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The Dielectric Constant of Liquid Sulphur*

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The dielectric constant and power factor of liquid sulphur were measured by a bridge method at four different audio-frequencies and over the temperature range 118°C to 350°C. The dielectric constant was found to be independent of frequency and equal to 3.520 ± 0.010 at 118°C. A study of the polarization curve shows that liquid sulphur is non-polar. A method was developed for differentiating between that part of the power factor which is due to conductivity

and that which is due to molecular friction. The former was found to be large at high temperatures and the latter small at all temperatures. The infrared spectrum of liquid sulphur contains definite absorption bands, which fact shows that its molecules are polar. It is difficult to understand this contradiction, since both measurements seem to give conclusive results.

INTRODUCTION

ACCORDING to Debye's theory, it should be possible to measure the electric moment of a substance according to the formula

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{d} = \frac{4\pi}{3} \frac{N}{M} \left(\alpha + \frac{\mu^2}{3kT} \right) = P,$$

where ϵ is the dielectric constant, d the density, N Avogadro's constant, α the molecular polarizability, μ the electric moment, k Boltzmann's constant, T the absolute temperature, and P the specific polarization. This formula has been found to apply quantitatively to gases and non-associated liquids, and qualitatively to associated liquids.

Debye¹ has further shown that if a liquid is quite viscous, the molecules may find difficulty in orienting themselves in the direction of the field. If such a liquid were placed in an alternating field and the frequency increased, a frequency would finally be reached where the molecules could no longer follow the alternations of the field, so that at this frequency the liquid would virtually become nonpolar. Debye calls this a region of anomalous dispersion, and predicts, among other things, that the power factor of the substance should increase markedly in

this region. Mizushima,² Kitchen and Müller,³ Smyth⁴ and others have obtained qualitative verifications of this theory.

It was thought that a study of an elementary substance might prove to be valuable in clearing up some of the difficulties which still remain; and it was for this reason that sulphur was chosen for the present study.

At the melting point, liquid sulphur is quite mobile. On heating, the viscosity remains approximately constant until about 160°C is reached, when it becomes very viscous, and reaches a maximum viscosity about 180°C, after which the viscosity decreases rapidly at first and then quite gradually up to the boiling point at 445°C. It is one of the few liquids which have a viscosity cycle. Molecular association is known to occur. According to Kellas⁵ the sulphur molecule contains eight atoms at the melting point. At 160°C the reaction $3S_8 \rightleftharpoons (S_8)_3$ takes place, and goes more strongly to the right as the temperature is increased, and reverses just before it reaches the boiling point.

Taylor and Rideal,⁶ from measurements on the heat of dissociation, the heat of vaporization, and the infrared absorption spectrum, conclude

² Mizushima, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 5, (79) 201 (1927); 9, (166) 209 (1928).

³ Kitchen and Müller, *Trans. Am. Inst. Elect. Eng.* 48, (2) 495 (1928).

⁴ Smyth, *Dielectric Constant and Molecular Structure*, The Chemical Catalog Company (1931).

⁵ Kellas, *J. Am. Chem. Soc.* 113, 903 (1918).

⁶ Taylor and Rideal, *Proc. Roy. Soc. A* 115, 589 (1927).

* Part of a dissertation presented for the degree of Doctor of Philosophy in Yale University.

¹ P. Debye, *Polar Molecules*, The Chemical Catalog Company (1929).

that the S_2 molecule is definitely polar. However, Rosenthal⁷ has measured the dielectric constant of liquid sulphur over a limited temperature range and at a very high frequency, and finds it to be nonpolar. Since the liquid becomes so viscous at high temperatures, one might expect that it would exhibit anomalous dispersion at low frequencies if it were polar. Therefore Rosenthal's result would not seem to be very conclusive. It was thought to be advisable to make the measurements at several low frequencies, and over a wide temperature range.

