit volume of the substance when placed in an electric field. Since energy can be considered to be the product of force times distance, we immediately look for some possibility of an electric displacement within the substance.

Since matter is composed of positive protons and

\(^1\) Paul Walden, Salts, Acids, Bases, 269.
negative electrons it becomes immediately apparent that a displacement of the electrons with respect to the protons would give rise to a dielectric constant greater than unity or in other words the displacement of the electric charges with respect to each other will be accompanied by the absorption of energy. If the centers of gravity of the electric charges in each atom are assumed to coincide, there will be no polarization in the absence of an electric field but by the application of a potential gradient these centers of gravity will be displaced with respect to each other and the substance will now possess a definite electric polarization. A mathematical investigation of this phenomenon leads to the conclusion that for all reasonably low potentials the polarization is a linear function of the potential, and only at very high voltages does one depart from it. It is conceivable that within a molecule the center of gravity of the negative charges will not exactly coincide with the center of gravity of the positive charges. In fact this is the fundamental assumption of the strong electrolytes and of all ionic lattices. The molecules then have permanent dipoles, and if they are placed in an electric field the molecule itself will tend to orientate in the field in addition to the displacement of electrons with respect to the protons above referred to, so that the energy absorbed will be greater than with non-polar molecules. As a matter of fact the energy absorbed due to the orientation of dipole molecules is usually of a considerably larger
order than that absorbed by non-polar molecules, or in other words, substances with permanent dipole moments have much higher dielectric constants than those without. Debye\(^1\) has assumed the correctness of the Clausius-Masotti expression
\[
\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4 \pi N}{3} \chi \quad \ldots \ldots \ldots (1)
\]
and has derived the equation
\[
P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4 \pi N}{3} \left( \chi + \frac{\mu^2}{3kT} \right) \ldots \ldots (2)
\]
in which \( P \) = the molar polarization
\( \varepsilon \) = dielectric constant
\( M \) = molecular weight
\( d \) = density
\( N \) = Avogadro's number
\( \chi \) = the polarizability of the molecule at such high frequencies that it cannot orientate in the electric field.
\( \mu \) = the permanent electric moment of the molecule
\( T \) = absolute temperature
\( k \) = Boltzmann's constant

The molar polarization can readily be seen to be the sum of two quantities, one depending upon the displacement of electrons in the atom and the other upon orientation of the molecules. It can be seen readily from equation two that in case a substance has no permanent dipole moment the dielectric constant will be independent of temperature, whereas with polar substances the dielectric constant will decrease with increasing temperature.

\(^1\) F. Debye, *Polar molecules.*
This fact provides ready means of differentiating the two classes of substances.

Now, if we consider the rate of oscillation of the applied field to increase steadily, it is readily understandable that the dipole molecules can follow the oscillations of the field. So long as the turning moment on the molecules is large compared with the viscous drag, they will easily orient themselves to the field. With higher and higher frequencies, a point will eventually be reached where the viscous drag will become so important that the molecules can no longer completely orientate themselves with respect to the field, and therefore with increasing frequency the dielectric constant will decrease. At these frequencies we say that the substance has anomalous dispersion.

Debye has arrived at an expression for the dielectric constant, taking into consideration the frequency:

\[
\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = \frac{4\pi N}{3} (\alpha + \frac{M^2}{3\varepsilon T} \cdot \frac{1}{1 + i\omega \tau}) \quad \ldots \ldots (3)
\]

where \( \omega = 2\pi \) times the frequency, and \( \tau \) is a constant with the dimensions of time. From equation three, it is readily seen that at the very high frequencies the dielectric constant becomes that of a substance without permanent dipole \( \varepsilon_0 \) whereas at zero frequency equation three becomes identical with equation two.
The dielectric constant may be considered to be the sum of two quantities, one real and the other imaginary.

$$\varepsilon = \varepsilon' - i\varepsilon''$$

It can be shown that

$$\varepsilon' = \varepsilon_o + \frac{\varepsilon_1 + \varepsilon_o}{1 + \left(\frac{\varepsilon_1 + 2}{\varepsilon_o + 2}\right)^2 \omega^2 \gamma^2} \quad \cdots (4)$$

$$\varepsilon_o = \varepsilon \text{ at optical frequency},$$

$$\varepsilon_1 = \varepsilon \text{ at zero frequency},$$

and

$$\varepsilon'' = (\varepsilon_1 - \varepsilon_o) \frac{\varepsilon_1 + 2}{\varepsilon_o + 2} \cdot \frac{\omega \gamma}{1 + \left(\frac{\varepsilon_1 + 2}{\varepsilon_o + 2}\right)^2 \omega^2 \gamma^2} \quad \cdots (5)$$

By application of Stokes calculation for frictional rotation of a sphere in a viscous medium, Debye obtained the expression

$$\tau = \frac{4 \pi \eta a^3}{k T} \quad \cdots (6)$$

where $\eta$ is the viscosity of the medium and $a$ is the radius of the sphere.
Variation of Dielectric Constant with Wave Length 
and its Physical Significance

As was stated above, $\gamma$ in equation three has the dimensions of time, and from equation six it is to be noted that it is directly proportional to the viscosity of the medium. Upon inquiring more carefully into the significance of this time constant, it becomes evident that it is a function of the time required for molecules to orientate themselves with respect to an applied field.

Debye has given mathematical expression for the relationship of $\gamma$ to the time of orientation of the molecules and defines it as the length of time required for the orientation of molecules in an electric field to reach one $\epsilon$th of their initial degree of orientation after the field is suddenly destroyed.

