as is the case in water, variation in density will largely govern the variation in the polarizability. Furthermore, water in the liquid state is a substance in which the molecules show a great tendency toward association, which doubtless varies with the temperature. The Debye equation which would apply when the molecules are free to assume a random orientation, has no significance for a substance of this kind. An attempted calculation of the electric moment only serves to make this evident.

Any significance which may be attached to the above values is best left until more data are obtained.

Acknowledgment is made to the National Research Council of Canada for a bursary and studentship held by one of us, during the tenure of which the above work was carried out.

Summary

A resonance method for the measurements of the dielectric constant of pure liquids is described, involving the use of a variable dielectric cell in which lead and end effects are eliminated and the dimensions of which can be altered over wide limits.

The dielectric constants of ether, benzene, chlorobenzene and nitrobenzene were measured at 25°. The dielectric constant of water was determined between 0 and 75°. The step-by-step method used made it possible to make absolute determinations based on air as unity.

The polarizability of water was calculated from the dielectric constant data. The futility of applying the Debye equation for this substance was pointed out.

MONTREAL, CANADA

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY, MCGILL UNIVERSITY]

HYDROGEN PEROXIDE. VII. THE DIELECTRIC CONSTANTS, REFRACTIVE INDICES AND IONIZING POWER OF HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS

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RECEIVED AUGUST 2, 1929 PUBLISHED FEBRUARY 6, 1930

Dielectric Constants.—The measurements referred to in the title may most conveniently be taken up in separate sections.

The determination of the dielectric constants of hydrogen peroxide and its aqueous solutions presents two difficulties: the tendency of the peroxide to decompose and conduction of the solutions due to impurities. The first of these was very largely overcome by constructing a cell similar to the one described elsewhere[1] but made of tin. The second difficulty was eliminated by paying particular attention to the purification of the peroxide. It was found that of all metals very pure tin showed the least

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[1] Cuthbertson and Maass, THIS JOURNAL, **52**, 483 (1930).

catalytic effect in causing decomposition. Every part of the condenser which had contact with the peroxide was therefore made from tin. The stator plates of the three-plate condenser were tin soldered to two tin tubes which were reinforced by inner brass rods, the upper ends of which were tightly clamped to a plate of bakelite. The center of the rotor plate was similarly fastened to a rod which passed through a bushing and then fastened to a vernier dial. This ensured the necessary rigidity and reproducibility in the setting of the cell. All the measurements were carried out at zero in order to minimize decomposition, which after a long immersion made itself evident by the formation of small bubbles of oxygen on the plates of the condenser.

The peroxide used was distilled from alkaline solution and subsequently recrystallized after concentration. The aqueous solutions were obtained by diluting with distilled water. It might be mentioned in this connection that conductivities higher than 10^{-5} made measurements difficult. In order to indicate the reproducibility and accuracy of the results the experimental data are given in Table I. The calculations of the dielectric constants are based on 84.4 for water at 0°. The relationship between percentage of hydrogen peroxide and dielectric constant is shown in Fig. 1.

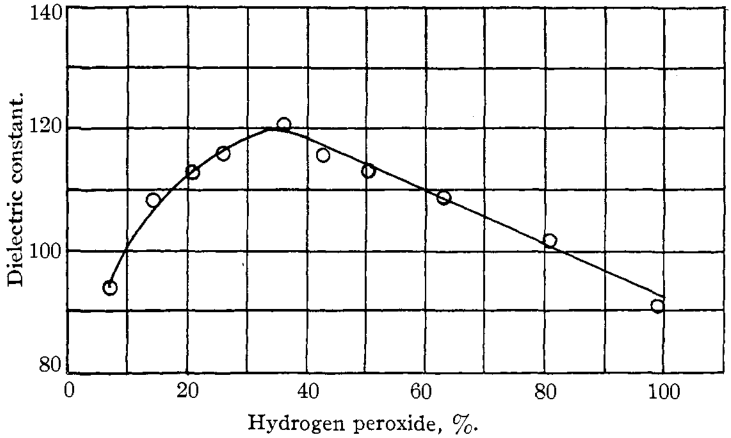

Fig. 1.

