

MEASUREMENTS OF THE DIELECTRIC CONSTANTS
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ABSTRACT

It is possible to build small, rigid circuits which have natural periods determined by the medium in which they are immersed. If $T\gamma$, the product of the natural period of the circuit and the conductivity of the medium, is sufficiently small, this period is proportional to the square root of the dielectric constant of the latter. On the basis of this fact measurements have been made of the dielectric constant of water from 0° to 100°C to an accuracy of 0.2 percent or better and covering a range of frequency from $T = 1.4 \cdot 10^{-8}$ to $81 \cdot 10^{-8}$. If $T\gamma$ is not sufficiently small, the period is affected by the conductivity of the medium in a complicated way and cannot be used to obtain the dielectric constant. With the smallest circuits used measurements of the dielectric constants of liquids having conductivities as high as 100 times that of water can be made.

A FEW months ago I became interested in the question of the measurement of the dielectric constants of solutions of certain biological substances, chiefly various proteins which can be prepared in very pure form. Such measurements have an interest in view of existing speculations.¹

The materials in question are for the most part best available in aqueous solution, where they behave like ampholytes containing very weak acid and basic groups.² Under the most favourable conditions concentrated solutions (20–30%) can be obtained having conductivities as low as ten times that of distilled water. They are, moreover, laborious to prepare in more than small quantities. Any method suitable for the study must therefore (1) be appropriate for use with material having a conductivity approaching that of a dilute salt solution and (2) be applicable to small amounts of the substance to be investigated.

The method described in this paper seems to be the simplest and most accurate one which meets these requirements and ought to be generally useful. It has, moreover, some interest in connection with the behaviour of circuits at high frequencies. The following other methods may be mentioned briefly.

The well-known bridge method of balancing the resistance and capacity of a cell containing the unknown liquid for an alternating e.m.f. of fixed frequency has been developed in great detail by Nernst.³ It requires only

¹ Debye, *Polar Molecules*, Chemical Catalogue Co., New York, 1929.

² E. J. Cohn, *Physiological Reviews* **5**, 350 (1925).

³ See Nernst, *Zeits. f. Phys. Chemie* **14**, 622 (1894). The method has been used by B. B. Turner, *Zeits. f. Phys. Chemie* **35**, 428 (1900), to measure the dielectric constant of water and several other liquids. It has also been used by Ratz, *Zeits. f. Phys. Chemie* **19**, 94 (1896) and

small amounts of material but it is not suitable for frequencies above about 10^6 sec^{-1} , such as are necessary for measurements on liquids having conductivities much greater than that of distilled water.

Another well-known method makes use of standing waves produced by resonance in parallel wires. The wave-length on the wires is inversely proportional to the square root of the dielectric constant of the surrounding medium provided conductivity effects may be neglected. This method may be used at very high frequencies (greater than $3 \times 10^8 \text{ sec}^{-1}$) in connection with spark oscillators, but it requires considerable amounts of material and its accuracy is not very great.⁴

A modification of this method, developed by Drude, requires much less material; but the accuracy is no greater than that of the original method and there is the disadvantage that the apparatus must be calibrated with known liquids.⁵

One of the earliest of the electrostatic methods is based on a comparison of the attraction between the plates of a condenser charged to a given difference of potential and separated first by air and then by the unknown liquid. The magnitude of the attraction is proportional to the dielectric constant of the medium between the plates. The method has been used successfully with direct and alternating sources of e.m.f. The only apparent objection to it is that it is inconvenient for small amounts of material.⁶

A modification of this method makes use of the torque acting on a small conducting body (Fürth gives this body the form of an ellipsoid of revolution) suspended in the field between the plates of a condenser. The magnitude of this torque is a function of the dielectric constant of the medium separating the plates.⁷

Harrington, *Phys. Rev.* **8**, 581 (1916) on water. More recently it has been used by C. P. Smyth, *Journ. Amer. Chem. Soc.* **49**, 1030 (1927), **50**, 1536 (1928), in the study of organic liquids and liquid mixtures; also by Sack, *Phys. Zeits.* **28**, 199 (1927) in the study of salt solutions.