If then, the time for one alternation of the polarity of the field is of the order of magnitude of $\gamma$ the molecules will not be able to orientate themselves completely with respect to the field before polarity has changed and the orientation will be reversed. Therefore the full effect of the orientation as measured by the dielectric constant will not be realized and an increasing frequency or decreasing wave length will produce a decrease in the dielectric constant. This is very
readily understood when one considers that as the time of one alternation in potential decreases, the ratio of this time to \( \tau \) will become smaller and smaller and therefore the average degree of orientation in the electric field will be smaller.

Taking the terminology of physics optics in which normal dispersion of light connotes a decrease in refractive index with increase in wave length and considering the close relationship of refractive index and dielectric constant (the dielectric constant is the square of the refractive index when there is no absorption) the variations of dielectric constant or refractive index in this region when the time of alternation is of the order of magnitude of \( \tau \) will be opposite to that normally described as normal dispersion, and therefore this region is termed the region of anomalous dispersion. Figure 1 represents the variation in dielectric constant with \( \log \frac{\lambda}{\nu} \), where \( \lambda \) is the wave length. Here there are two curves drawn with different \( \tau \) which illustrates the shifting of the region of anomalous dispersion due to a change in \( \tau \), or in other words, due to a change in temperature or in viscosity. With water, the region of anomalous dispersion extends from approximately one-tenth of a millimeter to ten centimeters wave length at room temperature.

The viscosity of the medium has been referred to frequently and is found in the expression for \( \tau \). That cannot be construed to mean the viscosity as measured by ordinary apparatus, but is rather a measure of the viscous drag on a
single molecule. Some investigations by Johnstone and Williams indicate that the value of $\eta$ is lower than that measured by macroscopic means. Nevertheless it is reasonable to assume as a first approximation at least that $\eta$ is a linear function of the macroscopic viscosity, and therefore the latter quantity may be used in estimating variations in $\tau$.

The expression \textbf{six} for $\tau$ was derived assuming that the molecules are spherical, which of course is only an approximation, but the assumption is quite well justified by experimental results.

It is a well known fact that viscosity increases rapidly with decrease in temperature, and since in expression \textbf{six} $\tau$ varies directly as viscosity and inversely as the temperature, it is evident that with a decrease in temperature it should increase very rapidly, so that at low temperatures the region of anomalous dispersion should be at very much longer wave length than at elevated temperatures. His prediction is very well verified by the investigations of Kitchen and Mueller on rosin and by that of Mizushima on alcohols, to cite two illustrations only.

3 Sanichiro Mizushima, \textit{Bulletin of the Chemical Society of Japan}, p. 47, 82, 115, 143, 163 (1926)
The exact physical meaning of adsorption cannot be given and the probabilities are that several explanations are valid for various phases of adsorption. It may be that adsorption under some conditions is due to very different processes than adsorption under others. Usually it is considered to mean a physical bond between a molecule or colloidal particle and a surface. However, many discussions of adsorption seem very definitely to employ the possibility of primary chemical bonds existing between the adsorbed molecule and the solid surface. It is very probable that also under certain circumstances the secondary valency bonds or residual bonds are brought into play and perhaps this is the most general type of adsorption.

The influence of these various types of binding to the surface on the freedom of rotation of the adsorbing molecule and therefore upon its dielectric constant is quite apparent. In case the bond is purely an electrostatic attraction, or in other words, a concentration of molecules in an electrostatic field near the surface of a solid, it seems that the freedom of rotation of the molecule will be comparatively little hindered although it is quite reasonable to assume that there will be some hindrance and therefore that the molecule will find itself in a somewhat more viscous medium than if it were entirely free in the gaseous or liquid state. On the other hand, if the
binding is by means of residual bonds, it seems that there must be some measurable hindrance to the movements of the molecule and perhaps its freedom to orientation itself in a field will be considerably hampered. One would expect in the case of primary bonds that the molecule will be in practically the same condition as in a solid and that its freedom to rotate in an oscillating electric field will be very small and therefore the region of anomalous dispersion will extend to very long wave lengths.

Errera\(^1\) has shown that in ice, water molecules are held very rigidly, but if one chooses a sufficiently slowly oscillating field the molecules can follow it. Probably if a more unsymmetric molecule than water were used, it would be found more difficult for them to rotate and it seems quite to be expected that long chain molecules would be unable to orientate themselves in an applied field at all.

Since chemical bonds are assumed to be electrostatic in nature, even non-polar molecules must be polarized in the adsorbed state. Magnus\(^2\) has investigated this possibility mathematically but so far there has been no attempt to measure the degree of polarization or to measure the effect of adsorption on dielectric constant. Whether the electric forces at a surface may reach sufficient magnitude to cause dielectric saturation is uncertain. Probably the reason why no attempt

1 J. Errera, *Journal de Phys.*, 504.
has so far been made to measure the dielectric constant of adsorbed molecules is that in the adsorbed condition we cannot separate the contribution to dielectric constant of the solid adsorbent from that of the adsorbed phase and therefore it seems almost hopeless to measure the latter in absolute units.

Kallmann and Dorsch\(^1\) conducted some very fine measurements on dielectric constants of exceedingly thin films of liquids, hoping to find an effect due to the orientation of the molecules in the surfaces of the electrodes, but found nothing, as would be expected if the adsorption or orientation at the surface is only one or two molecules deep.