APPARATUS

A diagram of the measuring apparatus is shown in Fig. 1. Part A represents a Hartley oscillator

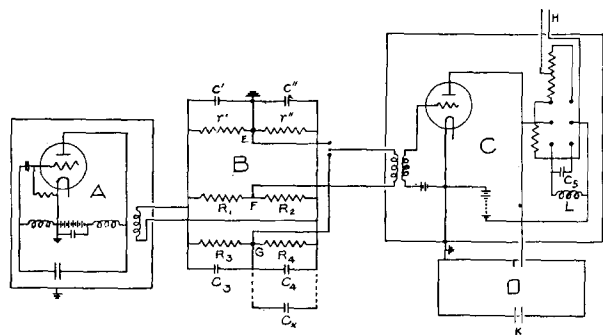


Fig. 1. Diagram of apparatus.

capable of giving a large number of frequencies between 200 and 4000 cycles, placed in a grounded metal box. Part B represents a capacitance bridge of the parallel resistance type. The upper arms consist of resistances R_1 and R_2 , which are matched coils of 4000 ohms each. The lower arms consist of condensers C_3 and C_4 shunted by resistances R_3 and R_4 . C_3 is a variable air condenser, C_4 is a standard variable air condenser recently accurately calibrated at the Bureau of Standards, and R_3 and R_4 are 100,000 ohm resistance boxes. r' , r'' , c' , and c'' make up a Wagner ground. C_x is the measuring cell, arranged so that it may be placed in parallel with C_4 . Every resistance and condenser in the bridge is in a separate grounded metal case, and the arrangement symmetrically placed to diminish the interaction between the various parts.

⁷ Rosenthal, Acad. Pol. Sci. et Let. Bull. 8a, 377 (1928).

Current from the bridge is fed through a transformer to an amplifier C. In the plate circuit of this tube is a combination frequency bridge and wave filter. C_5 is a mica capacitance box, and L is a Brooks inductometer used as a self-inductance. When the double pole-double throw switch is thrown up, the arrangement is a frequency bridge of the usual type and may be balanced for a particular frequency by placing phones at the point H. When the switch is thrown down, the condenser and inductance are put in parallel across the output of the amplifier and act as a wave filter which allows only that frequency to pass. The frequency bridge was calibrated to an accuracy of about 1 percent by means of a General Radio Company calibrated low-frequency oscillator. This arrangement made it a simple matter to measure the frequency and set the wave filter.

The output of this amplifier is fed into another amplifier, which is a 3-stage resistance-coupled amplifier of the usual type. Both amplifiers are placed in separate grounded metal boxes, and high-frequency low pass filters put in the input leads of both. These precautions eliminate external disturbances.

The measuring cell consists of three concentric aluminum cylinders approximately 10 cm in diameter. The outer and inner cylinders are rigidly screwed to an aluminum base, and together make up one plate of the condenser. The middle cylinder, which is shorter than the other two, is separated from them by quartz spacers, and comprises the other plate. The liquid is placed between the outer and inner cylinders and thus completely surrounds the middle one. This eliminates end effects. The effect due to the lead to the middle electrode was found to be negligible. This lead is surrounded by a quartz tube which acts as a spacer and extends outside of the condenser. Thus any leak across the surface of the liquid is eliminated. The spacers were very accurately ground, so that the condenser may be taken apart and reassembled without affecting its capacitance.

The spacers used in the condenser are quartz. Upon investigation it was found that they have an appreciable power factor above 350°C. Moulded magnesium oxide spacers were found to be far superior even at quite low temperatures,

but since sulphur was found to have a very high conductivity above 300°C , the error introduced by the quartz spacers is negligible, and they are used in preference to magnesium oxide on account of their superior mechanical properties.

The measuring cell is placed in a resistance furnace which is run from storage batteries and may be maintained at any desired temperature to within one degree throughout the cell. A thermocouple for measuring the temperature is placed in the liquid sulphur.