⁴ This method is based on the work of Lecher and of Blondlot on waves in wires. It was first used by Cohn u. Heerwagen, *Wied. Ann.* **43**, 343 (1891), and later more extensively by Drude, *Wied. Ann.* **55**, 633 (1895); **58**, 1 (1896); **59**, 17 (1896). See also *Zeits. f. Phys. Chemie* **23**, 270 (1897). It has also been used by Marx, *Wied. Ann.* **66**, 603 (1898), Colley, *Phys. Zeits.* **10**, 471 (1909); **10**, 657 (1909); **11**, 324 (1910), Rudop, *Ann. d. Physik* **42**, 489 (1913), Weichman, *Phys. Zeits.* **22**, 535 (1921), and Mie, *Phys. Zeits.* **27**, 792 (1926), for the most part on water. It has been applied by Deubner, *Ann. d. Physik* **84**, 429 (1927) to the study of dilute aqueous salt solutions.

⁵ This method is described by Drude in *Zeits. f. Phys. Chemie* **23**, 270 (1897). The value of the dielectric constants for a large number of substances obtained by the two methods are given. The method has been employed recently by R. Fürth, *Ann. d. Physik* **70**, 63 (1923) for the study of several organic and biological substances, and still more recently by Voigt, *Zeits. f. Physik* **44**, 70 (1927) for obtaining measurements on dilute salt solutions.

⁶ Much of the early work on water and other liquids was carried out by this method: Cohn and Aarons, *Wied. Ann.* **33**, 14 (1888); Tereschin, *Wied. Ann.* **36**, 792 (1888); Heerwagen, *Wied. Ann.* **49**, 272 (1893); Franke, *Wied. Ann.* **50**, 163 (1893). More recently Carman, *Phys. Rev.* **24**, 396 (1924) has revived the method and used it on water at a frequency of 60 cycles. Schmidt, *Phys. Rev.* **30**, 925 (1927), following the procedure of Carman, has applied it to dilute salt solutions.

⁷ The method was used at the suggestion of Nernst by Smale, *Wied. Ann.* **57**, 215 (1897)

A reflection method using polarized waves of very short wave-length (about 3 cm) has been used by Cole⁸ and Merczing⁹ to study the absorption bands of water. It is very inexact and of doubtful validity.

There is a very accurate method based on the principle of standing waves in wires described by Drake Pierce and Dow in a preceding paper of this journal. This method however requires very large amounts of material and is for this reason unsuited to the present requirements.

There is lastly another form of resonance method, which is of more interest in the present connection. A circuit, which we will call the *resonator*, containing the unknown, is brought to resonance with an *oscillator*, maintained at a fixed frequency, by adjustment of a variable condenser. This condenser is calibrated and placed in parallel with the cell or fixed condenser for the unknown, and from its settings when the cell is filled first with air and then with the unknown, the dielectric constant of the latter is calculated. Unfortunately this method is unsatisfactory at high frequencies, owing to stray capacity effects in the resonator. These increase with the frequency and may be expected to change with adjustments of the variable condenser. They can never be determined directly and can only be allowed for by calibration of the whole resonator in terms of known liquids introduced into the cell. This procedure, however, has the following disadvantages: (1) it limits the accuracy and range of all new determinations to that of previous measurements of the standard liquids; (2) it is impossible to get good standards of high dielectric constants (greater than about 30) since water itself is not known to great accuracy; (3) it is constantly necessary to check up on the calibration of the circuit.¹⁰

In order to avoid these difficulties and at the same time profit by the accuracy with which it is possible to make settings by a resonance method it was suggested to me by Professor G. W. Pierce that it might be possible to make a small, rigid resonator which could be entirely immersed in the liquid to be studied, so that all capacities of the circuit would be included alike in the medium. The plan then demands an inversion of the usual procedure of tuning the resonator to the oscillator; instead of this, the frequency of the oscillator is to be varied until it corresponds with the natural period of the resonator, first in air, then in the liquid. These frequencies can then be used to obtain the dielectric constant.

on water. It has been discussed at length by Fürth, *Zeits. f. Physik* **22**, 98 (1924). Peckhold, *Ann. d. Physik* **83**, 427 (1927), has employed it in the study of salt solutions.

⁸ Cole, *Wied. Ann.* **57**, 290 (1896).

⁹ Merczing, *Ann. d. Physik* **33**, 1 (1910); **34**, 1015 (1911).