Although an absolute measure of dielectric constant of adsorbed molecules seems not to be attainable, it seems certain that some very valuable evidence as to the state of the molecules when adsorbed can be obtained by studying changes in dielectric constant with wave length. Thus it should be possible to prove definitely whether or not adsorbed molecules are loosely bound at a surface or are held with the rigidity of a solid. In the former case the relaxation time as measured by the region of anomalous dispersion in the dielectric constant curve should be relatively little affected by adsorption while in the latter case the adsorbed molecule should have relaxation time of a very different order of magnitude from that of the unadsorbed.

\(^1\) H. Kallmann I.K.E. Dorsch, Z. physik. Chem. v. 122, 305. (1927)
In seeking for suitable material to study it seemed advisable to find something in which adsorption would be quite uniform. Silica gel and charcoal are very common adsorbents but in neither case is it safe to assume that the first molecules adsorbed are held in the same way that the latter molecules are. In fact it is most certainly quite the contrary. There is a series of minerals called the zeolites, however, in which water is held quite firmly but from which it may be driven without destruction of the crystalline structure. It is normally assumed that this water is held as water of hydration and that when the water is driven out it merely finds an exit through large passages in the crystal lattice. When it is reabsorbed the assumption has been that it reenters the crystal lattice and assumes its normal position. If this is the case there should be little difference between the forces holding the first water entering and those holding the last, and this assumption is borne out by the fact that practically all of the water is adsorbed at approximately constant vapor pressure.

Here is a case in which it seems reasonable to assume a very large change in the relaxation time of the water due to adsorption. Chabazite contains about twenty-six per cent water by weight and of this, approximately twenty-two per cent may be reversibly removed at an elevated temperature. It was therefore chosen for these experiments.

Due to the fact that a granular substance between the plates of a condenser will display varying dielectric
constant, depending upon the arrangement of the granules and the
closeness of packing, it was first attempted to obtain plates
of chabazite sawed from large crystals. The services of Mr.
Sperisen in San Francisco were enlisted and he made numerous
attempts to saw plates of approximately one millimeter thick-
ness from the faces of chabazite crystals, however he found
that none of the crystals available were sufficiently perfect.
All of them had flaws running through them so that plates of
only three or four millimeters in diameter could be obtained.
These seemed too small to work with so that we finally decided
to use granulated chabazite and try to perform as many experi-
ments as possible on one condenser full without disturbing the
arrangement. As will be seen later the results obtained with
one condenser full did not check those from another series of
experiments, but still there is a residue of information which
we may glean from these experiments.

Methods of Measuring Dielectric Constant

In general there are four distinct methods for measuring
the dielectric constant of a substance. One, the electric force
acting through a dielectric is measured. Two, the dielectric
constant is calculated from the velocity of propagation of el-
ectromagnetic waves through the material. Three, the capacity
of a condenser is measured empty and again full of the substance
and the dielectric constant is the ratio of the capacity full to
that empty. The fourth method is by the deflection of molecular beams upon passing through a non-homogeneous electric field. The first method was first described by Silow and has more recently been modernized and improved by Carmen. In their experiments the charged vains to an electrometer are immersed in the liquid whose dielectric constant is to be measured and their rotation in an electric field observed. Quincke measured the force of attraction between parallel plates of a condenser, while Färth measured the rotation of an ellipsoid of revolution when suspended in the liquid at an angle of forty-five degrees with the field. For one reason or another this method has not proved popular. Carmen has apparently demonstrated the applicability of his apparatus to measurement of conducting solutions but beyond that no modern measurements use this method.

The second method was first described by Drude. He generated high frequency, alternating current by a spark discharge between two semi-circular electrodes. An induced alternating current was formed in a circle of wire surrounding these electrodes and standing waves were produced on the free ends of this circle brought out parallel to each other. The distance between the nodes of these standing waves was measured in air.

1 Carmen, Physical Review, v.24, 396 (1924)
2 Quincke, Wied. Ann. v.32 529 (1897), v.34, 801 (1898)
3 h. Färth, Z. Physik, v.22, 88 (1924), v.25, 670 (1924)
4 P. Drude, Z. F. Phys. Chem. v.23, 267 (1927)
and when the wires were immersed in the liquid under investigation. A Geissler tube was used as indicator.

The method is subject to fair accuracy, but requires a very large quantity of the liquid investigated and in general is not applicable to the investigation of solids.

The third method in which the capacity of a condenser is measured before and after filling with the substance is the one that is most generally used. This method may be divided into several divisions depending upon the arrangements of the circuits. It is probably only necessary here to mention measurement with damped and undamped waves. Modern practice is in the direction of undamped waves, and it is considered that a good many of the anomalies observed in dielectric constant measurements are due to the use of damped waves. In the generation of undamped oscillations radio tubes are used almost exclusively. A single current may be employed in what is termed the resonance method, in which case the capacity of the condenser may be calculated by the frequency of the exciting current and by the known constants of the circuit. Usually a hot wire galvanometer is used as an indicator of the resonance peak. The heterodyne beat method has come into prominence particularly where the measurement of minute changes in capacity is necessary or where very small condensers are desirable. It is subject to almost limitless refinement and the degree of accuracy attainable is mainly dependent upon the number of precautions one is willing to take.

1 K. Widdington, Philosophical Magazine, v.40, 634.
In this system two circuits are used, each oscillating at almost the same frequency. The frequency of one is fixed and that of the other which possesses the capacity to be measured is varied until an audible beat note is obtained between the two circuits. If, for example, one circuit is oscillating at one million cycles per second and the other is set to oscillate at one million one thousand, a note will be heard in the receiver of one thousand cycles a second. Now if the second circuit is changed to one million one thousand and one, the beat note will change by one cycle, which can be detected if a tuning fork is used as a standard frequency. In other words, the setting of the second circuit with respect to the first can be measured accurately to within one part in a million.

