

1936

# The dielectric constant and the specific conductance of pure liquid hydrogen sulphide

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THE DIELECTRIC CONSTANT AND THE SPECIFIC CONDUCTANCE OF  
PURE LIQUID HYDROGEN SULPHIDE

BY

WILLIAM GLENN BICKFORD

A Thesis Submitted to the Graduate Faculty  
for the Degree

DOCTOR OF PHILOSOPHY

Major Subject Inorganic Chemistry

Approved:

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Iowa State College  
1936

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THE DIELECTRIC CONSTANT AND THE SPECIFIC CONDUCTANCE OF  
PURE LIQUID HYDROGEN SULPHIDE

I. INTRODUCTION

It has appeared important to precisely determine the dielectric constant and the specific conductance of pure liquid hydrogen sulphide by means of an alternating current bridge method. Recent advances in precision methods have been brought about by the introduction of the vacuum tube generator as a source of alternating current of symmetrical wave form, by the use of vacuum tube amplifiers for increasing the sensitivity of the detecting instrument, and by the introduction of shielded networks incorporating the Wagner earthing device for minimizing and balancing stray couplings between various branches of the network, and between these branches and earth.

Shedlovsky (1) has made a mathematical analysis of the theory of earth capacity errors in the A. C. Wheatstone bridge and has described a completely shielded bridge network with which measurements of high precision can be made. The most important contribution of this work however, was the proof that properly designed electrostatic screening could be used without error. This point had been seriously questioned by Jones and Josephs (2), who



had previously described a network for the Kohlrausch method that made use of the new vacuum tube features, a suitable earthing circuit, and dispensed with the use of the circular slide wire (which produces an inductive asymmetry in the balancing circuit). The work of Jones and Josephs is probably the first most important contribution in the field of electrolytic conductance since the time of Kohlrausch. In the writer's opinion, no one should attempt conductance work until he has thoroughly reviewed the above cited literature. In fact the data from these two papers (and from the more recent publications of Jones and of Shedlovsky) are of such a nature as to make questionable the validity of all prior conductance work.

The reported values for the electrical conductance of liquid hydrogen sulphide (3)(4)(5)(6), vary from  $0.1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^3$  to  $1 \times 10^{-11} \text{ ohm}^{-1} \text{ cm}^3$ ; obviously these are not in good agreement. The attempts of earlier investigators to establish a value for the conductance by means of the conventional Kohlrausch method resulted only in indifferent success because of the extremely high resistivity of the liquid. The later investigators therefore resorted to the artifice of a galvanometer method employing a direct current. This device is undesirable because of polarization phenomena and because a value so obtained cannot be significant in the interpretation of

conductance data obtained on solutions of the liquid by the use of alternating current and a bridge method.

The dielectric constant of the liquid has not heretofore been reported at the temperature of  $-78.5^{\circ}\text{C}$ . Since this is the temperature at which the properties of solutions in the liquid have been investigated most extensively, it would appear that a knowledge of the constant at this particular temperature would be of importance.

The problem of obtaining values for the dielectric constant and specific conductance of the liquid resolved itself primarily into the choice of an alternating current bridge method suitable for the measurement of very large resistance and capacitance, and into the selection of a method for the production of chemically pure hydrogen sulphide.

After consulting the literature relative to bridge methods and to dielectric theory (7)(8), it was found expedient to treat the liquid as an imperfect dielectric showing leakage conductance, and to construct a condenser bridge network by which the power factor and dielectric constant of the liquid could be measured. From these values the equivalent parallel resistance was computed, and transformed in the conventional way to specific conductance.

## II. THE PREPARATION OF CHEMICALLY PURE LIQUID HYDROGEN SULPHIDE

It has been the practice in this laboratory to prepare liquid hydrogen sulphide from hydrochloric acid and iron sulphide by the method of Antony and Magri (9) as modified by Quam (10). This method is quite satisfactory for the production of a large quantity of the liquid which is to be used for solvent purposes. However, for conductance work, it seemed advisable to employ a simpler method for production of the liquid. The literature was therefore consulted with reference to methods for the preparation of hydrogen sulphide and to the purity of the product obtained by the methods.

Cardoso (11) found that hydrogen sulphide prepared from pure iron sulphide and hydrochloric acid is chemically impure, and still remained so after fourteen fractional distillations, because of the impossibility of removing the dissolved hydrogen and a slightly soluble oily material of higher boiling point (which he took to be hydrogen polysulphides). In an attempt to purify the gas Cardoso (12) absorbed the gas in sodium hydroxide solution and again liberated it by acidulation with hydrochloric acid. This process freed the gas from the dissolved hydrogen but a larger fraction of the higher boiling point substance (hydrogen polysulphides) was pro-

duced than before. The hydrogen sulphide was then absorbed in a magnesium hydroxide suspension and again liberated by heating the solution. The hydrogen sulphide thus prepared was nearly free from polysulphides and after fractional distillation gave a product that had a satisfactory critical point.

A consideration of Cardoso's experience would lead one to suspect that the polysulphides were formed because of the influence of the free acid used in the acidulation process for (a) polysulphides were found in the gas produced from iron sulphide and hydrochloric acid, (b) in the gas from sodium bisulphide and hydrochloric acid, but (c) polysulphides were practically absent from the hydrogen sulphide produced by the thermal decomposition of magnesium sulphide in aqueous solution. It is probable that polysulphides would have been entirely absent if they had not been contained in the hydrogen sulphide which was used in the formation of the magnesium sulphide.

From the foregoing it is to be concluded that chemically and thermodynamically pure hydrogen sulphide may be prepared by the hydrolysis of certain sulphides, for example aluminum sulphide (which may be easily synthesized from the elements). This ideal case is very nearly realized in the method of Habermann (13), who in 1890 produced hydrogen sulphide by treating calcium sulphide with a

saturated solution of magnesium chloride and heating the mixture to 60°C. The reaction is an exceedingly smooth one, and the rate of gas evolution may be easily controlled by varying the temperature of the reactants. We can heartily confirm the report of Randall and Bichowsky (14) that "the gas (hydrogen sulphide) is probably purer than that prepared by any other known method".

Satwaleker, Butler and Wilkinson (loc. cit.) have shown that traces of water exert a marked influence upon the conductance of liquid hydrogen sulphide. The apparatus used for the purification and liquefaction of hydrogen sulphide in this investigation was so designed that the liquid could be fractionally distilled directly into the test cell. This process eliminated the possibility of any contact with atmospheric moisture.

The apparatus employed is shown diagrammatically in Figure 1. All connections were either glass seals or ground glass joints, thereby preventing contact of the gas and rubber. As indicated, the gas was generated in flask (A), washed with water (B), barium sulphohydrate (C) for the removal of acid factors such as carbon dioxide, dried with calcium chloride (D), aluminum sulphide (E), and phosphorus pentoxide (F). It was then passed through a baffle (G) for the removal of entrained solids, liquefied