¹⁰ Resonance methods of this type have been used by the following observers: Thwing, *Zeits. f. Phys. Chemie* **14**, 286 (1894); Niven, *Proc. Roy. Soc.* **85A**, 139 (1911); Hyslop, and Carman, *Phys. Rev.* **15**, 243 (1920); Preuner and Pungs, *Phys. Zeits.* **20**, 543 (1919); Jackson, *Phil. Mag.* **43**, 492 (1922); Lattey, *Phil. Mag.* **41**, 829 (1921); Kerr, *Journ. Chem. Soc.* **128**, 2796 (1926); Williams, *Journ. Am. Chem. Soc.* **48**, 1888 (1926) and later; Fritts, *Phys. Rev.* **23**, 345 (1924); Walden, Ulrich, and Werner, *Zeits. f. Phys. Chemie* **115**, 177 (1925); Kjansky, *Zeits. f. Physik* **52**, 743 (1928); Hellmann and Zahn, *Ann. d. Physik* **86**, 687 (1928) and Kniekamp, *Zeits. f. Physik* **51**, 95 (1928) discuss the method.

After a certain amount of experimentation it was found possible to build compact all metal resonators having natural periods of the desired magnitude. The period of a resonator diminishes with its size, and for a given resonator the period is of course greater in liquids of high dielectric constant. Resonators having a frequency of about 10^8 sec^{-1} in water are small enough to be satisfactorily immersed in 15–20 cc of liquid. This amount of liquid is found to include enough lines of force so that the results are unaffected by parts of the field not included.

The question now arises as to the relation between the natural period of a resonator and the dielectric constant of the medium surrounding it. It is of course well known that if we can treat a circuit as composed of lumped capacity C , inductance L , and resistance R , arranged in series, it will have an impedance given by

$$(R^2 + (L\omega - 1/C\omega)^2)^{1/2}.$$

This will be a minimum at a frequency, called the resonant frequency, given by

$$\omega = 1/(LC)^{1/2}$$

corresponding to the natural period of the circuit.¹¹ If C_0 is the capacity of the circuit in air, and C_1 its capacity in a medium of dielectric constant ϵ , then

$$C_1 = \epsilon C_0.$$

If ω_0 and ω_1 give the corresponding natural periods, then, since L is constant,

$$\epsilon = \omega_0^2 / \omega_1^2. \quad (1)$$

If we could regard our resonators as circuits of lumped capacity, inductance, and resistance, this would make the determination of the dielectric constant

TABLE I. Dielectric constant ϵ of distilled water.

Type of Resonator	Temp.	Frequency	ϵ	ϵ^{*25°
Spiral	21.2	8.147×10^7	79.99	78.62
Cylinder	36.9	4.331×10^7	74.65	78.70
Spiral	38.2	4.344×10^7	74.06	78.51
Cylinder	25.0	2.230×10^7	78.49	78.49
Cylinder	21.3	0.9820×10^7	79.75	78.42
Cylinder	20.0	0.3698×10^7	80.29	78.49
(Cylinder)	18.4	0.1396×10^7	84.8	82.4)
				Av. 78.54

* Calculated from temperature data given below.

by the proposed plan very simple. Now there is evidence, to be given below, that we cannot make such an assumption about the resonators; nevertheless

¹¹ We use ω for convenience. It is to be noted that ω , the natural period T , the resonant frequency f , and the corresponding wave-length λ in free space are given by the relations $\omega/2\pi = f = 1/T = 3 \cdot 10^8/\lambda$.

it appears that, if we can neglect the conductivity of the medium, we can still use Eq. (1) to compute the dielectric constant. The justification of this lies in the fact that the results obtained on water with the use of this assumption are consistent among themselves and agree with other observations. The measurements on water were made at various frequencies with a variety