The molecular beam method was first suggested by Kallmann and Reiche. A beam of molecules is collimated by passing through pinholes in a highly evacuated space. It is then allowed to pass through a non-homogeneous electric field and the deflections of the molecules measured by some suitable device. The molecules may be frozen out on a glass surface or may be caused to react with some sensitive surface or to sensitize a surface for some other reaction. This method is not subject to high accuracy but in certain cases is very valuable for proving the presence or absence of a permanent dipole in gaseous molecules.

The heterodyne beat method was chosen in the present investigation due to the limited size of the measuring condenser, and

1 Kallmann & Reiche, *Z. Physik.*, v. 6, 352. (1921)
also on account of the fact that this method is particularly adapted to the measurement of changes in dielectric constant, and that, as pointed out above, is the only kind of measurement of significance in this work.

It was thought that due to the probability that the water in chabazite is held more nearly in the solid than in the liquid condition, a frequency well within the range where the heterodyne beat method is applicable could be used. Nevertheless, it was desirable to use as short wavelength as practical. A wavelength of approximately 50 m. was chosen. Unfortunately, the sensitivity to small changes in the constants of the circuits increases with this method with decrease in wavelength and without great care it is very difficult to use wavelengths much shorter than 50 m. When it is realized that the upper limit of the anomalous dispersion curve for water lies at about 0.1 m., one can understand that if adsorption does have an effect on the freedom of rotation of the molecules, only an effect of a large order can be observed at 50 m.

The diagram of the circuits used is shown in Figure 2.
Oscillator parts:

1. $T =$ Radio tube, UX201A
2. R.C.F. = Radio frequency coil, 3/4" dia. 250 turns, No. 120 D.C. wire
3. $L =$ Transmitting inductance, 3 3/8" dia., 11 turns, No. 18 gauge copper wire
4. $R_1 =$ Grid-leak, 10,000 ohms
   $R_2 =$ Rheostat, 6 ohms
5. \( C_1 \) = Calibrated condenser, Leads & Northup condenser,
   1,193 m.m.f.
\( C_2 \) = Variable "Hammarlund Jr" condenser, 50 m.m.f.
\( C_3 \) = Variable Condenser, 28.5 m.m.f.
\( C_4 \) = Fixed condenser, 250 m.m.f.
\( C_x \) = Test condenser
\( C_1 \) = Fixed condenser, 24 m.m.f.
\( C_2 \) = Fixed condenser, 2457 m.m.f.

6. \( A \) = Battery, 6 volts
   \( B \) = Battery, 96 volts

Receiving unit:
1. \( T_1 \) = Detector tube, UX201A
   \( T_2 \) = O.K. Amplifying tube, X-112-A
2. \( L \) = Receiving coil, 4.5 x 5 c.m. one turn, No.18 gage copper wire
3. \( C_1 \) = "National" variable condenser, 150 m.m.f.
   \( C_2 \) = Variable condenser, 250 m.m.f.
   \( C_3 \) = Variable condenser, 250 m.m.f.
   \( C_4 \) = Fixed condenser, 250 m.m.f.
4. \( r_1 \) = Grid-leak, 10,000 ohms
   \( r_2 \) = Grid-leak, 1 megoh.
   \( r_3 \) = 0.6 megoh.
   \( r_4 \) = Rheostat, 6 ohms
5. \( A \) = Storage battery, 6 volts
   \( B \) = Dry battery, 45 volts
6. \( F \) = Loud speaker.
At first heavy copper tubing was used as inductance, but this vibrated rather badly with vibrations in the building and made the readings unsteady so that it was later replaced with No. 18 gage copper wire wound on a paper cylinder and securely fastened to avoid any vibratory motion.

The capacities were calibrated against a Leeds-Northrup condenser that had been received with certificate of calibration. In order to increase the accuracy of reading, the measuring condenser, in parallel with a small variable condenser, was replaced in series with the standard condenser of 1.143 micromicrofarads capacity. In this way a change of a very small fraction of a micromicrofarad in the capacity of the measuring condenser was reflected by a change in the setting of the standard condenser of several micromicrofarads.

The measuring condenser was made of iron plates separated by a glass separator cut out of a microscope slide (Fig. 3) These were supported in the vacuum apparatus by the lead in

![Diagram](image-url)
wires as shown in figure 4. It was attempted to utilize alumi-
num plates, but they warped at the temperature attained in the
dehydration, and they were found to give off gas so sopiously that
a hard vacuum was almost unattainable.

By means of the apparatus pictures in figure 4 it was poss-
able to pump off the air and water vapor, heating the tube in
which the condenser is supported to about 400°C. After from
three to twelve hours of evacuation, the apparatus was placed
in a thermosat box and allowed to come to constant temperature.
The large carefully calibrated bulb could be filled with water
vapor at any desired pressure by controlling the temperature of
tube D. The stopcock between the tube and the bulb was then
closed and the cock from the bulb to the condenser chamber was
opened. Adsorption is remarkably rapid, requiring less than a
minute usually for the manometer to read less than a tenth of a
millimeter pressure. Adequate time was allowed for the water
vapor to be adsorbed and temperature to come to equilibrium,
after which the capacity of the condenser was measured.

The effect of a minute film of oil on water on the rate
of evaporation is strikingly illustrated by the time for equil-
ibrium to be established between the water in the water tube
and the vapor in the bulb in the presence and in the absence
of stopcock grease. In one of the heating operations, some
stopcock grease was allowed to melt and run down the tube. At
zero centigrade the grease was quite hard and there was no vis-
ible evidence of a film of it on the water. It required,
however, about ten minutes for the vapor pressure in the bulb to come up to 4.6 mm. After this tube was thoroughly cleaned out and fresh water admitted, the time was less than a minute, although usually three minutes were allowed.