It will be noticed that the calibration value for water remains constant in a series of readings but varies a little from one series to another for the same cell setting. This was due to permanent changes on the handling of the cell between runs and does not enter into the results as calculated for any one series. After each peroxide measurement a water determination was made.

Observation showed that only very slight decomposition occurred, so that after a five-minute interval no appreciable change could be detected. After standing for a period of two hours, however, the relative

TABLE I

CAPACITY VALUES FOR HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS RELATIVE TO WATER AT 0°

H_2O_2, %, 99.45		H_2O_2, %, 98.87		H_2O_2, %, 81.27	
Cell setting 80–20		Cell setting 80–20		Cell setting 80–20	
Relative capacity	Water value	Relative capacity	Water value	Relative capacity	Water value
33.20	31.30	34.85	32.10	38.85	
33.20	31.50	34.70	32.05	38.50	
33.30	31.40	34.65	32.30	38.60	
33.20	31.70	34.65	32.10	38.75	
33.30	31.60		32.10	38.80	
33.50	31.50			38.90	
33.10					
33.30					
33.30					
Av. 33.28	31.50	Av. 34.71	32.11	Av. 38.67	32.11
Dielectric constant, 89.2		Dielectric constant, 91.2		Dielectric constant, 101.6	

H_2O_2, %, 63.8		H_2O_2, %, 50.23		H_2O_2, %, 43.25	
Cell setting 80–20		Cell setting 80–20		Cell setting 60–20	
41.50		43.20	31.70	31.20	22.20
41.40		43.25	31.60	31.0	22.40
41.30		43.35	31.90	31.1	22.40
41.35		43.20	31.80	30.8	22.20
		43.20	31.60	31.70	22.20
			31.70	31.3	
Av. 41.39	32.11	Av. 43.24	31.71	Av. 31.0	22.32
Dielectric constant, 108.8		Dielectric constant, 115.0		Dielectric constant, 116.2	

H_2O_2, %, 36.3		H_2O_2, %, 32.0		H_2O_2, %, 25.8	
Cell setting 60–20		Cell setting 60–20		Cell setting 60–20	
31.80		31.70		30.70	
31.80		31.70		30.70	
31.80	22.32	31.50		30.60	22.32
		31.30			
		31.50	22.32		
Av. 31.80	22.32	Av. 31.54	22.32	Av. 30.67	22.32
Dielectric constant, 121.1		Dielectric constant, 119.0		Dielectric constant, 116.0	

H_2O_2, %, 20.8		H_2O_2, %, 14.0		H_2O_2, %, 6.9	
Cell setting 60–20		Cell setting 80–20		Cell setting 80–20	
30.00		43.40	33.80	37.70	
29.70		43.00	33.70	37.20	
30.30	22.32	43.70	33.70	37.40	33.62
		43.50	33.60		
		43.50	33.60		
Av. 30.00	22.32	Av. 43.42	33.62	Av. 37.40	33.62
Dielectric constant, 113.5		Dielectric constant, 108.5		Dielectric constant, 94.0	

capacity was measurably lowered due to the formation of bubbles, although the extent of the decomposition could not be detected analytically. All the measurements tabulated above were made before the capacity was altered by bubble formation.

The occurrence of a maximum in the curve relating the dielectric constant and percentage hydrogen peroxide was not anticipated. The phenomenon has, however, been observed before. Partington[2] showed that a maximum exists in the binary mixture benzoic acid and benzene. It is known that peroxide and water form a complex but whether this exists at so high a temperature as 0° and at the same time is responsible for the maximum is problematical. The maximum occurs at 35% hydrogen peroxide and this does not correspond with the composition of the molecular compound.[3] This fact however does not prove that the latter has no influence on the constant. The fact that the complex is bound to be dissociated and the hydrogen peroxide with its higher dielectric constant might have less influence on the slope of the curve.