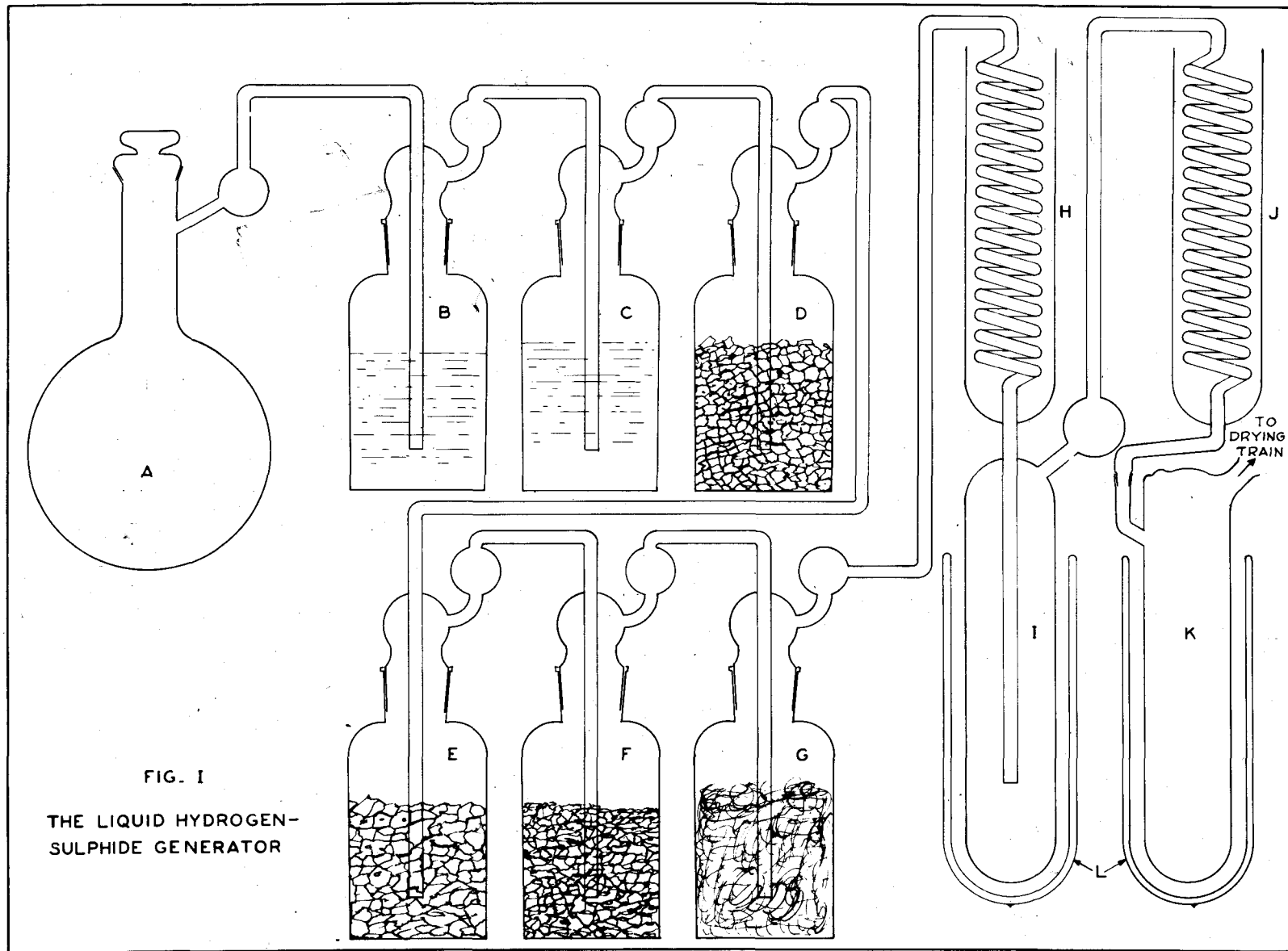


FIG. I  
THE LIQUID HYDROGEN-  
SULPHIDE GENERATOR

at atmospheric pressure by means of a dry ice-ether bath that surrounded the condenser (H), and collected in the container (I). It was then fractionally distilled, condensed at (J) and collected in the test cell (K). Dewar flasks (L) contained the cooling mixture.

The cell was blocked from atmospheric contamination by means of a suitable train connected to the cell outlet.

The calcium sulphide used was analysed for sulphide present by treating a weighed sample with 1:4 sulphuric acid and catching the evolved hydrogen sulphide in a neutral 3 percent cadmium sulphate solutions. The precipitated cadmium sulphide was treated with an excess of standard iodine solution and the excess iodine was titrated with standard sodium thiosulphate solution. Two determinations gave the values of 40.5 and 41.6 per cent calcium sulphide.

In calculating the yield of hydrogen sulphide from this method, one must take into consideration this low per cent of calcium sulphide in the reactant.

### III. THEORIES OF NETWORKS

Alternating current bridge measurements are made by arranging a network of conductors, which are referred to as the branches of the network, and supplying two points in the network with an alternating potential difference, while two other points are "bridged" by a conductor consisting of a detecting device. The various branches contain the test specimen and the standards of resistance, capacitance, etc. The constants of these branches are then adjusted until a condition of balance exists which is indicated by a zero current flow through the bridging instrument. The constants of the test specimen are then determined by calculations involving the balance conditions.

The networks herein considered are composed of various combinations of resistance and capacitance, and a statement of the current voltage relationships of these simple quantities when subjected to alternating stress will clarify the more complex relationship when these are considered in parallel and in series in networks.

The alternating current, and likewise the voltage responsible for it, used to supply the network is sinusoidal in character and hence is a simple harmonic function of time. It also flows in a certain sense in the network. Because of



these properties the voltage and the current may be represented by vectors.

Now consider the case of a condenser that has an instantaneous charge of  $q$ , and a capacitance of  $C$ , then the voltage

$$e = \frac{q}{C} \quad (1)$$

Differentiating,  $\frac{de}{dt} = \frac{1}{C} \frac{dq}{dt} = \frac{1}{C} i$  (2)

Which in vector notation (7) is,

$$j\omega e = \frac{1}{C} i \quad (3)$$

The impedance operator

$$z = -\frac{j}{\omega C} \quad (4)$$

The impedance

$$Z = \frac{1}{\omega C} \quad (5)$$

The phase angle

$$\phi = \tan^{-1}(-\infty) = -\frac{\pi}{2} \quad (6)$$

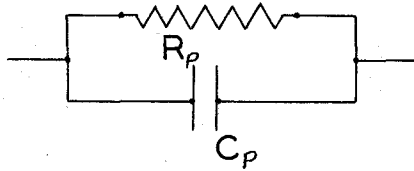
Therefore in a pure condenser the current is said to lead the impressed voltage by  $\frac{\pi}{2}$ , a quarter period; or in other words the current reaches a maximum a quarter period (90°) before the voltage.

In the case of a perfect resistance the maximum current

flow is attained at the instant of maximum voltage, obviously then the voltage and current are in phase, so that

$$Z = R = Z, \text{ and } \phi = 0 \quad (7)$$

It follows then that in a combination of these two quantities, for example a parallel arrangement as shown,



that the current through the resistance is in phase with the voltage while that through the capacitance is out by  $90^\circ$ .

The net result is that the total current through the system does not lead on the voltage by  $\frac{\pi}{2}$ , but differs by an angle  $\phi$  known as the angle of loss or phase difference.

For this combination ( $\omega = 2\pi \times$  frequency in c.p.s.)

$$z = \frac{R_p(1 - j\omega C_p R_p)}{1 + \omega^2 C_p^2 R_p^2}, \text{ and} \quad (8)$$

$$Z = \frac{R_p}{\sqrt{1 + \omega^2 C_p^2 R_p^2}}, \text{ and} \quad (9)$$

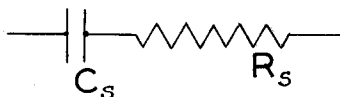
$$\phi = -\tan^{-1} \omega C_p R_p \quad (10)$$

This parallel combination is used in the Kohlrausch method for balancing the impedance of the filled conductance cell. The solution has an ohmic resistance, (Jones and

Bollinger (15) have shown Ohm's law to be valid for electrolytes; at least in the range of low potential gradients employed in standard conductance work) and the spacing of the electrodes gives rise to a geometric capacitance. However it is certain that the capacitance required in a network for balancing the reactance of the filled test cell is much larger than that called for by the geometric capacitance of the test cell. This excess is caused by polarization, which has the properties of capacitance since electrical energy is transformed into chemical energy during one-half of the cycle and reversed during the second half period.

Difficulties are introduced when the balancing resistance values become quite large (500,000 ohms) because of the impossibility of producing wire wound resistors of this order of magnitude that are reactance free. This difficulty may be overcome by using a series combination of capacitance and resistance to balance the impedance of the filled test cell.

For the series combination,



$$z = R_s - \frac{j}{\omega C} \quad (11)$$

$$Z = \frac{1}{\omega C_s} \sqrt{1 + \omega^2 C_s^2 R_s^2} \quad (12)$$

$$\phi = -\tan^{-1} 1/\omega C_s R_s \quad (13)$$

The series and parallel arrangements are simply related and so far as the effect in the network is concerned are equivalent. In whichever arrangement used for determining the constants of the filled cell the resistance is chosen to dissipate the same amount of energy as the cell, and in combination with the capacitance to give the same phase relationship. Obviously, the effective impedances are equal, so

$$R_s = R_p / (1 + \omega^2 C_p^2 R_p^2), \text{ and} \quad (14)$$

$$R_p = R_s (1 + 1/\omega^2 C_s^2 R_s^2) \quad (15)$$

An inspection of these equations will show that a very large parallel resistance, such as found in poorly conducting substances, may be determined in terms of a small series resistance providing the capacitance and the frequency are accurately known.

Fleming and Dyke (16) have conducted a research on the power factor and conductivity of dielectrics in which they make use of the series condenser method for determining the equivalent parallel resistance of the test specimen. Their network is a four condenser bridge in which condensers are used for the ratio arms, and appears to be an application of the Wien bridge. There are two difficulties encountered in such a bridge. The first of these is the capacitance-to-ground of the

parts, and the second is the equivalent series resistance of the standard condenser. Unless this is small compared to the resistance placed in series with the balancing condenser, its effect will not be negligible and must be considered as a correction factor.