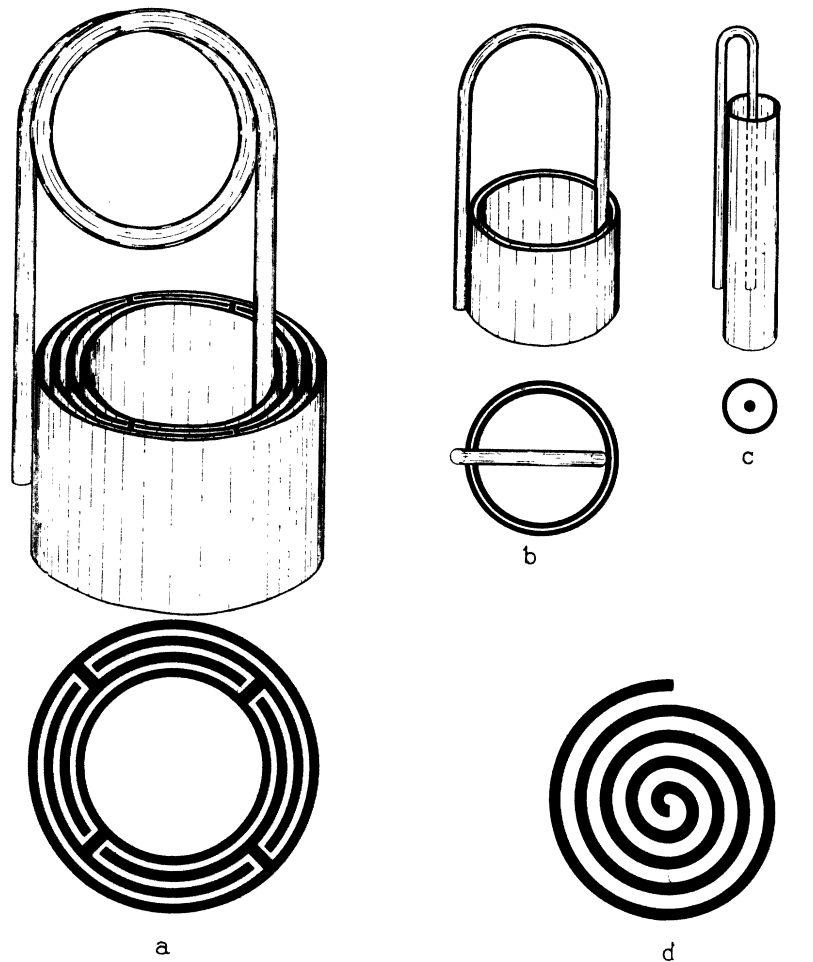


Fig. 1. Types of resonators. a, cylinder type: natural period in air, $8 \cdot 10^{-8}$ sec.; size 13×20 cm. b, cylinder type: natural period, 10^{-8} sec.; size 5×7 cm. c, cylinder type: natural period, $2 \cdot 10^{-9}$ sec.; size, $8 \cdot 6$ cm. d, spiral type: natural period, 10^{-9} sec.; diameter, 1.7 cm.

of resonators. Some of these had the form of concentric cylinders and others of spirals. (See Fig. 1.) The results obtained are given in Table I. The values of E were calculated from the observed frequencies by Eq. (1). With one exception they are all in agreement within the experimental error of the determination of the frequencies, and they also agree with values obtained by other methods. The one exception is in the case of the result obtained with

the largest resonator of all at a relatively low frequency. There is no doubt that the discrepancy in this case is due to the effect of conductivity which increases with decreasing frequency and may be expected on theoretical grounds to become evident at about this frequency for water. This close agreement in the values of ϵ is certainly a justification of the application of Eq. (1) to calculate the dielectric constant from the frequency in cases where conductivity of the dielectric may be neglected.

It should be observed in connection with this procedure that it is not possible in all cases to determine $\omega_0 = 2\pi f_0$ directly. If f_1 , the frequency of the resonator in water, is greater than about 1.4×10^7 , $f_0 = \epsilon^{1/2} f_1$ is greater than about 12×10^7 and lies above the upper range of the oscillator—about 12×10^7 . In such cases, however, it is easy to obtain f_0 by determining f_i , the frequency of the resonator in any intermediate liquid l , whose dielectric constant is immediately measured by a larger resonator for which f_0 is known directly. This liquid may be chosen as having low conductivity, and so introduces no trouble on that ground. It need have no especial purity or composition, since its dielectric constant is determined for the occasion. This practice was made use of in determining the values of f_0 for the smaller resonators and is involved in the above determinations of ϵ for water at the higher frequencies. The auxiliary liquid employed was acetone or a mixture of acetone and gasoline. Of course it is evident that each additional measurement of a frequency introduces errors which are accumulated in the final result and such extra steps are to be avoided if possible.

There is no need to describe the vacuum tube oscillator in detail. It was built about a 299X Cunningham tube with the base removed for operation at higher frequencies. The oscillation was set up between the plate and the grid; its frequency was controlled by interchangeable inductances and a rotating condenser driven by a reducing gear and equipped with a dial bearing a vernier. At the lowest frequencies a Hartley circuit was sometimes employed.