METHOD OF MEASUREMENT

The dielectric constant of sulphur is determined by measuring the capacitance of the measuring cell with air as the dielectric and again with sulphur as the dielectric. The ratio of these two capacitances gives the dielectric constant.

A strict substitution method is employed in making the measurements so that all lead capacitances and so forth are eliminated. The resistance boxes R_3 and R_4 were found to have so low an inductance that they introduced an inappreciable error. An individual reading of the capacitance is correct to 0.1 percent. In the measurement of the dielectric constant, the effect of the quartz spacers in the measuring cell had to be taken into consideration. There are six spacers at the top and six at the bottom, but three at each end are sufficient to hold the electrodes rigidly in place. The procedure is to measure the capacitance of the air condenser with all 12 spacers in place at a number of temperatures; then remove three at each end and repeat the process. The difference in capacitance at any temperature gives the effect of half the spacers, and by interpolation the true capacitance of the condenser can be found.

It is known that a number of the properties of liquid sulphur depend on its past history. Thus, in order to get consistent results, it was thought advisable to start each run with c.p. crystals of sulphur, melt them very carefully at a temperature just above the melting point; and increase the temperature at about the same rate on all runs. However, it was found that if the sulphur was allowed to stand at a fixed temperature for from two to five hours, depending on the viscosity, the dielectric constant and power

factor are independent of its past history. The latter procedure was finally adopted, each run taking about two weeks to complete.

The measurement of the power factor presented some difficulty. A leaky condenser is conventionally represented either as a resistance in parallel or in series with a perfect condenser. When the power factor is small, it makes very little difference which representation is used; but when it is large, it makes a very appreciable difference. Errors in the measured capacitance of greater than 100 percent may be made in this way. It is then necessary to represent the condenser as a combination of resistances in series and parallel with a perfect condenser. Two different types of power losses in condensers with liquid dielectrics are well recognized; the first being due to an ionic conductivity, and the second to molecular friction. It seems reasonable to assume that the former can best be represented by a parallel resistance, and the latter by a series resistance. In his theory Debye completely ignores the conductivity due to ions, and considers the power factor as due entirely to molecular friction. If ionic conductivity is large, it may completely mask the effect due to molecular friction. It was found to be necessary to devise a method of measurement which would separate these two power factors, and at the same time allow a measurement of the true dielectric constant if power factor measurements were to be compared with those predicted by Debye's theory, since the ionic conductivity of sulphur at high temperatures is quite large. For this reason, corrections to the measured capacitance are much smaller in a parallel resistance bridge method than in a series method.

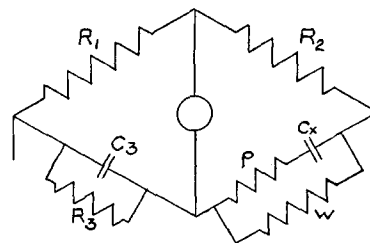


FIG. 2. Equivalent bridge diagram.

Fig. 2 shows the equivalent bridge, where ρ is the fictitious resistance due to molecular friction,

and w that due to ionic conductivity. The bridge shown assumes a nonsubstitution method, but the transition to a substitution method is readily made. The conditions for balance are:

$$\frac{1}{w} \left[\frac{1 + \omega^2 \rho (\rho + w) C_x^2}{1 + \omega^2 \rho^2 C_x^2} \right] = \frac{1}{R_3}, \quad (1)$$

$$\frac{C_x}{1 + \omega^2 \rho^2 C_x^2} = C_3, \quad (2)$$

where ω is 2π times the frequency, and $R_1 = R_2$.

From these it is found that

$$\rho = 1/\omega C_x [(C_x - C_3)/C_3]^{1/2} \quad (3)$$

and

$$1/w = 1/R_3 - \omega [C_3(C_x - C_3)]^{1/2}. \quad (4)$$

Since there are three unknowns, certain assumptions will have to be made. Assume first that the ionic conductivity is not a function of the frequency; that is, that w is constant. Next assume that the frictional resistance varies inversely as the frequency; that is $\rho = \alpha/\omega$, where α is a constant.