Because of these considerations it appeared best to employ an equal-arm bridge having resistors for ratio arms, in which capacitance-to-ground is cared for by screening and by the use of a Wagner earth. The circuit of Figure 2 was employed in the earlier part of this investigation.  $R_8, R_9 - C_8, C_9$  is the Wagner earth unit;  $R_1, R_2$  are the ratio arms;  $C_3$  is the precision condenser;  $C_4$  is the balancing condenser;  $C_x$  is the test cell.  $R_3, R_4$  and  $R_x$  respectively represent the equivalent series resistance of these condensers.  $C_7$  and  $C_6$  represent the capacitance-to-earth of the shields of condensers  $C_3$  and  $C_4$ , while  $R_7$  and  $R_6$  represent the resistance factor of these impedances.  $R_5$  is the resistor which when placed in series either with  $C_7$  or  $C_6$ , by shifting contact d from e to f, will balance the in-phase component of the current through arm a - c or f - b, as the case may be.

This circuit employs the parallel substitution method for comparing the test cell  $C_x$ , with the precision condenser  $C_3$ . This method is preferred above other methods for comparing condensers because it is less liable to error, since

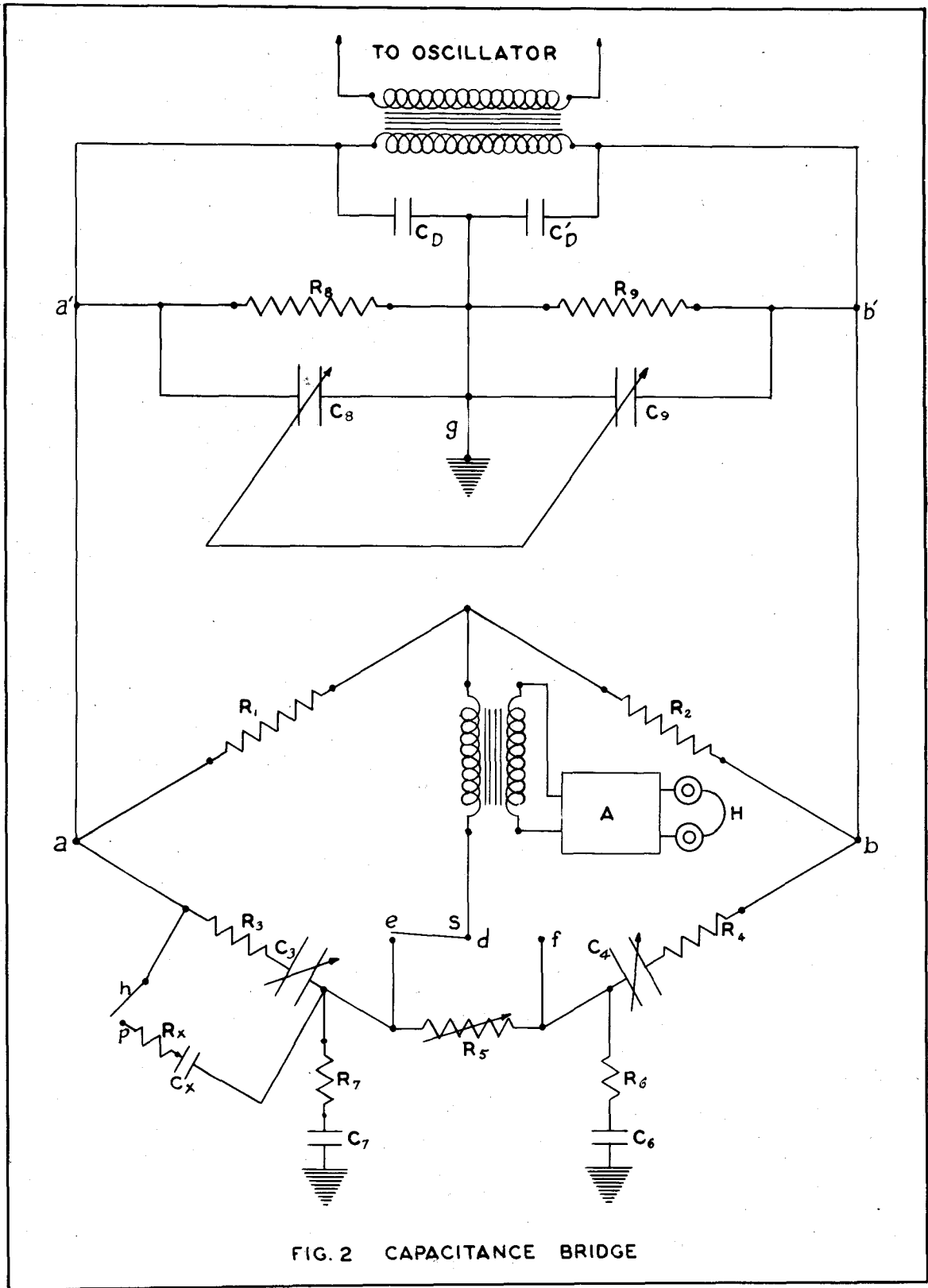


FIG. 2 CAPACITANCE BRIDGE

only one means is used in balancing the bridge. However in this method it is necessary to know the law of variation of the resistance with the capacitance of the precision condenser, although it is not necessary to know the actual phase angles at the various settings of this condenser. For a detailed account of the modified substitution method and the derivation of the bridge equations see Field (17).

It was found that the capacitance of certain of our cells, when empty and when filled with the standard dielectric benzene (18), could be checked over the entire range of the precision condenser, but that the apparent value of  $R_x$  varied with the setting of this condenser. There was also an abnormal shift of  $R_x$  with the frequency. We were at a loss to understand this variation in  $R_x$  while  $C_x$  remained so nearly constant. In an attempt to locate its cause we substituted a General Radio air condenser for the test cell and found that the variation still persisted. This could only mean that there was a defect in the network. We therefore recalibrated our oscillator, rebuilt our bridge and introduced interbridge transformers of astatic construction to isolate the source and detector from the bridge proper. Much to our dismay, the error remained. We then found that Siskind (19), while using the same type of network, had observed the same effect on  $R_x$ . He anticipated the existence

of "stray capacitance" error, and derived the bridge equation assuming a capacitative shunt,  $R_7C_7$  or  $R_8C_8$  as the case may be, across the added resistor  $R_5$ . This analysis yielded the astonishing result that the effect of such a "stray capacitance" is not compensated by the Wagner ground. It has a negligible effect upon the capacitance determination of  $C_x$ , but enters as a serious correction factor in the evaluation of  $R_x$ .

Siskind (loc. cit.) has recommended a network for the determination of power factor that makes the use of the added resistor,  $R_5$ , unnecessary and therefore eliminates the above mentioned source of error. We have modified our network accordingly and the circuit is shown in Figure 3. This network makes use of the parallel substitution method, and of a Wagner ground.  $R_1$  and  $R_2$  are the ratio arms and are shunted by shielded condensers  $C_1$  and  $C_2$ .  $C_3$  is the precision condenser and  $C_4$  is a balancing condenser.  $C_x$  is the test cell, A is the amplifier, and H indicates the telephones.  $T_1$  and  $T_2$  are respectively the shielded input and output transformers. The Wagner ground is composed of resistors  $R_7$ ,  $R_8$  and  $R_9$  and condensers  $C_7$  and  $C_8$ .