The frequency of the oscillator was determined in terms of the frequency of a quartz crystal according to a method described by Pierce.¹² The oscillator was permanently coupled, inductively, with the crystal circuit so as to give audible beats whenever set to the frequency of one of the harmonics of the crystal. These harmonics serve as standard frequencies and are identified by means of a wave meter. From the dial readings of the oscillator corresponding to several nearby harmonics of the crystal, the frequency corresponding to any intermediate setting of the oscillator may be determined by graphical interpolation. The frequency of every setting of the oscillator during the course of a measurement was always obtained directly in this way.

In the above measurements the criterion for resonance was maximum reaction of the resonator on the oscillator. The resonator, suspended by a fine thread in the medium in question, is placed in the field of the oscillator at a distance of 15 to 50 cm from its coil. The frequency of the oscillator is then varied until there is a sudden drop, or rise, in the plate current. This

¹² Pierce, Proc. Amer. Acad. Arts and Sciences 59, No. 4 (1923).

effect on the plate current of the oscillator undoubtedly accompanies a sharp change in the oscillatory current itself and is taken as the indication of maximum reaction. The corresponding frequency of the oscillator is then determined, according to the method just described, without altering the positions of resonator or oscillator. That in the case of water, or any medium whose conductivity may be neglected under the conditions of measurement, the frequency giving maximum reaction back on the oscillator is the same which gives maximum current in the resonator, corresponding to Eq. (1), was determined by means of a resonator containing a hot wire element (described below). It was found in a test case with water that maximum current was induced in the resonator at a wave-length $\lambda = 5.125$ M; whereas maximum reaction on the oscillator occurred at $\lambda = 5.124$ M. This result accords with the applicability of Eq. (1) to settings obtained by the reaction method.

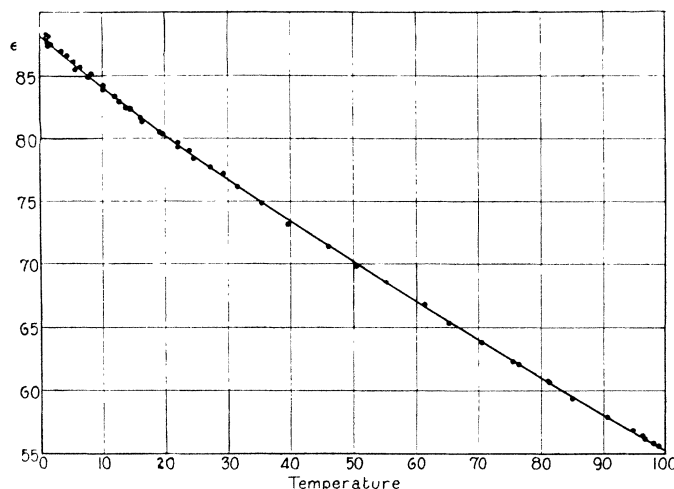


Fig. 2. The dielectric constant of water (ϵ) as a function of temperature.

The sharpness of any resonance setting is of course greater the lower the conductivity of the medium in question. In the case of distilled water the accuracy of a resonance setting at a frequency greater than about 4×10^6 is nearly equal to the accuracy of the determination of the frequency—that is, good to about 0.02 percent. The accuracy of the determination of the resonance frequency itself is thus about 0.04 percent. Any determination of the dielectric constant of water involves the determination of not less than two resonance frequencies, one in air and one in water. The best individual values of the dielectric constant of water obtained by this method are therefore accurate to about 0.1 percent.

The study of water was extended over a range of temperature from about 0°C to 100°C . The results are shown graphically in Fig. 2. The value of the dielectric constant as a function of temperature is expressed with an accuracy equal to that of the experimental results by the equation

$$\epsilon = 78.54[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2] \quad (2)$$

It is gratifying that these values are in good agreement with those obtained by Drake, Pierce, and Dow (preceding paper) over the range of temperature covered by these observers. They are also in reasonably good agreement with the results of earlier observers given in The International Critical Tables.

We now come to the results obtained on dilute salt solutions where conductivity effects are appreciable. Here the situation is much more complicated and shows (1) that the frequencies corresponding to maximum current in the resonator and maximum reaction on the oscillator are different when the conductivity of the dielectric is appreciable, and (2) that the resonators cannot in general be treated as circuits of lumped capacity, resistance, and inductance.