These assumptions are justified by their application to sulphur and by the measurements of Bryan⁸ who plotted the power factors of a number of liquids against the frequency and found their component parts to vary in this way. Next assume that

$$\rho = (1/\omega C_3) [(C_x - C_3)/C_3]^{1/2}.$$

This amounts to expanding C_x in a power series and dropping the fourth and higher order term in C_3 , since C_3 is very small. This assumption greatly facilitates the solution of the equations.

Writing the Eqs. (3) and (4) for two different frequencies, and solving for α and C_x we get

$$\alpha = (1/R_3 - 1/R'_3) / (\omega C_3^2 - \omega' C_3'^2) \quad (5)$$

and

$$C_x = C_3(1 + \alpha^2 C_3^2 + 4\alpha^4 C_3^4 + \dots). \quad (6)$$

where primes indicate quantities having to do with the second frequency.

Also, $\tan \phi_1 = \omega \rho C_x = \alpha C_x$; $\tan \phi_2 = 1/\omega R_3 C_x$,

where ϕ_1 is the phase angle due to molecular friction, and ϕ_2 is the total phase angle, since $R_1 = R_2$. These are the angles between the impedance vector and the resistance vector. To obtain the

power factor, which is the cosine of this angle, one merely employs a table of natural trigonometric functions.

Values of α , obtained by computations on different pairs of frequencies, show that it is not strictly a constant. The procedure which was adopted is to call the value of α obtained from two different frequencies the correct value for a frequency which is the mean of the two measured frequencies. By plotting the values obtained from several pairs of frequencies on an α -frequency graph, values of α at any frequency may be obtained. It was found that measurements at four different frequencies are sufficient to determine α over the frequency range used.

Values of the dielectric constant and power factor which were obtained from the first few runs did not agree at all above about 300°C. After a careful investigation it was found that the effect of slight impurities and the past history of the sulphur had nothing to do with this disagreement, as was at first supposed, but the trouble was due to a peculiar polarization phenomenon at the electrodes. It occurred at different temperatures on different runs, and resulted in a greatly increased dielectric constant and frictional power factor in a fairly narrow temperature range. It was found that when a very thick coating of oxide had formed on the aluminum electrodes, successive runs agreed to within the experimental error. To make sure that these were the true values, another aluminum condenser was built having a capacitance about two-thirds that of the original one. After the electrodes had been well oxidized, measurements with this condenser agreed exactly with those of the original one. If any electrode effect had been present, the apparent dielectric constant would certainly have varied with the electrode distance.

RESULTS

The results for a frequency of 312 cycles from one of the first runs is shown in Fig. 3. Curve 1 represents the dielectric constant, curve 2 the frictional power factor, and curve 3 the total power factor. The reason for the concern about the values in the neighborhood of 300°C is quite obvious, as it appears to be a region of anomalous dispersion.

⁸ Bryan, Phys. Rev. 22, 399 (1923).

Curves from one of the later runs are shown in Fig. 4. The curves shown are for a frequency of 312 cycles; curves for different frequencies

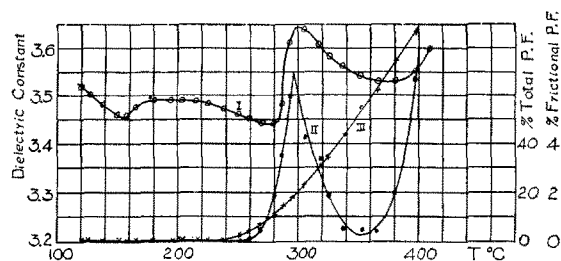


FIG. 3. Results of a preliminary run. I, dielectric constant; II, frictional P.F.; III, total P.F.