The bridge is operated by setting  $C_4$  at some convenient value, placing contact h on point p, contact S on point f, and adjusting the precision condensers  $C_2$  and  $C_3$  until



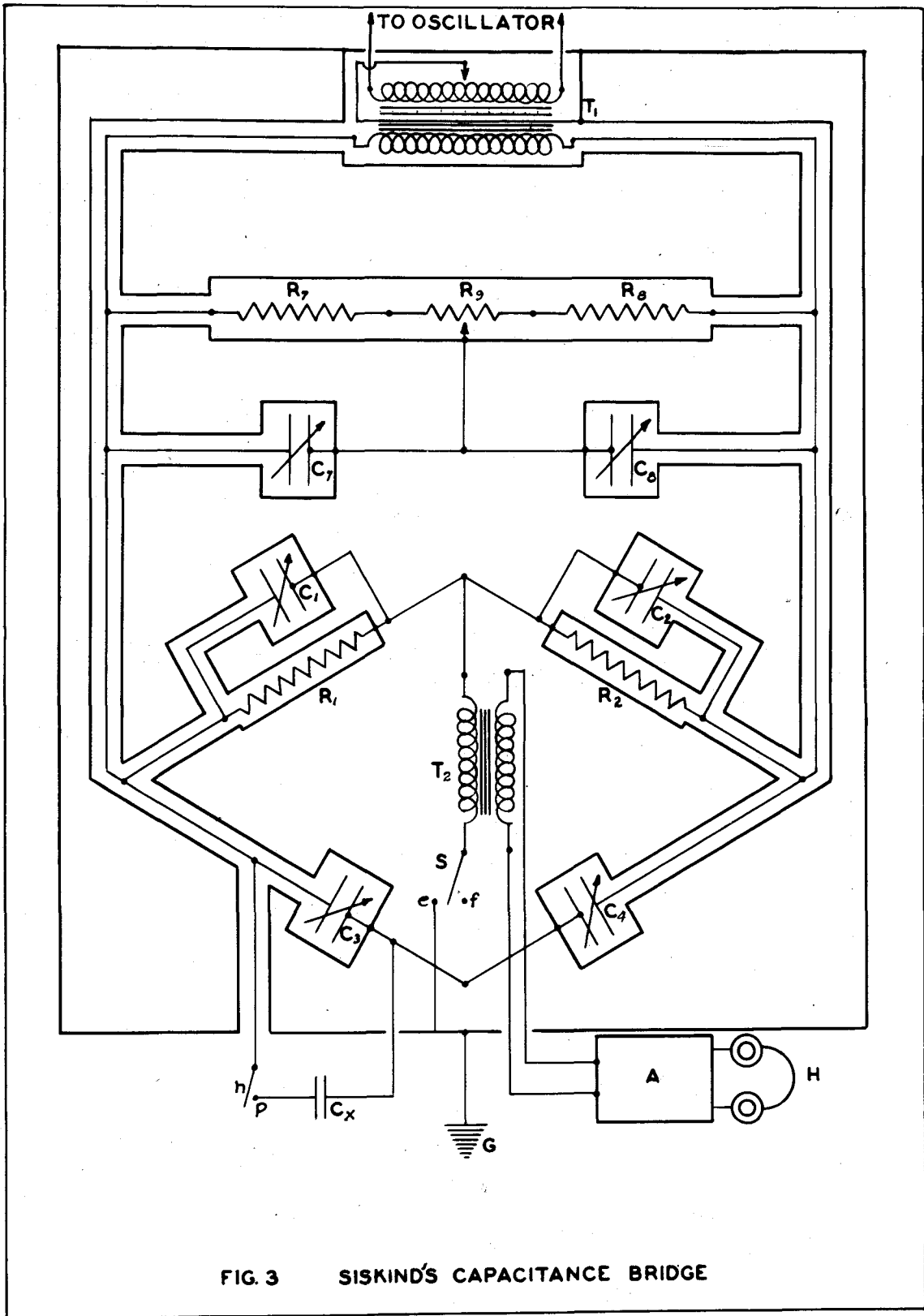


FIG. 3 SISKIND'S CAPACITANCE BRIDGE

balance is secured. Next the Wagner-ground balance is secured by throwing switch S to contact e and adjusting  $R_3$  and  $C_3$ . Switch S is then returned to point f, and the final balance obtained by adjusting  $C_3$  and  $C_2$ . This method is then repeated with contact h barely removed from point p. This requires the development of a new technique, and is the most important single operation of the procedure. Extreme care must be used to exactly duplicate the removal of h from p, otherwise observational errors will be introduced. The capacitance of  $C_x$ , and the power ratio  $\eta_x$  (ratio of equivalent series resistance to reactance) are found by the equations,

$$C_x \doteq C_3' - C_3 \quad (16)$$

$$\eta_x \doteq \omega [C_3'/C_x] [R_2(C_2 - C_2') - R_1(C_1 - C_1')] \quad (17)$$

The primes denote the capacitance obtained when contact h is barely removed from point p. If  $R_1$  and  $R_2$  are of equal value (which is true in our network), then the equations reduce to,

$$C_x \doteq \Delta C_3 \quad (18)$$

$$\eta_x \doteq \omega R_1 (\Delta C_1 - \Delta C_2) (C_3'/C_x) \quad (19)$$

In case the power ratio,  $\eta_x$ , is low then equation 19 gives the power factor directly, otherwise,

$$(\text{power factor})_x = \sin \tan^{-1} \eta_x. \quad (20)$$

The equivalent series resistance,  $R_x$ , of the test condenser is given by,

$$R_x = \eta_x / \omega C_x \quad (21)$$

and  $R_x$  is transformed into equivalent parallel resistance by equation 15.

#### IV. THE CELL CONSTANT

The cell constant,  $k_c$ , of a cell whose electrode separation is  $d$ , and whose uniform cross section is  $A$  is expressed by the equation,

$$k_c = \frac{d}{A} \quad (22)$$

This relationship, although questioned by Parker (20) has been shown to be valid by Jones (21). The numerical value of  $k_c$  is usually determined by measuring the conductance of a solution whose specific conductance is known, i.e., various dilutions of potassium chloride.

The evaluation of a constant for a cell of large cross section and of very small electrode separation, such as those used for very poorly conducting solutions, is a matter of some difficulty and quite often an impossibility by the conventional methods because of the phenomena (such as polarization, heat effects, etc.) encountered during the measurement of quite small resistances, even when the most dilute of standard salt solutions is employed. It therefore became obvious that a special method must be established for obtaining the cell constant for a cell whose dimension would be suitable for the measurement of the specific conductance of

liquid hydrogen sulphide.

Equation 22, expressing the cell constant, is very simply related to the equation for the electrical capacitance  $C_{cm}$  of a parallel plate condenser whose cross section is  $A$ , and whose plate separation is  $d$  and which is filled with a medium of dielectric constant  $K$ .

$$C_{cm} = \frac{KA}{477d} \quad (23)$$

Since one micro-micro-farad is equivalent to 0.9 centimeter, equation 23 in terms of micro-micro-farads becomes

$$C_{\mu\mu F} = \frac{KA}{(.9)477d} \quad (24)$$

solving equation 24 for  $\frac{d}{A}$  it is found that

$$\frac{d}{A} = \frac{K}{(.9)477} \times \frac{1}{C_{\mu\mu F}} \quad (25)$$

In case the measurement of capacitance is carried out when the cell is air filled (dielectric constant of air is 1) equation 25 reduces to,

$$\frac{d}{A} = \frac{0.08841}{C_{\mu\mu F}} \quad (26)$$

but  $\frac{d}{A}$  is the cell constant, so

$$k_c = \frac{d}{A} = \frac{0.08841}{C_{\mu\mu F}} \quad (27)$$

This derivation may be extended to the case of a cell having two coaxial cylinders for electrodes.

Let  $\bar{A}$  = mean area of the two coaxial cylinders

$$\bar{A} = r_m \times L \times 2\pi \quad (28)$$

Where  $L$  = length of coaxial cylinders and  $r_m$  = mean radius

$$r_m = \frac{r_2 - r_1}{\ln r_2/r_1} \quad (29)$$

in which  $r_2$  is the radius of the larger cylinder and  $r_1$  is the radius of the smaller, then

$$\bar{A} = \frac{2\pi L(r_2 - r_1)}{\ln r_2/r_1} \quad (30)$$

Substituting the value for  $\bar{A}$  in equation 22, the cell constant,  $k_c^*$ , for two coaxial cylinders is

$$k_c^* = \frac{(r_2 - r_1)}{\frac{2\pi L(r_2 - r_1)}{\ln r_2/r_1}} = \frac{\ln r_2/r_1}{2\pi L} \quad (31)$$

The electrical capacitance of a condenser having two coaxial cylinders for electrodes of length  $L$ , radii  $r_1$  and  $r_2$ , and filled with a dielectric of constant  $K$  is

$$C_{\mu\mu F}^* = \frac{K}{(.9)(4\pi)} \times \frac{2\pi L}{\ln r_2/r_1} \quad (32)$$

solving equation 32 for  $\frac{\ln r_2/r_1}{2\pi L}$  which is the value for the cell constant  $k_c^*$ , of a cell having two coaxial cylinders for electrodes, it is found that

$$k_c^* = \frac{\ln r_2/r_1}{2\pi L} = \frac{K}{(.9)(4\pi)C_{\mu F}} \quad (33)$$

Equation 33 is found then to be identical with equation 25, and in case the cell is air filled, equation 33 reduces to

$$k_c^* = \frac{0.08841}{C_{\mu F}} \quad (34)$$

which is identical with equation 26.