Since chabazite adsorbs water at a pressure less than 0.1 mm. until it is nearly saturated, no corrections had to be made due to the volume of the chamber holding the condenser, and the course of the change in dielectric constant could be followed without difficulty.

In order to demonstrate the presence of anomalous dispersion, readings were made at both 33 and 75 meters wavelength. Also in addition to these measurements at constant temperature, a series was run at the two wavelengths and different temperatures down to about -80°C. It was hoped to demonstrate the decided effect of temperature on the relaxation time by this means, and in case the water within the chabazite were liquid to show its freezing point by a sudden drop in dielectric constant.
Results and Conclusions

Throughout the school year and the following summer many measurements were made, but with unsatisfactory results. Figure 5 shows only a few of the better ones at constant temperature. A troublesome lack of consistency in the readings interfered for months, and it was only after completely rebuilding the apparatus that the cause of the trouble became apparent. At such high frequencies as 50 m. small capacities and inductances may become important. It was found that the lead wires into the thermostat and to the measuring condenser had sufficient capacity and inductance to give the effect of a second circuit capacitatively coupled to the first. The relationship between the three condensers in the circuits no longer was simple, but was defined by a very complex function so that the calculation of the actual changes in the capacity of the chabazite became next to impossible.
$dC_a$ - Weight of $H_2O$

College of the Pacific
August 30th, 1931
K. Inada

I. Data 1. Short wave
Weight of Chabazite = 1011 gr.
Capacity of $n$ = 667 mm scatter

II. Data 2, 3
Weight of Chabazite = 1089 gr.
Capacity of $n$ = 447 mm scatter
(a) Short wave
(b) Long wave

Fig. 5

Weight of $H_2O$ in mg
### Table 1

**Short Wave**

<table>
<thead>
<tr>
<th>Pressure (m.m.)</th>
<th>Temperature (Centigrade)</th>
<th>Weight of Chabazite (m.g.)</th>
<th>Capacity of Chabazite (m.m. fd.)</th>
<th>Weight of Chabazite (m.m. fd.)</th>
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### Table 2

**Long Wave**

<table>
<thead>
<tr>
<th>Pressure (m.m.)</th>
<th>Temperature (Centigrade)</th>
<th>Weight of Chabazite (m.g.)</th>
<th>Capacity of Chabazite (m.m. fd.)</th>
<th>Weight of Chabazite (m.m. fd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22.5</td>
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<td>22.308</td>
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<td>184.081</td>
<td>4.22</td>
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</tbody>
</table>

Note: The table values are rounded to the nearest decimal place.
Table 3 (a)

**Short Wave**

Constant temperature 22°C  
Weight of chabazite 1.039 gr.  
Capacity of chabazite 4.47 m.m.f.d.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Temperature</th>
<th>Weight of water (g)</th>
<th>dx</th>
<th>Total dx (m.m.f.d.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.m.</td>
<td>Centigrade</td>
<td>dw</td>
<td></td>
<td>dw</td>
</tr>
<tr>
<td>0</td>
<td>18.7</td>
<td>0</td>
<td>1.30</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>19.4</td>
<td>39.418</td>
<td>33.218</td>
<td>1.50</td>
</tr>
<tr>
<td>0</td>
<td>20.1</td>
<td>20.328</td>
<td>59.596</td>
<td>1.90</td>
</tr>
<tr>
<td>0</td>
<td>20.4</td>
<td>20.587</td>
<td>80.142</td>
<td>2.50</td>
</tr>
<tr>
<td>0</td>
<td>20.7</td>
<td>20.965</td>
<td>101.109</td>
<td>3.10</td>
</tr>
<tr>
<td>0</td>
<td>21.0</td>
<td>21.267</td>
<td>123.275</td>
<td>3.40</td>
</tr>
<tr>
<td>0</td>
<td>23.9</td>
<td>24.209</td>
<td>147.584</td>
<td>3.92</td>
</tr>
<tr>
<td>0.5</td>
<td>24.2</td>
<td>24.297</td>
<td>174.981</td>
<td>4.30</td>
</tr>
<tr>
<td>2.5</td>
<td>24.5</td>
<td>25.679</td>
<td>205.660</td>
<td>4.55</td>
</tr>
<tr>
<td>11.5</td>
<td>24.7</td>
<td>11.683</td>
<td>207.343</td>
<td>4.55</td>
</tr>
</tbody>
</table>

Table 3 (b)