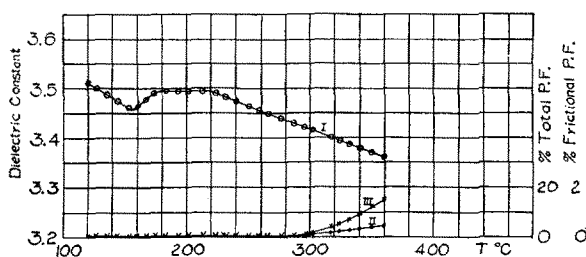


FIG. 4. Results of a final run. I, dielectric constant; II, frictional P.F.; III, total P.F.

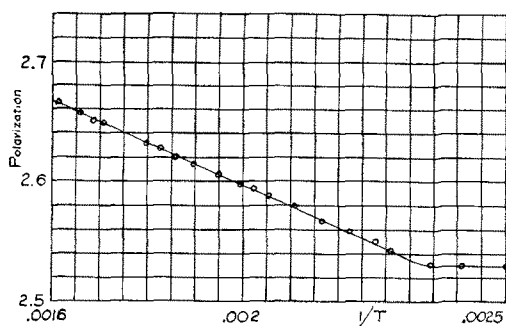


FIG. 5. Polarization curve.

being identical to within the experimental error. Curve 1 gives the dielectric constant, curve 2 the frictional power factor, and curve 3 the total

power factor. It will be seen that the apparent anomalous dispersion has now entirely disappeared. The density of sulphur at different temperatures was taken from an article by Kellas⁵ which appeared to be the best available. From this the polarization could be computed. This was plotted against the reciprocal of the absolute temperature in Fig. 5, the data being taken from Fig. 4.

Table I shows a typical set of results for a temperature of 231°C. The table is self-explanatory, and values given there may be checked by using the formulas given above.

The error in the measured capacitance of the unknown condenser in each case is estimated at less than 0.1 percent. Values of the dielectric constant obtained on different runs check to within 0.3 percent, and this was taken as the experimental error. The estimated error in the total power factor is 1 percent, and that in the frictional power factor is 5 percent.

It will be seen from the polarization curve that for temperatures from 118°C to 158°C the polarization is independent of the temperature and has a value of 0.2528 ± 0.0008 cc/g. In the region 148°C to 120°C, Rosenthal⁷ gives the value 0.2628 by direct measurement at high frequency, and the value 0.318 by measurements on dilute solutions of sulphur in carbon disulphide.

It will also be noted from the polarization curve that above 158°C the polarization decreases directly as $1/T$, instead of increasing as it would if it were a polar substance. This, together with the fact that the frictional power factor is always quite small, shows that liquid sulphur is definitely nonpolar.

It is interesting to compare these results with the results of Taylor and Rideal⁶ on the infrared absorption spectrum of sulphur in various forms. They found the same definite absorption bands

TABLE I.

Temp.	Freq.	Meas. cap. $\mu\mu F$	$\frac{1}{R_3} \times 10^{10}$	$\alpha \times 10^{-5}$	Corr. cap. $\mu\mu F$	Diel. const.	% Fr. P.F.	% Total P.F.	Dens.	P cc/g
231	312	2173.9	170	6.4	2169.8	3.486	0.14	0.40	1.7390	0.2605
231	548	2172.4	215	6.9	2168.3	3.485	0.15	0.27	1.7390	0.2604
231	1248	2169.9	372	6.5	2165.8	3.482	0.14	0.22	1.7390	0.2602
231	2829	2168.2	531	2.8	2164.1	3.480	0.06	0.14	1.7390	0.2601

appearing in all forms. Shaefer and Matossi,⁹ in discussing these results, assume that S_2 is the fundamental entity in all forms of sulphur, that it has a large electric moment, and always

⁹ Shaefer and Matossi, *Das Ultrarote Spektrum*, Julius Springer (1930).

remains free to rotate. Thus these results seem to directly contradict the results given above. Similar contradictions have previously been noted and are very interesting, although no plausible explanation of them can be offered at the present time.