The evidence to support the above statements comes from the use of resonators, already referred to, containing a hot wire element. These resonators are of the cylindrical type. A small section of the metal loop joining the

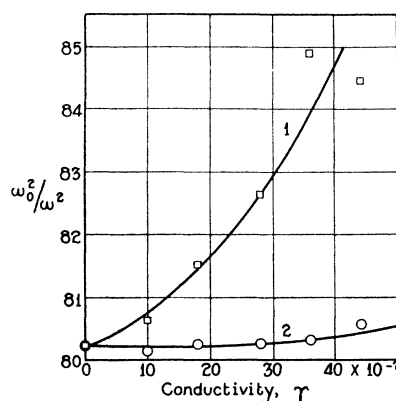


Fig. 3.

two cylinders is removed and replaced by a condensite tube of the same size. This serves to hold the two halves of the resonator rigidly in their former position and at the same time to enclose a piece of 40 gauge copper wire which connects the two cut ends of the loop and restores the connection in the circuit. To the midpoint of this wire are welded the ends of two lengths of 40 gauge wire, one copper and one constantan, which enter through the walls of the tube. These form one junction of a thermo-couple, which is a sensitive detector of any current in the resonator. If the resonator is suspended in water and placed at a distance of two feet from the coil of a power oscillator tuned to the right frequency, sufficient heat is developed in the hot wire to give a full scale deflection of a table galvanometer.

With such a resonator it is possible to tune the oscillator to give either maximum current in the resonator or maximum reaction back on the oscillator. As we have already seen, the two settings are identical for water at a frequency of about 6×10^7 ($\lambda = 5$ M.) When, however, we turn to dilute salt solutions at about the same frequency, the two methods of tuning no longer

give identical results. Instead, the frequency required to produce maximum current in the resonator is greater than that required for maximum reaction on the oscillator, and the difference between the two increases with the conductivity of the solution. This is shown by the results given in Fig. 3. The upper curve corresponds to maximum reaction; the lower to maximum current. It should be noted that a power oscillator was used to get settings by the first method, and the small oscillator to get settings by the second method.

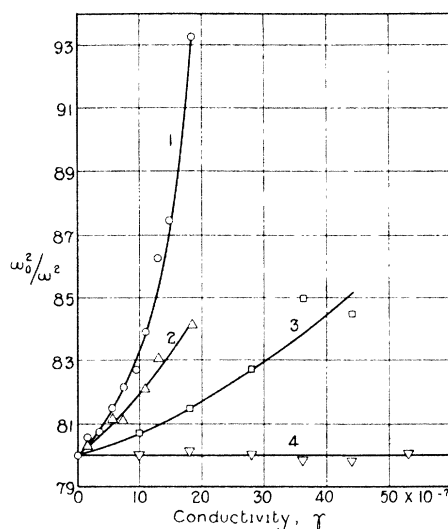


Fig. 4. Values of ω_0^2/ω^2 at varying conductivities obtained by the reaction method of determining resonance. Each curve was made with a different resonator. The natural periods in air of the corresponding resonators, expressed in seconds, are: 1, $11.40 \cdot 10^{-9}$; 2, $5.060 \cdot 10^{-9}$; 3, $1.914 \cdot 10^{-9}$; 4, $1.373 \cdot 10^{-9}$.

Such results are not unexpected in a general way. Suppose we have two circuits 1 and 2, 1 being the oscillator and 2 the resonator. We assume that the circuits are coupled inductively, and that the oscillator is subjected to an impressed E.M.F. of amplitude

$$E = e^{j\omega t}$$

Then, if $Z_1 = R_1 + jX_1$ is the impedance 1, $Z_2 = R_2 + jX_2$ the impedance of 2, and M the mutual induction between them, the complex current amplitudes are given by

$$A_1 = E / [Z_1 - (Mj\omega)^2 / Z_2]$$

$$A_2 = A_1 M j\omega / Z_2.$$

In determining the condition for A_2 maximum, we may certainly neglect changes in A_1 , if circuit 1 is a power oscillator. The frequency ω_2 corresponding to A_2 maximum is then seen to be given by the equation

$$\frac{d}{d\omega} \left(\frac{(R_2^2 + X_2^2)^{1/2}}{\omega} \right) = 0. \quad (3)$$