The dielectric constant of pure hydrogen peroxide is 89.2 at 0°, based on a value of 84.4 for water. There is a reference in the literature to a value obtained by Calvert[4] of 84.7 for a 45.9% solution at 18°. This value has been extrapolated for the 100% solution. Measurements at temperatures other than 0° will be attempted in the near future.

Refractive Indices.—The measurements were carried out with a goniometer using the method described previously.[5] A hydrogen tube was used and the refractive indices were measured by means of the three lines 6563, 4861 and 4340. The values are given in Table II.

TABLE II

REFRACTIVE INDICES 24.5°

		H lines	
H_2O_2, %	6563	4861	4340
13.85	1.3409	1.3476	1.3515
35.48	1.3557	1.3623	1.3657
55.60	1.3701	1.3768	1.3814
74.79	1.3851	1.3914	1.3984
89.36	13.957	1.4032	1.4091

The above values were plotted against concentration of hydrogen peroxide and the refractive indices of 20, 35, 40, 60, 80 and 100% hydrogen peroxide were taken. n_α was obtained for the above concentrations by extrapolation by means of the Cauchy Formula and MR_α was calculated.

The curves relating refractive index to concentration show no abnormalities as observed in the dielectric constant determination. The same

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[2] Partington, *Phil. Mag.*, [7] 1, 1035 (1926).

[3] Maass and Herzberg, THIS JOURNAL, **42**, 2569 (1920).

[4] Landolt–Börnstein, "Tabellen."

[5] Maass and Hatcher, THIS JOURNAL, **42**, 2548 (1920).

Table III

Refractive Powers and Polarizability

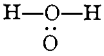
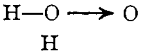
H_2O_2, %	n_α	MR_α	Polarizability
0	1.3239	3.610	17.38
20	1.3360	3.854	18.01
35	1.3460	4.110	18.50
40	1.3495	4.154	18.70
60	1.3637	4.533	19.55
80	1.3756	4.964	20.71
100	1.3910	5.643	22.52

holds true for n_α plotted against concentration. All the values fall approximately on continuous gentle sloping lines and the largest deviation occurs in the case of the blue line for H_2, viz., 4340. This is undoubtedly due to the experimental error because the blue image was not as well defined as the other two and therefore increased somewhat the difficulty of focusing the cross hairs of the telescope on it.

Maass and Hatcher[6] obtained 1.4140 for the refractive index of pure peroxide for the sodium D line and 1.4043 at 96.81%. From the values given the latter is in good agreement but the first is too high. On recalculating the value for pure peroxide from the prism and angle of minimum deviation in their paper an arithmetical error was found. Recalculation gave 1.4063, in agreement with the above results.

The change in the value as originally published is too slight to affect the argument relating MR_D and constitution. The value of the molecular refractive power 5.805 is too large for two hydroxyl oxygens and too small for a quadrivalent oxygen if the value found by Miss Homfray[7] in pyrone salts be accepted. The dispersive power also gives values for hydrogen peroxide not truly additive on the basis of hydroxyl oxygens. The dispersive power between the H lines—6563 and 4340—equals 0.410. The atomic dispersions for the same lines amount to 0.036 and 0.019 for hydrogen and hydroxyl oxygen, respectively. This gives a calculated value of 0.110 compared to an observed of 0.410.

Neither the refractive power nor dispersive power of hydrogen peroxide appears to offer decisive proof as to the correct formula for this substance. Some evidence of value may, however, be obtained by a consideration of Sugden's[8] parachor. On the basis of the following formulas the calculated values of the parachor are given.

Formula	HO—OH	 $\underset{\overset{\cdot\cdot}{O}}{H-O-H}$	 $\underset{H}{H-O\longrightarrow O}$
Parachor calcd.	74.1	97.7	72.5
Parachor obs.	69.6	..	..

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[6] Maass and Hatcher, This Journal, **42**, 2548 (1920).

[7] Homfray, *J. Chem. Soc.*, **87**, 1443 (1905).

[8] Sugden, *ibid.*, **125**, 1185 (1924); *ibid.*, **127**, 1525 (1925).