It would appear then that the constant for a cell of any shape may be found in terms of its electrical capacitance. However, there are certain limitations to this method which must be observed in practice. Equation 34 holds when the distance between the cylinders is small compared to the radius of the electrode, and makes no attempt to correct for edge effect, i.e. fringing, which in such a case would be small.

In the cell designed for and used in this research, the edge effect has been made a constant by the use of suitable guard rings, and is independent of the dielectric constant of the medium which fills the cell. Equation 34 holds rigorously under these conditions.

#### V. THE TEST CELL

A cell that is to be used for the determination of the power factor and dielectric constant of a liquid differs somewhat in design from a cell that is used strictly for conductance measurements. It is primarily an air condenser whose capacitance and power factor can be measured when empty and then when filled with the liquid in question.

The ratio of the capacitance when filled to that when empty is the specific inductive capacity or dielectric constant of the liquid. (Perhaps a better term would be dielectric ratio rather than constant for the value is a function of the temperature and is not a constant.) The power factor of the liquid is computed from the values obtained on the filled and empty cell.

Jones and Bollinger (21) have conducted an important research on the design of conductance cells. They have made a mathematical analysis of errors in conductance cells due to electrical shunts, and have found a cure, by the proper designing of cells, for the distressing anomaly known as the "parker effect". They, however, were not concerned with the design of cells for poorly conducting solutions, and in



addition to their findings there are two other important sources of error in the customary type of cell that is used on such solutions for the determination of conductance and dielectric constant.

One of these errors is caused by fringing at the electrode edges, and the second, which is more important from the conductance view point, is caused by capacitance and leakage losses introduced by solid dielectric supports of the electrodes. If these losses are ohmic in nature and are small they may be allowed for in the conductance calculations without much sacrifice in precision. If, however there is a capacitative reactance involved, which is usually the case, the magnitude of error will be a function of the frequency and of the dielectric constant of the medium. This will lead to unsatisfactory results. It is the belief of the writer, based upon experience and reasoning, that far too little attention has been paid to these sources of error by co-workers in the field of limited conductance. An example drawn from many such instances contained in our note books will illustrate the point.

Cell K-3 was designed in this laboratory according to specifications found in the chemical literature for cells that are used for dielectric constant and low conductivity

measurements, and was built for us by a reputable commercial firm. It consisted of three concentric platinum cylinders held apart by small mica wedges, which were sealed into a Pyrex glass container. The outermost of these cylinders was connected to the low potential point in the bridge network and the power factor and capacitance measurements were made on a shielded network similar to the General Radio type 216 capacity bridge (17).

The power factor of this absolutely dry and clean cell at 995 c.p.s. was 0.003, and varied in an absurd and unpredictable manner with the frequency. Upon the suggestion of Professor R. F. Field of The General Radio Company, who kindly furnished us with data on the power factors of mica and Pyrex glass and with the following equation for computing the theoretical power factor of our test cell, we made an analysis of the capacitance distribution in the test cell. It was found that at a frequency of 995 c.p.s. the capacitance due to the free electrode area was  $47.8 \mu\mu\text{F}$ , and that due to the mica wedges and glass supports was  $13.4 \mu\mu\text{F}$ . About 25 per cent of the total cell capacitance was due to the electrode spacers, and this in itself is of course entirely unsatisfactory for precision work.

Substituting these values and that for the power factor of mica in the equation,

$$R\omega C = \frac{(R\omega C)_a C_a + (R\omega C)_m C_m}{C_a + C_m} = \frac{(R\omega C_m) C_m}{C_a + C_m} \quad (35)$$

(in which  $R\omega C$  is the approximate power factor of the test cell,  $(R\omega C)_a$  is the power factor of a pure air condenser and is equal to zero,  $(R\omega C)_m$  is the power factor of mica and is 0.0004,  $C_a$  is the capacitance of the free electrode space in the condenser, and  $C_m$  is capacitance due to mica.  $R$  is the equivalent series resistance, and  $\omega$  is equal to  $2\pi$  x frequency in c.p.s.) gave a theoretical value of 0.00001 for the power factor. Using the same equation and 0.006 for the power factor of Pyrex glass gave 0.0013 for the theoretical value. The measured power factor was 0.003.

The power factor of an imperfect condenser is  $\sin \theta$  and for small values is equal to  $\tan \theta$ . ( $\theta$  is the loss angle in the condenser.) The equivalent parallel resistance  $W$  of the test cell is given by (7),

$$\tan \theta = \frac{1}{\omega W C_p} \quad (36)$$

and in the case of the cell under consideration had a value of approximately  $1 \times 10^9$  ohms. Since the specific resistivity of liquid hydrogen sulphide was found by Satwalaker (loc. cit.) to be of the order of  $1 \times 10^{11}$  ohms, it is obvious that the equivalent resistance of the cell would enter as a serious correction factor. In fact the energy loss in the cell would

be approximately equal to that of the liquid being measured since the cell constant was approximately  $1 \times 10^{-2}$ . If the loss in the cell had been proportional to the frequency, it might have been considered strictly ohmic in nature and a suitable correction made. As it was, the cell was probably showing absorption and a correction for its effect upon the conductance would be difficult to make, and would undoubtedly lead to erroneous results. The cell also showed a shift of capacitance with the temperature and frequency.

An ideal cell would be one that has a zero loss angle, and a capacitance that would be as nearly constant as theoretically possible. Such a cell would have guard rings to take care of the fringing effect at the electrode edges, and would have no solid dielectric supports between the high and low potential electrodes. Field (22) has described such a cell, and given a consideration of the capacitance network that it represents. Our test cell is essentially the same as this, except that the electrode area has been modified to increase the "direct" capacitance and the container has been changed to meet our specific needs. The cell is shown diagrammatically in Figure 4. We have found it satisfactory in every respect. It has a zero loss angle at low voltages, and changes in its geometrical capacitance cannot be detected in the range of frequencies between 995 and 3020 c.p.s. The