**Long Wave**

Constant temperature 33°C  
Weight of chabazite 1.039 gr.  
Capacity of chabazite 4.47 m.m.f.d.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Temperature</th>
<th>Weight of water (g)</th>
<th>dx</th>
<th>Total dx (m.m.f.d.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.m.</td>
<td>Centigrade</td>
<td>dw</td>
<td></td>
<td>dw</td>
</tr>
<tr>
<td>0</td>
<td>18.7</td>
<td>0</td>
<td>1.30</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>19.4</td>
<td>39.418</td>
<td>33.218</td>
<td>2.20</td>
</tr>
<tr>
<td>0</td>
<td>20.1</td>
<td>20.328</td>
<td>59.596</td>
<td>2.60</td>
</tr>
<tr>
<td>0</td>
<td>20.4</td>
<td>20.587</td>
<td>80.142</td>
<td>3.07</td>
</tr>
<tr>
<td>0</td>
<td>20.7</td>
<td>20.965</td>
<td>101.109</td>
<td>3.27</td>
</tr>
<tr>
<td>0</td>
<td>21.0</td>
<td>21.267</td>
<td>123.275</td>
<td>2.57</td>
</tr>
<tr>
<td>0</td>
<td>23.9</td>
<td>24.209</td>
<td>147.584</td>
<td>4.10</td>
</tr>
<tr>
<td>0.5</td>
<td>24.2</td>
<td>24.297</td>
<td>174.981</td>
<td>4.35</td>
</tr>
<tr>
<td>2.5</td>
<td>24.5</td>
<td>25.679</td>
<td>205.660</td>
<td>4.65</td>
</tr>
<tr>
<td>11.5</td>
<td>24.7</td>
<td>11.683</td>
<td>207.343</td>
<td>4.85</td>
</tr>
</tbody>
</table>
The leads were shortened as much as possible and every effort made to eliminate this source of error. It became apparent, however, that only by a radical rearrangement of the entire apparatus could entirely consistent results be obtained. The time had passed when this was physically possible, so that it became necessary to accept the data as it could be gotten. The standard condenser was set at a fixed value and changes in the capacity of the chabazite measured by changes in the parallel condenser.

In spite of the lack of satisfying results, there is a residuum of results from the work of sufficient value to warrant certain conclusions, and as a piece of pioneering research it seems that the knowledge gained has been worth the effort.

Figure 5 shows conclusively that the region of anomalous dispersion for water in the adsorbed condition in chabazite does not extend to 33 meters wavelength, the shortest that we used. This means that the relaxation time for water in the adsorbed state in chabazite is less than 500 times the relaxation time in liquid water at normal temperature. This is a powerful argument against the attachment of the water molecules by primary bonds, or even against a firm bond of any kind. Since the relaxation time of ice at \(-2^\circ \text{C}\), is of the order of 2,000,000 times that for liquid water\(^1\) it is perfectly evident that the water in chabazite is much more like liquid water than it is like ice.

Hoping further to show the character of the water, the values of the dielectric constant at low temperatures were

\(^1\) J. Errera, *Journ. de Phys.* v.5, 204 (1924)
$d\chi - \text{Temperature}$

- Short wave
- Long wave

---

College of the Pacific
August 30th, 1931
R. Jamalik

Temperature in Centigrade

Fig. 6
## Capacity - Temperature

### Table 4(a)

**Empty Condenser**

#### Short Wave

<table>
<thead>
<tr>
<th>Temperature (Centigrade)</th>
<th>$C_3 - C_1$ (m.m. ft)</th>
<th>$dx$ (m.m.fld.)</th>
<th>Total $dx$ (m.m. ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Test condenser</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.8</td>
<td>30.90</td>
<td>-1.93</td>
<td>0</td>
</tr>
<tr>
<td>25.8</td>
<td>16.50</td>
<td>-1.93</td>
<td>0</td>
</tr>
<tr>
<td>25.8</td>
<td>16.60</td>
<td>-1.93</td>
<td>0</td>
</tr>
<tr>
<td>25.7</td>
<td>-11.10</td>
<td>-2.00</td>
<td>-0.07</td>
</tr>
<tr>
<td>25.6</td>
<td>-25.29</td>
<td>-2.15</td>
<td>-0.15</td>
</tr>
<tr>
<td>25.6</td>
<td>-40.75</td>
<td>-2.42</td>
<td>-0.27</td>
</tr>
<tr>
<td>25.6</td>
<td>-53.52</td>
<td>-2.60</td>
<td>-0.18</td>
</tr>
<tr>
<td>25.6</td>
<td>-66.71</td>
<td>-2.75</td>
<td>-0.15</td>
</tr>
<tr>
<td>25.5</td>
<td>-77.21</td>
<td>-2.77</td>
<td>-0.02</td>
</tr>
<tr>
<td>25.4</td>
<td>-83.35</td>
<td>-2.75</td>
<td>0.02</td>
</tr>
</tbody>
</table>

### Table 4(b)

#### Long Wave

<table>
<thead>
<tr>
<th>Temperature (Centigrade)</th>
<th>$C_3 - C_1$ (m.m. ft)</th>
<th>$dx$ (m.m.fld.)</th>
<th>Total $dx$ (m.m. ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.8</td>
<td>30.90</td>
<td>-0.63</td>
<td>0</td>
</tr>
<tr>
<td>25.8</td>
<td>16.50</td>
<td>-0.75</td>
<td>-0.12</td>
</tr>
<tr>
<td>25.8</td>
<td>16.60</td>
<td>-0.62</td>
<td>-0.13</td>
</tr>
<tr>
<td>25.7</td>
<td>-11.10</td>
<td>-0.88</td>
<td>-0.26</td>
</tr>
<tr>
<td>25.6</td>
<td>-25.29</td>
<td>-1.08</td>
<td>-0.40</td>
</tr>
<tr>
<td>25.6</td>
<td>-40.75</td>
<td>-1.13</td>
<td>-0.17</td>
</tr>
<tr>
<td>25.6</td>
<td>-53.52</td>
<td>-1.25</td>
<td>-0.03</td>
</tr>
<tr>
<td>25.5</td>
<td>-66.71</td>
<td>-1.38</td>
<td>-1.15</td>
</tr>
<tr>
<td>25.4</td>
<td>-77.21</td>
<td>-2.51</td>
<td>-1.15</td>
</tr>
<tr>
<td>25.4</td>
<td>-83.35</td>
<td>-1.68</td>
<td>-0.83</td>
</tr>
</tbody>
</table>
### Table 5(a)