The calculated value for the parachor corresponding to (3) most nearly approaches the observed value of 69.6. This formula represents what is termed a coördinate link, *i. e.*, the electrons shared by the two oxygen atoms come from the oxygen atom attached to the two hydrogen atoms.

It appears reasonable then to suppose that the calculated values of the molecular refractive and dispersive power of hydrogen peroxide would agree, were the atomic refractive power of a coördinate linked oxygen atom known. On the basis then of the deviation shown in all three cases for Formulas 1 and 2, 3 is to be taken as correct, and the atomic refractive power of a coördinate oxygen linked to another is 2.1.

The electric moments calculated by the Debye equation for aqueous solutions of hydrogen peroxide of various strengths were all found to have approximately the same value. This value has no significance in view of the fact that one is dealing with a binary mixture both the components of which are highly associated. The interest of such a calculation lies in that it makes evident that even if a maximum occurs in the dielectric constant no such maximum need be expected in n_∞. The polarizability is given by $\frac{E-1}{E+2}\cdot\frac{M}{d}$, where M is calculated on the basis of molar fractions and, although E passes through a maximum on varying the concentration of peroxide, the polarizability increases continuously when E is large.

Ionizing Power.—In measuring the conductivity of solutions in which peroxide is the solvent, care must be taken to avoid decomposition at the electrodes. Tin has proved to be the most suitable metal and to avoid polarization a method was employed the principle of which is described by Bouty[9] and Sheldon.[10] In outline the apparatus used in this investigation consisted of a glass cell into which four tin electrodes could be inserted. A current of less than 0.001 ampere was passed through the solution, the circuit being made through the two outer electrodes, which may be termed the primary ones. A quadrant electrometer connected to the other two (secondary electrodes) made possible the measurement of the potential difference between two fixed points in the solution. By means of a double throw switch connected to the electrometer and across a resistance box which is in series in the primary circuit, it was possible to measure the drop of potential across both the fixed electrodes and the known resistance. The ratio of the quadrant electrometer readings in the two cases made possible the calculation of the resistance of the solution in question since the same current is flowing through both.

Figure 2 gives a diagrammatic sketch of the cell in the form of a U-tube with two other glass tubes sealed into the horizontal portion and in

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[9] Bouty, *J. de phys.*, **3**, 325 (1884).

[10] Sheldon, *Ann. Physik*, **34**, 122 (1888).

the same plane as the two outer arms. In the outer arms the primary electrodes were inserted while the drop of potential was measured across the two inner ones by means of the electrometer. The current was supplied by a number of dry cells and passed through the resistance box R and solution on closing the switch S. The double switch K made possible the quick comparison of the potential drop across E, E or R.

Owing to the irregularities in the semi-circular scale and the position of the electrometer relative to it, the scale deflections were not exactly proportional to the potential differences measured. The following method of correction was applied. Three dry cells were used. Each in turn was connected across the quadrants of the electrometer and the deflection determined in all three cases. Two were then connected in series and finally the deflection was noted for all three in series. A graph of the necessary correction for any deflection was then used.

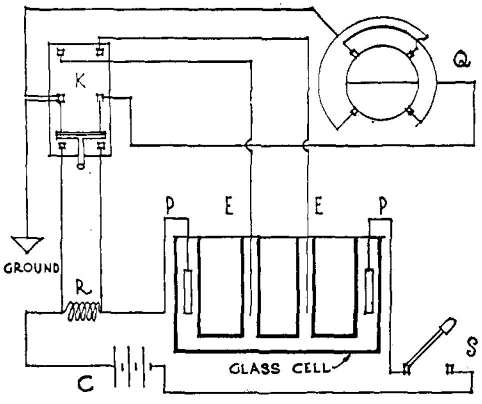

Fig. 2.