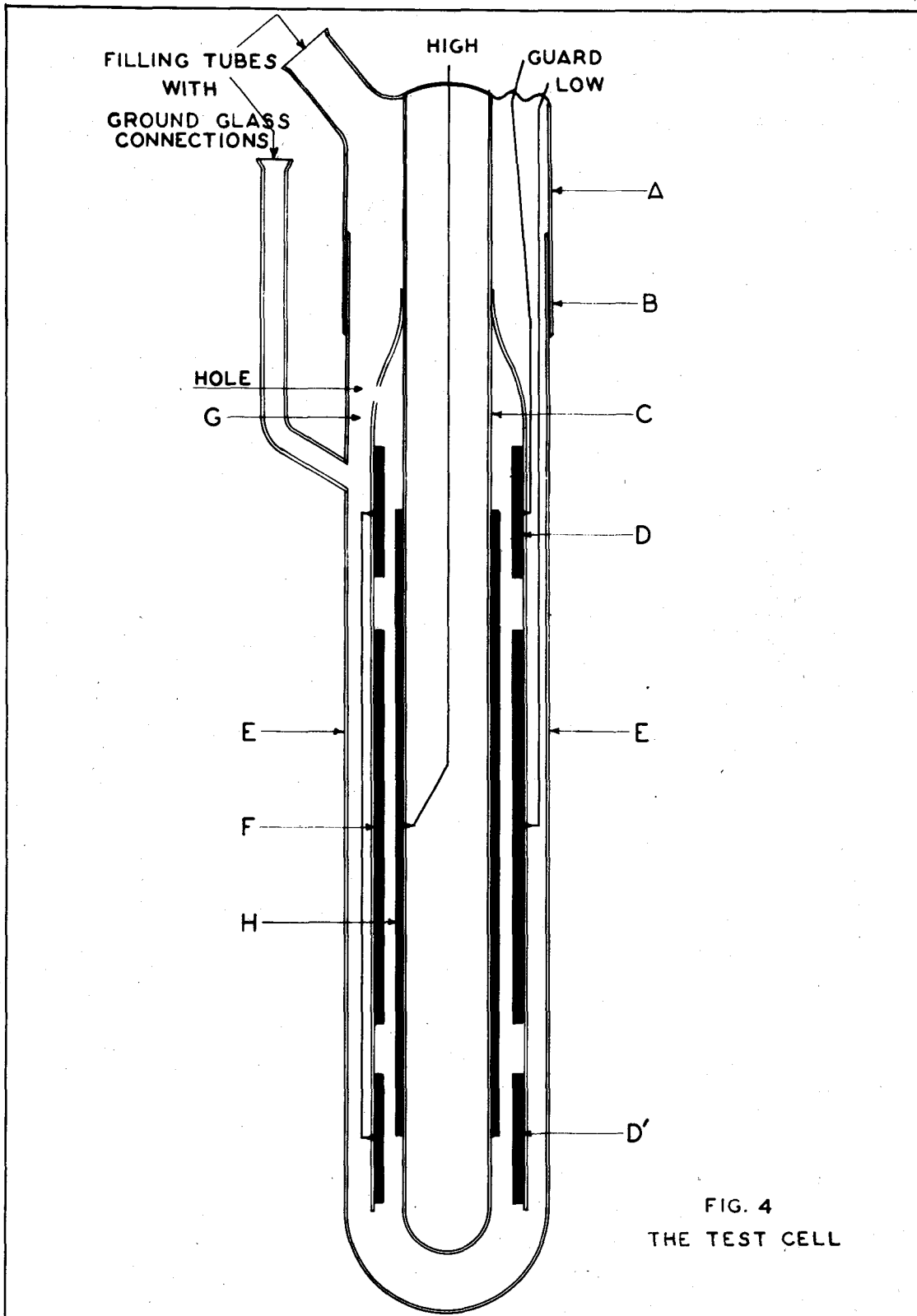


FIG. 4  
THE TEST CELL

electrodes and lead wires are nickel metal. All connecting wires are spot-welded to the electrodes. The high potential electrode H has a length of 16 cm. and an external diameter of 2.5 cm. It is held rigidly in place by shrinking onto Pyrex tube C. The low potential electrode F has a length of 10 cm. and an internal diameter of 2.9 cm. It is firmly embedded in Pyrex tube G. The guard rings D and D' are each 5 cm. in length and 2.9 cm. internal diameter. They are likewise embedded in Pyrex tube G. The space between the guard rings and the low potential electrode is 1.5 cm. A is the cap of the cell to which the Pyrex supports are sealed and through which the leads are brought out by means of tungsten wires. E is the container, made of Pyrex glass and fits into the cap by means of the ground seal B. The filling tubes are likewise provided with ground connections for connecting the cell with the generator. The overall length of the cell is 30 cm. and the external diameter is 4.8 cm. The liquid capacity of the cell is 200 c.c.

The important feature in the construction of the cell is the absence of solid supports directly between the high and low electrodes. There is an indirect path between these two electrodes through the Pyrex tubes C and G. However it is to be noted that the guard ring D is interposed here. Since this ring is maintained at earth potential it follows

that there is no "direct leakage" between the high and low potential electrodes.

The test cell has a "direct capacitance" of 40.4<sub>0</sub>  $\mu$ F. The "direct capacitance" is that capacitance which is measured between electrodes F and H.

## VI. THE SCREENED AUDIO-FREQUENCY CAPACITANCE BRIDGE

The theoretical aspects of this network have been discussed elsewhere in this paper. The bridge proper is self contained within its shield and is connected to the shielded oscillator and detector by means of duplex cables in earthed shields. All shields are earthed at a common junction. As suggested by Figure 3, page 20, all component parts are contained in individual compartments of an earthed copper alloy box. When individual shielding of lead wires between compartments was not used, they were run through one inch holes and were rigid enough to be self-supporting. Interbridge transformers of astatic construction contained in individual copper shields were used in connecting the bridge with the source and detector. All controls are at earth potential and this reduces bodily capacitance effects to a minimum. Extreme care was used in soldering all electrical connections, and in the placing of the components of the network. Such a device as herein described is an instrument of very high precision.

1. The Oscillator. Dr. Theodore Shedlovsky of the Rockefeller Institute for Medical Research very kindly



furnished us with constructional details of the improved audio-frequency oscillator that he is using. It is an Eccles and Jordan circuit adapted to audio-frequency by Dr. N. Frank of the Massachusetts Institute of Technology. It is said to have a very good wave form and a more constant frequency than the one tube type. Both these features were important to us because the solution for equivalent parallel resistance in the power factor equation contains a frequency term. The frequency must therefore be known and constant.

After constructing our oscillator from the best parts obtainable in the market, we calibrated its frequencies against a General Radio Master Oscillator at Radio Station WOI, and also examined its wave form on the oscillograph at WOI. It proved to have a very nearly sinusoidal wave and the second harmonic present was barely audible with multi-stage amplification after the capacitance bridge was balanced for the fundamental. We have found this oscillator suitable in every respect and recommend it highly for low voltage conductance work. The oscillatory is shown diagrammatically in Figure 5.

2. The Detector. The detector was constructed in this laboratory from standard parts. It consists of a two-stage amplifier and Western Electric high impedance telephones. The first stage is transformer coupled and the second is resistance coupled. The volume control,  $C_1$ , on

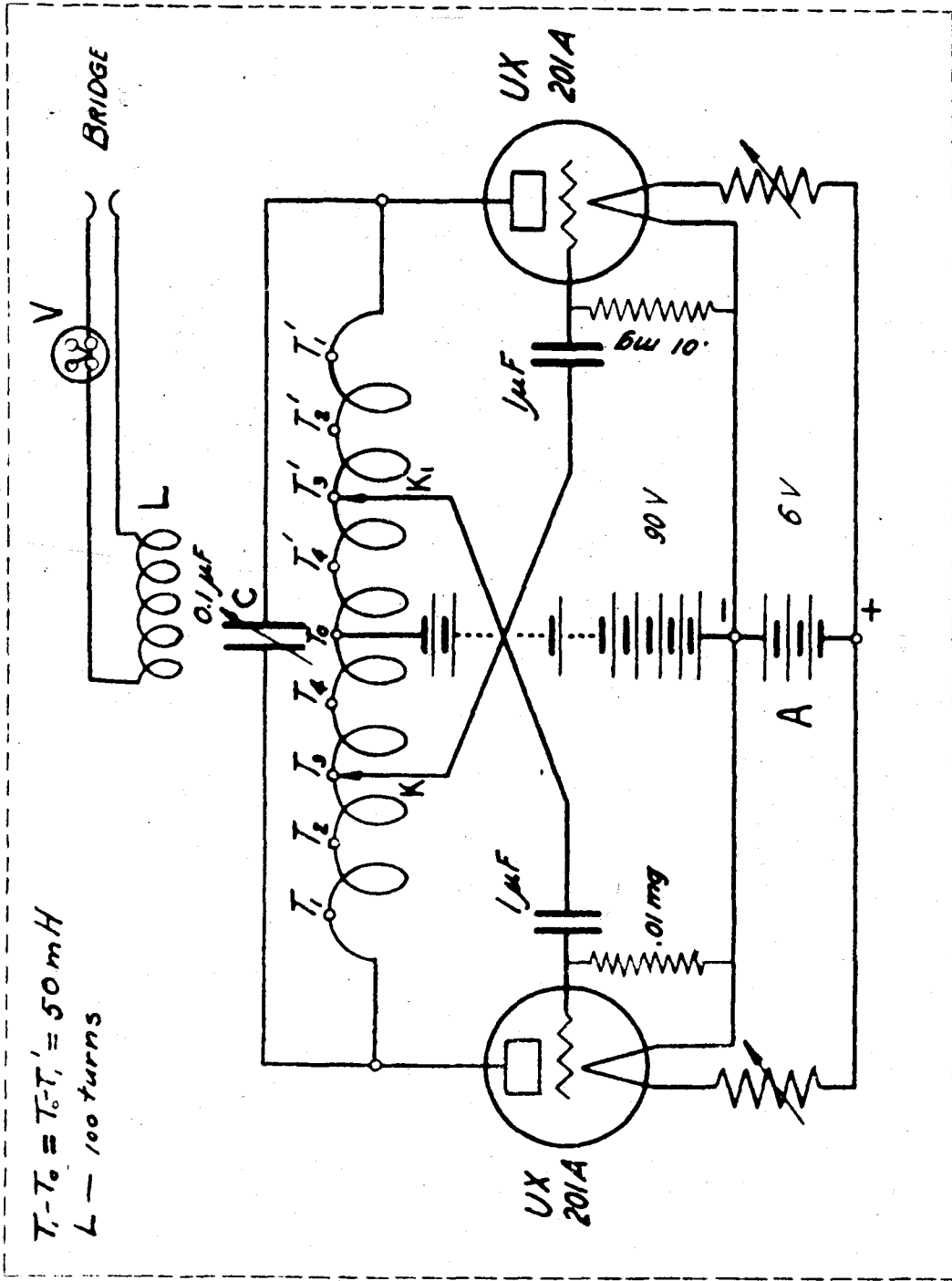


Fig. 5

the secondary of the input transformer is of distinct advantage during the preliminary balancing of the bridge. The circuit is shown in Figure 6. We do not know that this circuit is published elsewhere, and claim no originality for it. It is built along general principles for amplifiers, and has proven quite satisfactory. Jones and Bollinger (23) have published an account of an improvement in their detector; we have not found it necessary to make any such changes in our instrument. An A.C. operated detector was considered, but the idea was given up because of the difficulty that would be found in detecting the last fading note of the fundamental due to the sixty cycle hum in such instruments.