The determination of ω_1 , corresponding to A_1 maximum, is far less simple, but in general we may expect ω_1 and ω_2 to be different. It is suggestive, however to observe that in the case of a resonator of lumped capacity, inductance, and resistance immersed in a non-conducting medium, we may expect ω_1 and ω_2 to be equal. In this case the impedance of the resonator is $R + j[L\omega - (1/C\omega)]$. Conductivity of the dielectric being negligible, R is simply the resistance of the all-metal circuit, and may be neglected in comparison with L and C . ω_2 is then found to be equal to $1/(LC)^{1/2}$. If, on the other hand, we assume that the condition for A_1 max. is governed primarily by the second term in the denominator, we find that ω_1 is also equal to $1/(LC)^{1/2}$, provided we again neglect R in comparison with L and C .

It is, however, as we have pointed out, impossible to regard the resonators as circuits of lumped capacity, inductance, and resistance when conductivity is appreciable. We will now, in conclusion, consider this point. Values of ω_0^2/ω^2 , the apparent dielectric constant, for dilute salt solutions of various concentrations obtained by the two methods of determining resonance

TABLE II. Values of ω_0^2/ω^2 for solutions of potassium chloride at 20°C.

Resonator 1: $T_0 = 1.914 \cdot 10^{-9}$ sec.				
% conc. KCl	$\gamma \cdot 10^{-7}$	ω_0^2/ω^2	$f(h)$	$f(h)^2\omega_0^2/\omega^2$
0.000	0.3	80.22	1.000	80.22
.005	10.	80.16	1.001	80.32
.010	18.	80.28	1.001	80.44
.015	28.	80.29	1.004	80.73
.020	36.	80.32	1.006	81.28
.024	44.	80.60	1.009	82.06
.029	53.	80.76	1.013	82.86
.034	62.	80.81	1.017	83.56
Resonator 2: $T_0 = 2.495 \cdot 10^{-9}$ sec.				
% conc. KCl	$\gamma \cdot 10^{-7}$	ω_0^2/ω^2	$f(h)$	$f(h)^2\omega_0^2/\omega^2$
0.000	0.3	80.22	1.000	80.22
.005	10.	80.19	1.001	80.35
.010	18.	80.01	1.003	80.49
.015	28.	80.62	1.006	81.59
.020	36.	80.62	1.010	82.23
.024	44.	80.89	1.015	83.31
Resonator 3: $T_0 = 6.629 \cdot 10^{-9}$ sec.				
% conc. KCl	$\omega \cdot 10^{-7}$	ω_0^2/ω^2	$f(h)$	$f(h)^2$
0.000	0.3	80.22	1.000	80.22
.001	2.	80.22	1.001	80.38
.002	4.	80.09	1.001	80.25
.003	6.	80.17	1.002	80.49
.004	8.	79.86	1.004	80.50
.005	10.	79.70	1.005	80.50
.006	11.	79.89	1.007	81.02
.008	15.	79.31	1.012	81.22
.010	18.	78.47	1.017	81.15
.012	22.	78.12	1.025	81.11

are shown graphically in Figs. 4 and 5. The values obtained by the reaction method are in general higher than those from the thermal procedure and both sets of results vary among themselves. We will discuss only the latter, where the theory is far simpler. These are given in Table II.

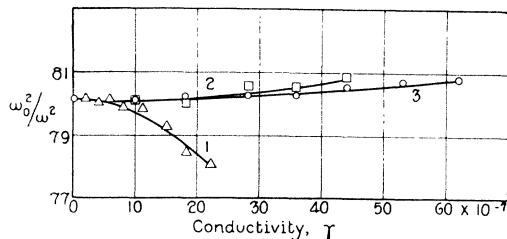


Fig. 5. The same, obtained by the thermal method. Corresponding natural periods in air are: 1, $6.629 \cdot 10^{-9}$; 2, $2.495 \cdot 10^{-9}$; 3, $1.914 \cdot 10^{-9}$.