Without Water Vapor

**Short Wave**

<table>
<thead>
<tr>
<th>Td.</th>
<th>((C_5-C_r)-(C_3-C_x)) dx</th>
<th>Total dx</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m.m.f.d.</td>
<td>m.m.f.d.</td>
</tr>
<tr>
<td>0.56</td>
<td>-0.56</td>
<td>-0.07</td>
</tr>
<tr>
<td>0.47</td>
<td>-0.07</td>
<td>-0.04</td>
</tr>
<tr>
<td>0.67</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.45</td>
<td>-0.45</td>
<td>-0.05</td>
</tr>
<tr>
<td>0.50</td>
<td>-0.45</td>
<td>-0.10</td>
</tr>
<tr>
<td>0.45</td>
<td>-0.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>0.51</td>
<td>-0.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>0.56</td>
<td>-0.56</td>
<td>-0.07</td>
</tr>
<tr>
<td>0.50</td>
<td>-0.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>0.45</td>
<td>-0.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>0.50</td>
<td>-0.50</td>
<td>-0.10</td>
</tr>
<tr>
<td>0.45</td>
<td>-0.45</td>
<td>-0.10</td>
</tr>
<tr>
<td>0.40</td>
<td>-0.40</td>
<td>-0.10</td>
</tr>
<tr>
<td>0.45</td>
<td>-0.14</td>
<td>-0.05</td>
</tr>
<tr>
<td>0.25</td>
<td>-0.25</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

**Long Wave**

<table>
<thead>
<tr>
<th>Td.</th>
<th>((C_5-C_r)-(C_5-C_x)) dx</th>
<th>Total dx</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m.m.f.d.</td>
<td>m.m.f.d.</td>
</tr>
<tr>
<td>0.67</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.64</td>
<td>-0.64</td>
<td>-0.01</td>
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<tr>
<td>0.62</td>
<td>-0.62</td>
<td>-0.02</td>
</tr>
<tr>
<td>0.57</td>
<td>-0.57</td>
<td>-0.05</td>
</tr>
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<td>0.48</td>
<td>-0.48</td>
<td>-0.09</td>
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<tr>
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<td>-0.50</td>
<td>-0.08</td>
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<td>-0.50</td>
<td>-0.10</td>
</tr>
<tr>
<td>0.45</td>
<td>-0.50</td>
<td>-0.05</td>
</tr>
<tr>
<td>0.25</td>
<td>-0.25</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

**Note:**
- Negative values indicate energy loss, positive values indicate energy gain.
Table G(a)  
Amount of water vapor & salts  
Weight of chabazite 1.089 gr.  
Capacity of chabazite 4.47 m.m.f.d.

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>(C&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;r&lt;/sub&gt;)-(i-C&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;x&lt;/sub&gt;)</th>
<th>dx</th>
<th>Total dx</th>
</tr>
</thead>
<tbody>
<tr>
<td>room Test condenser</td>
<td>m.m.f.d.</td>
<td>m.m.f.d.</td>
<td>m.m.f.d.</td>
</tr>
<tr>
<td>25.1</td>
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<td>0</td>
</tr>
<tr>
<td>25.5</td>
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<td>-0.05</td>
</tr>
<tr>
<td>25.6</td>
<td>0.33</td>
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<tr>
<td>25.0</td>
<td>-18.19</td>
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<td>-0.30</td>
</tr>
<tr>
<td>24.8</td>
<td>-24.14</td>
<td>3.15</td>
<td>-0.40</td>
</tr>
<tr>
<td>25.0</td>
<td>-29.63</td>
<td>2.97</td>
<td>-0.15</td>
</tr>
<tr>
<td>25.0</td>
<td>-50.44</td>
<td>2.76</td>
<td>-0.24</td>
</tr>
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<td>-0.33</td>
</tr>
<tr>
<td>24.9</td>
<td>-77.20</td>
<td>2.20</td>
<td>-0.20</td>
</tr>
<tr>
<td>24.2</td>
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<td>2.05</td>
<td>-0.15</td>
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</table>

Table C(b)  
Long Wave

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>(C&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;r&lt;/sub&gt;)-(i-C&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;x&lt;/sub&gt;)</th>
<th>dx</th>
<th>Total dx</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.1</td>
<td>22.80</td>
<td>4.60</td>
<td>0</td>
</tr>
<tr>
<td>25.5</td>
<td>17.72</td>
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<td>25.0</td>
<td>-18.19</td>
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<td>4.37</td>
<td>-0.40</td>
</tr>
<tr>
<td>25.0</td>
<td>-29.63</td>
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<td>-0.40</td>
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<td>-0.37</td>
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<td>-0.20</td>
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<td>-77.20</td>
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<td>-0.01</td>
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<tr>
<td>24.2</td>
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<td>2.92</td>
<td>-0.20</td>
</tr>
</tbody>
</table>
### Table 7(a)

Amount of water vapor 12 bulbs  
Weight of chabazite 1.0L  
Capacity of chabazite 6.67 m.m.f.d.