The meaning of the notations in Figure 6 is given below:

- $T_1$  -- Step-up transformer (ratio 1:3)
- $C_1$  -- Volume control
- 1H -- Choke coil (1 Henry)
- H -- Head phones
- UX230 and UX232 -- Vacuum tubes
- F -- Micro-farad
- $\sim$  -- Ohm
- V -- Volt

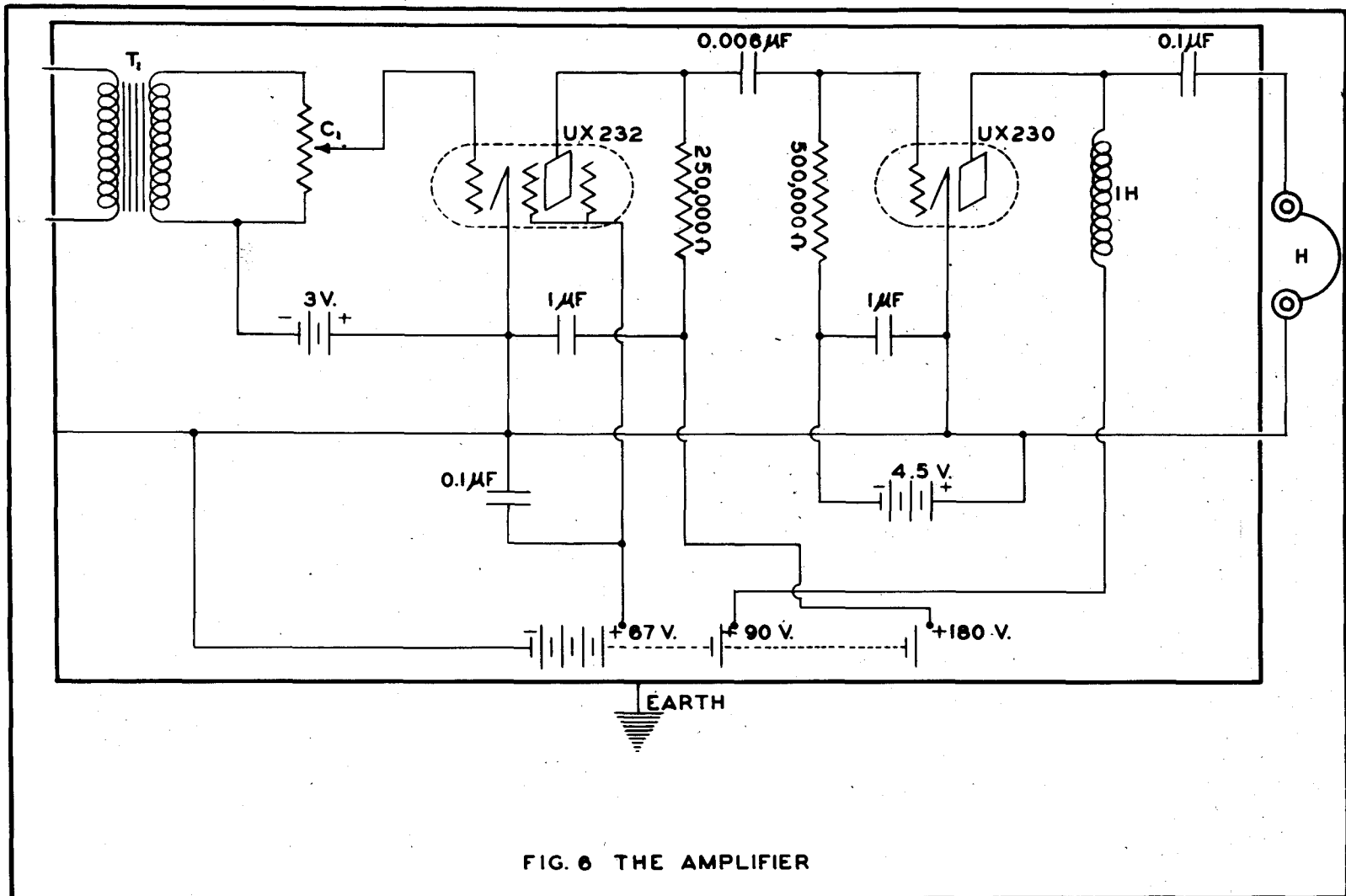


FIG. 6 THE AMPLIFIER

3. Interbridge Transformers. A good discussion of the theory and use of shielded transformers for impedance bridges is found in the General Radio Experimenter (24). The input and output transformers used to connect the source and detector with the bridge are standard parts from the General Radio type 216 capacity bridge. They are of astatic construction and tend to isolate these instruments from the bridge, as well as to match impedances between these parts. The importance of their use is now generally recognized.

4. The Wagner-Ground Circuit. This circuit consists of two ( $R_7$  and  $R_8$ ) Ayrton-Perry coils (General Radio) of 5000 ohms each connected by a 10 ohm rheostat, and of two ( $C_7$  and  $C_8$ ) 500  $\mu$ F air condensers. Earth connections are made as indicated in Figure 3, page 20.

5. Ratio Arms. The ratio arms ( $R_1$  and  $R_2$ ) are each 5000 ohm coils wound on a flat bakelite card. This unit is a standard part from the General Radio type 216 capacity bridge, and is mounted symmetrically within its shielded compartment by means of a pin that passes through its center to the walls of the shield.

6. The Balancing Condensers. Condensers  $C_1$  and  $C_2$  are the phase adjusters and shunt coils  $R_1$  and  $R_2$ . They are connected with their shielded sides to the midpoint of the ratio arms.  $C_1$  is a type 246L General Radio calibrated

condenser and  $C_2$  is a Leeds and Northrup type 1186 air condenser, Number 120146, that is calibrated within  $\pm 1 \mu\text{F}$  and may be read to 0.1 division.

Condensers  $C_3$  and  $C_4$  are both General Radio instruments.  $C_4$  is a type 539B condenser and is calibrated.  $C_3$  is the type 222L precision condenser and was calibrated by the makers to within  $1 \mu\text{F}$  absolute capacitance. It was recalibrated in this laboratory in terms of a small air condenser so that a capacitance difference could be obtained to an accuracy of  $0.2 \mu\text{F}$  or 0.1 per cent, whichever is the larger (24). This accuracy is brought about by the fact that this condenser can be read to 1 part in 25,000.

VII. THE ELECTRICAL CONSTANTS FOR  
LIQUID HYDROGEN SULPHIDE

The test cell, E-4, after being thoroughly cleaned and dried was filled with pure liquid hydrogen sulphide by the previously described method. Every precaution was observed to insure the anhydrous state of the liquid. The filled cell was then transferred to the network and the following observations made by the procedure outlined for Siskind's capacitance network. The primes indicate the balance when the test cell is removed from the circuit. The condensers  $C_1$  and  $C_4$  were set at a convenient value and were not varied at any time during the determinations. These capacitances do not enter into the calculations.

SAMPLE I

Frequency .....3000 c.p.s.

Condenser	Reading	Capacitance ( $\mu\mu\text{F}$ )
$C_3$	1000.5	574.2
$\downarrow$		
$C_3$	1611.5	938.0
$\downarrow$		
$C_2$	93.0	1096.2
$\downarrow$		
$C_2$	21.0	288.2
$C_3$	1000.0	574.0
$\downarrow$		
$C_3$	1611.0	937.7
$\downarrow$		
$C_2$	100.0	1166.0
$\downarrow$		
$C_2$	27.5	359.0
$C_3$	1000.5	574.2
$\downarrow$		
$C_3$	1611.5	938.0
$\downarrow$		
$C_2$	93.0	1096.0
$\downarrow$		
$C_2$	21.0	288.2



SAMPLE II

Frequency ..... 2000 c.p.s.

Condenser	Reading	Capacitance ( $\mu\mu\text{F}$ )
C <sub>3</sub>	1100.0	634.0
C <sub>3</sub>	1702.0	1000.0
C <sub>2</sub>	95.0	1119.0
C <sub>2</sub>	79.0	931.0
C <sub>3</sub>	1100.0	634.0
C <sub>3</sub>	1702.0	1000.0
C <sub>2</sub>	50.0	608.0
C <sub>2</sub>	32.0	419.0
C <sub>3</sub>	1100.0	634.0
C <sub>3</sub>	1702.0	1000.0
C <sub>2</sub>	95.0	1119.0
C <sub>2</sub>	79.0	931.0

Repeated tests conducted on the air filled test cell for the evaluation of its "direct capacitance" and power factor gave the following result:

Frequency ..... 995 and 3000 c.p.s.