Let us consider the behavior of an ideal resonator of lumped capacity, inductance, and resistance and compare the predictions with the results given above. Such a circuit placed in a conducting dielectric will behave as if the plates of the condenser were short circuited by a resistance r . If R denote the resistance of the metallic part of the circuit as before, and C and L its capacity and inductance, then it can be shown that the impedance of the circuit suspended in the conducting dielectric is

$$R + \frac{r}{1 + r^2 C^2 \omega^2} + j \left(L\omega + \frac{r^2 C \omega}{1 + r^2 C^2 \omega^2} \right).$$

The frequency corresponding to maximum current amplitude in the resonator may be obtained from Eq. (3) and is given by

$$\omega^2 = \frac{1}{2LC} \left(1 \pm \left(\frac{2LC}{r^2 C^2} + 1 \right)^{1/2} \right),$$

provided we neglect the ratio R/r . Now it can be further shown that for any condenser filled with a medium of dielectric constant ϵ and conductivity γ , the equivalent resistance r between the plates is given by

$$rC = \epsilon / 4\pi\gamma. \text{ }^{13}$$

Therefore, taking account of the fact that $C = \epsilon C_0$, where C_0 is the capacity of the resonator in air, and that $1/C_0 L = \omega_0^2 = 4\pi^2/T_0^2$, where T_0 is the natural period of the resonator in air, we obtain finally

$$\frac{\omega^2}{\omega_0^2} = \frac{1}{2\epsilon} \left\{ 1 \pm \left(1 + \frac{2}{\epsilon} (2T_0\gamma)^2 \right)^{1/2} \right\}.$$

Since if $\gamma = 0$ this must reduce to $\omega^2/\omega_0^2 = 1/\epsilon$, we discard the $-$ sign before the radical. This result may be compactly expressed by

$$\omega/\omega_0 = f(h)/\epsilon$$

¹³ I am indebted to Professor Pierce for this result.

where $f(h)$ has been tabulated for values of h .¹⁴ If $h=0$, $f(h)=1$. If h is less than about 0.12, $f(h)$ is not greater than 1.001, and ω_0^2/ω^2 is equal to ϵ to an accuracy of 0.2 percent or better.

For distilled water where $\gamma=3 \times 10^6$ e.s.u., approximately, we should be able to express ϵ by ω_0^2/ω^2 to an accuracy of 0.2 percent in the case all measurements for which T_0 (corresponding to ω_0) is less than 10^{-7} secs, or for which λ_0 , the corresponding wave-length in free space, is less than 30M. For liquids, e.g. salt solutions, for which γ is greater, $f(h)$ increases more rapidly with T_0 and we should be obliged to use smaller resonators having higher natural periods. But the main thing to notice is that as $T_0\gamma$ becomes appreciable and increases, ω_0^2/ω^2 becomes increasingly less than ϵ , according to Eq. (4).

If we attempt to correct the experimental values according to Eq. (4), we obtain the results given in the last column of Table II. Now it is pretty clear that these corrected results cannot give the true values of the dielectric constants of the solutions. The reason for this is that if they did, we should be obliged to assume the dielectric constant to vary with the frequency over the range covered by the measurements and to be greater than that of pure water. The results of Drake, Pierce, and Dow, however, show that the dielectric constant of dilute salt solutions is independent of frequency over the range in which we are interested and is in fact the same as that of water to an accuracy of about 1 percent up to a concentration of 1/70 normal KCl. These results are obtained by a method in which the theory is much simpler and the correction factor known. We are therefore justified in concluding that although the resonators may be treated as circuits of lumped capacity, inductance, and resistance in cases where the conductivity of the dielectric is negligible, i.e., where $T_0\gamma$ is small, they do not in general have the properties of such circuits, but behave in a much more complicated way. It is possible indeed that they are rather to be regarded as lines, if of a complicated type. The analysis of the behavior of even the simplest types of lines is, however, very complex under the circumstances of the above measurements and no attempt has been made to carry it out.

In any case, from the experimental results on the salt solutions, it is clear that we can use ω_0^2/ω^2 directly to express ϵ in the case of frequencies determined by the thermal method up to conductivities many times that of water, provided we use resonators having small natural periods. Table II shows that anomalies begin to appear at conductivities corresponding to values of $T_0\gamma$ for which the correction term $f(h)$, obtained from the analysis of the ideal circuit, begins to become significant. This is not unexpected. It appears that we are safe in equating ω_0^2/ω^2 and ϵ for values of h not greater than about 0.1. This means that if we use a resonator having a natural period in air of about 10^{-9} sec, we can employ the method up to conductivities about 100 times that of water. On the other hand if we make settings by the reaction methods we run into difficulties considerably sooner. Here we are probably safe up to conductivities 20–30 times that of water.

¹⁴ G. W. Pierce, Proc. Amer. Acad. Arts and Sci. 57, No. 7 (1922).