**Short Wave**

<table>
<thead>
<tr>
<th>Temperature (Centigrade)</th>
<th>((C_2-C_6))</th>
<th>(dx)</th>
<th>Total (dx)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m.m.f.d.)</td>
<td></td>
<td>(m.m.f.d.)</td>
</tr>
<tr>
<td>Room Test condenser</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.2</td>
<td>23.80</td>
<td>4.55</td>
<td>0</td>
</tr>
<tr>
<td>25.2</td>
<td>9.64</td>
<td>4.20</td>
<td>-0.35</td>
</tr>
<tr>
<td>25.2</td>
<td>-4.30</td>
<td>3.73</td>
<td>-0.47</td>
</tr>
<tr>
<td>25.2</td>
<td>-21.14</td>
<td>3.28</td>
<td>-0.45</td>
</tr>
<tr>
<td>25.2</td>
<td>-33.55</td>
<td>2.97</td>
<td>-0.31</td>
</tr>
<tr>
<td>25.2</td>
<td>-49.74</td>
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<td>25.2</td>
<td>-64.52</td>
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<td>-0.24</td>
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<td>-78.65</td>
<td>2.30</td>
<td>-0.13</td>
</tr>
<tr>
<td>24.8</td>
<td>-80.23</td>
<td>2.13</td>
<td>-0.17</td>
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</table>

### Table 7(b)

**Long Wave**

<table>
<thead>
<tr>
<th>Temperature (Centigrade)</th>
<th>((C_2-C_6))</th>
<th>(dx)</th>
<th>Total (dx)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m.m.f.d.)</td>
<td></td>
<td>(m.m.f.d.)</td>
</tr>
<tr>
<td>25.2</td>
<td>23.80</td>
<td>4.95</td>
<td>0</td>
</tr>
<tr>
<td>25.2</td>
<td>9.64</td>
<td>4.60</td>
<td>-0.35</td>
</tr>
<tr>
<td>25.2</td>
<td>-4.30</td>
<td>4.05</td>
<td>-0.55</td>
</tr>
<tr>
<td>25.2</td>
<td>-21.14</td>
<td>3.62</td>
<td>-0.45</td>
</tr>
<tr>
<td>25.2</td>
<td>-33.55</td>
<td>3.35</td>
<td>-0.27</td>
</tr>
<tr>
<td>25.2</td>
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measured and plotted in Figure 6. Here the variation of the capacity of the empty condenser was measured down to the temperature of solid carbon dioxide in ether, it was then filled with chabazite, all water pumped off and the capacity curve again obtained. Water was admitted, not to saturation but to several fractions below saturation, and the influence of the water on the capacity determined. Here it seems evident from Fig. 6 that at the lower temperatures the dielectric constant of the water is greater at the longer wave-lengths, showing that at low temperatures the region of anomalous dispersion extends up to 75 meters.

The remarkable fact becomes obvious that although the water within the chabazite is almost as mobile as liquid water in an oscillating field, it cannot be frozen at temperatures as low as -80°C. If freezing had occurred, it would have been evident from a sudden break in the dielectric constant curve. One would expect some undercooling, since water in capillaries tends to undercool more strongly than in larger masses but the paradoxical results here obtained certainly were not expected. These results fall into line with observations by Gortner and numerous others that there is a fraction of the water in colloids that will not freeze. No adequate explanation has yet been given.

2 R. A. Gortner, J. Phys. Chem., v.36, 297 (1932)
Although chabazite is definitely crystalline, we have evidence that the water is held similar to that in colloids. It has been often assumed, and in fact so defined, that crystals are fundamentally different from colloids, the latter being assumed to be a manifestation of the amorphous state, and yet here is an example of a crystal in which the water is held like in the hydrophyl colloids. It will be exceedingly interesting to pursue this investigation still further and see if the water in various of the simpler crystals may behave in the electric field in the same manner.

It is conceivable that within the relatively open crystal lattice of chabazite and allied zeolites water may be held in true chemical combination, but the binding is from one direction only, perhaps from one single atom, and the water molecule thus supported on a pinnacle, so to speak, will be free to swivel about and make a generous contribution to the dielectric constant even at relatively high frequencies. Of course such water molecules could not "freeze" so that the change of dielectric constant with temperature would give a smooth curve. Probably the viscosity term in the equation for the relaxation time (equation 6) will remain nearly constant unless the water molecules are so thick in the lattice structure as to interfere with each other's movements, which means that the decrease in the dielectric constant with temperature will be much slower than in the case of liquids, a fact to be observed in figure 6.
The above hypothesis regarding the condition of the water in chabazite would offer a ready explanation of another observation. In figure 5 it is evident, in spite of the lack of coincidence of the curves, that the first additions of water contribute more per milligram to the dielectric constant than the later ones. This observation is quite contrary to what would be expected if it is assumed that later additions are more weakly bound and therefore more mobile. Certainly the heat of adsorption of the last water is less than that of the first. If, however, the water molecules are held on certain atoms in the lattice, as more and more water is added they will be more and more frequently found on adjacent atoms and therefore the interference with each other's freedom to orientate will steadily increase. For very long wavelengths this will produce no measurable effect on the dielectric constant, but for high frequencies the greater the quantity of water already present the less will an addition affect the dielectric constant. This interference can as well come from the other side of a channel as from along side of a molecule.
Summary

A brief review of the relation of dielectric constant to physical and chemical properties of a substance is given. The availability of dielectric constant measurements as a powerful tool in the investigation of matter is pointed out, and the four methods of measurement are outlined.

Adsorbed water is found to have a relaxation time much more nearly that of liquid water than that of ice. It will not freeze, and its dielectric constant has a relatively small temperature coefficient.

It is concluded that water is held in the zeolites by attachment of the molecules to atoms or points in the rigid lattice, where they may pivot freely, thus possessing a small relaxation time much less dependent upon temperature than is normally the case in liquids.

In conclusion we would like to express our appreciation of the kindness of the Stanford University Chemistry Department, and especially of Dr. J. W. McBain, for lending us the apparatus used in this investigation.
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