Condenser	Reading
$C_3$	1200.0
$C_3^*$	1261.8
$C_2$	49.0
$C_2^*$	49.0
$C_3$	1000.0
$C_3^*$	1067.7
$C_2$	75.0
$C_2^*$	75.0

$$\Delta C_3 = 67.75 \text{ divisions} = 40.4 \mu\mu\text{F}$$

$$\Delta C_2 = 0$$

The "direct capacitance" of the test cell is therefore  $40.4 \mu\mu\text{F}$  and its power ratio ( $\gamma_x$ ) is zero since  $C_2$  remained constant. The cell therefore exerts no shunting effect upon the liquid being measured.

Substituting the cell capacitance in equation 34,

page 26, gives the cell constant for E-4.

$$k_c^o = \frac{0.08841}{40.4_0} = 2.18_8 \times 10^{-3} \quad (37)$$

The precision of this measurement is  $0.2 \mu\text{F}$ ; this variance would give cell constant values from 0.002193 to 0.002183. 0.002188 was taken as the cell constant.

The data secured on Sample I by the improved bridge method for calculating the dielectric constant and the specific conductance of pure liquid hydrogen sulphide are summarized below.

$$-\Delta C_2 = C_2 - C_2'$$

$\bar{C}_X$  = Cell capacitance when  $\text{H}_2\text{S}$  filled

$C_X$  = Cell capacitance when air filled

3000 c.p.s. = The frequency

$-78.5^\circ\text{C}$ . = The temperature

$$R_1 = 5000 \checkmark$$

$$-\Delta C_2 = 808 \mu\text{F}$$

$$C_2' = 938 \mu\text{F}$$

$$\bar{C}_X = 363.8 \mu\text{F}$$

$$C_X = 40.4_0 \mu\text{F}$$

Substituting the value of  $\eta_x$  from equation 19, page 21, into equation 21, page 22, gives for the equivalent series resistance of the test specimen,

$$R_X = \frac{R_1 (\Delta C_1 - \Delta C_2) C_3'}{\bar{C}_X^2} \quad (38)$$

Since condenser  $C_1$  was not varied  $C_1$  is equal to zero, and equation 38 becomes,

$$R_X = \frac{R_1 (-\Delta C_2) C_3'}{\bar{C}_X^2} \quad (39)$$

Simplifying equation 15, page 15, (see Hague (7) page 136) letting  $R_X = R_S$  and  $\bar{C}_X = C_S$ , it is found that the equivalent parallel resistance of the sample is

$$R_p = \frac{1}{\omega^2 \bar{C}_X^2 R_X} \quad (40)$$

Substituting in equation 40 the value of  $R_X$  from equation 39 it is found that the  $\bar{C}_X^2$  term drops out and the reduced equation for  $R_p$  is

$$R_p = \frac{1}{\omega^2 R_1 C_3' (-\Delta C_2)} \quad (41)$$

Applying equation 41 to the data for Sample I, it is found that

$$R_p = \frac{1}{[5000][(2)(3.1416)(3000)]^2 [938 \times 10^{-12}][808 \times 10^{-12}]}$$

$$R_p = \text{antilog } 6.87080$$

The specific conductance  $S$  is given by

$$S = \frac{k_p^2}{R_p} \quad (42)$$

Substituting in this equation it is found that the specific conductance of Sample I is

$$S = \frac{2.188 \times 10^{-3}}{\text{Antilog } 6.87080}$$

$$S = 2.9_5 \times 10^{-10} \text{ ohm}^{-1} \text{ cm.}^3$$

The dielectric constant of a material is found by the ratio of the "filled" to the "empty" capacitance. That is,

$$K = \frac{\bar{C}_x}{C_x} \quad (43)$$

Applying this equation to the data on Sample I yields

$$K = \frac{363.80}{40.4_0} = 9.0_5$$

The dielectric constant of Sample I is therefore  $9.0_5$ .

The data secured on Sample II are summarized below, and the calculations are carried out in the same manner by application of equations 41, 42, and 43.

Frequency = 2000 c.p.s.

Temperature =  $-78.5^\circ\text{C}$ .

$R_1 = 5000 \checkmark$

$$-\Delta C_2 = 188 \mu\mu F$$

$$C_3' = 1000 \mu\mu F$$

$$\bar{C}_x = 366 \mu\mu F$$

$$C_x = 40.4_0 \mu\mu F$$

$$R_p = \frac{1}{[(2)(3.1416)(2000)]^2 [5000][1000 \times 10^{-12}][188 \times 10^{-12}]}$$

$$R_p = \text{antilog } 6.82850$$

$$S = \frac{2.188 \times 10^{-3}}{\text{antilog } 6.82850}$$

$$S = 3.31 \times 10^{-10} \text{ ohm}^{-1} \text{ cm.}^3$$

The dielectric constant K for Sample II is

$$K = \frac{366}{40.4_0} = 9.0_6$$

The values obtained on pure liquid hydrogen sulphide by the aid of Siskind's network are

Sample	Dielectric Constant	Specific Conductance
1	9.0 <sub>5</sub>	$2.95 \times 10^{-10} \text{ ohm}^{-1} \text{ cm.}^3$
2	9.0 <sub>6</sub>	$3.31 \times 10^{-10} \text{ " "}$

These values are in good agreement and are well within the limits of experimental error.

The average of the data secured by the use of cell E-3,

and the network of Figure 2 are summarized below. It has already been pointed out that the conductance was thought to be in error because of the shunting effect of the solid supports in the cell and also because of the capacitance error in the network. The capacitance measurements by this bridge were satisfactory although there was some question as to how to allow for the capacitance of the solid supports of the test cell in the dielectric constant calculations.

Dielectric constant    8.37, or 9.1<sub>2</sub>

Specific conductance    1.17 x 10<sup>-9</sup>

The difference in the dielectric constant is due to the difference in the estimated "external capacitance" of cell E-3. By "external capacitance" is meant such capacitances as that caused by the solid supports and leads of the cell. The evaluation of the capacitance distribution in this cell that gave the value of 9.1<sub>2</sub> for the dielectric constant of hydrogen sulphide obviously was not greatly in error. However, it is to be noted that the "apparent conductance" of the liquid is greater in cell E-3 than in cell E-4. This is accounted for by the shunting effect of cell E-3.

The following values have been reported for the specific conductance of liquid hydrogen sulphide.

0.1 x 10<sup>-6</sup> ohm<sup>-1</sup> cm. <sup>3</sup>

(3)

less than  $4 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^3$  (4)

$3.7 \times 10^{-11}$  " " (6)

$1 \times 10^{-11}$  " " (5)

For the dielectric constant

10.2 (4)

9.4 (25)

Kemp and Dennison (25) observed the dielectric constant at the melting point ( $-82.5^\circ\text{C.}$ ) while our observation is made at  $-78.5^\circ\text{C.}$ , which perhaps accounts for the difference, although Kemp and Dennison only claim an accuracy of ten per cent. Obviously the value of Magri (4) is widely in error.

Probably the best previous measurements on the specific conductance have been made by Wilkinson and co-workers (5)(6) in this laboratory. Their reported values are somewhat less than the present observation. This is to be expected in view of the fact that they employed a direct current galvanometer method and encountered some polarization. Taking this into account the agreement between the new and old data from this laboratory is good.

The constants for pure liquid hydrogen sulphide at  $-78.5^\circ\text{C.}$  are

dielectric constant 9.0<sub>5</sub>

specific conductance  $3.1 \times 10^{-10} \text{ ohm}^{-1} \text{ cm.}^3$



### VIII. SUMMARY

1. A method is described for the production of chemically pure liquid hydrogen sulphide.
2. The theories of the series and parallel arrangements of capacitance and resistance for conductance work are discussed, and it is experimentally shown that Siskind's capacitance bridge can be applied to conductance work.
3. A new method for obtaining the "cell constant" of a test cell in terms of its electrical capacitance is described, and it is experimentally shown that this method is precise for certain types of conductance cells.
4. A properly designed test cell for the measurement of dielectric constant and electrical conductance is described, and it is experimentally shown that such a cell has no influence on the conductance of the medium.
5. A completely screened audio-frequency bridge for the measurement of conductance, dielectric constant, and power factor is described.
6. The dielectric constant and the specific conductance of pure liquid hydrogen sulphide are reported and compared with the data obtained by earlier investigators.

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