The method used in the determination of the cell constant will illustrate the general method employed in the conductivity measurements. A solution of $N/10$ potassium chloride was poured into the cell and the four tin electrodes were placed in position. The two outer electrodes were connected in the circuit of the cell C and the resistance R. R had in this case a value of 22,000 ohms. The secondary electrodes were connected to one pair of end terminals of the double throw switch K while the other two shunted the resistance R. One of the center terminals was connected to ground, the other to one pair of quadrants. The other pair of quadrants was grounded. The switch K was thrown in turn across the secondary electrodes E, E and the resistance R and the corrected scale readings 4.02 and 13.65 were obtained. Hence the resistance of the cell was $(4.02/13.65) \times 22{,}000 = 6471$ ohms, and the cell constant k becomes $= 6471 \times 1.17 \times 10^{-2} = 75.82$, where 1.17×10^{-2} is the specific conductivity of a $N/10$ potassium chloride solution at 20°. The solution in the cell was then replaced by a $N/100$ potassium chloride solution and deflections of 15.42 and 5.72 were obtained for the secondary electrodes and resistance. Hence the specific conductivity of this solution is

$$(75.82) \div \left(\frac{15.42}{5.72} \times 22{,}000\right) = 1.278 \times 10^{-3}$$

which is in agreement with the established value.

It might be mentioned here that in a series of measurements involving the same cell and electrodes, any change in the position of the secondary electrodes was obviated by having the electrodes of such a length that they did not reach the main body of the liquid in the horizontal portion of the cell.

Varying the position of the primary electrodes between measurements makes no difference in the ratio of the deflections.

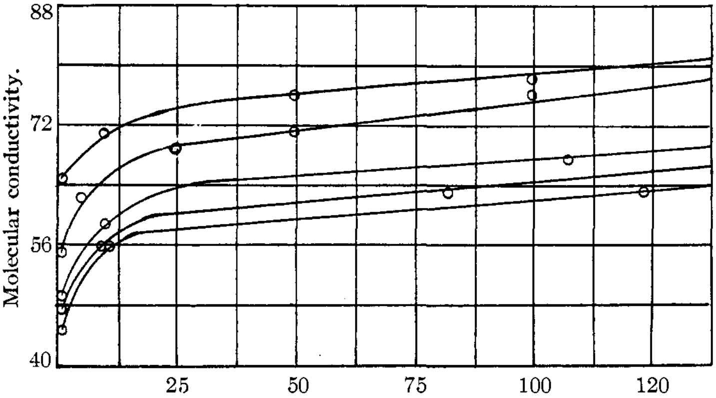

Fig. 3.

By varying the cross section of glass connection several cells were made having widely different constants and these cells were used according to the resistance of the solution. As a source of current dry cells up to 30 volts were employed and their number and the resistance up to 100,000 ohms chosen in such a way that deflections of proper magnitude were obtained. With the small currents used, no variation in the current could be detected during long periods. In any case the measurements as carried out are quite independent of the current, provided it does not change during the short interval required to measure the two deflections.

Excellent results were obtained by means of the above method. Especially noticeable was the accuracy with which solutions having a very low conductivity could be measured.

The specific conductivity of freshly crystallized peroxide was found to be of the order 2×10^{-6}. This must be taken as the upper limit since the crystallization and measurements were carried out in glass vessels. This conductivity would correspond to a hydrogen-ion concentration of 4×10^{-6} or less than one-tenth of that given by boric or carbonic acids but fifty times as great as pure water. If therefore hydrogen peroxide is an acid it is an exceedingly weak one. On diluting the peroxide the concentration of some of the solutions was found to increase if they were allowed to stand in glass vessels.

In the case of solutions of low conductivity, for which the results are given below, the conduction of the solvent was determined so that proper corrections could be applied. This was only necessary in the case of the acetic acid solutions and very dilute potassium chloride solutions.

TABLE IV

CONDUCTIVITY OF POTASSIUM CHLORIDE IN HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS AT 0°

H_2O_2, %	Dilution in liters	Spec. cond.	Mol. cond.
22.26	0.500	9.62×10^{-2}	48.1
	1.020	5.36×10^{-2}	54.7
	5.00	1.26×10^{-2}	62.8
	25.0	2.64×10^{-3}	69.5
	50.0	1.41×10^{-3}	70.5
	100.0	7.63×10^{-4}	76.3
35.48	1.10	4.84×10^{-2}	53.3
	10.10	5.88×10^{-3}	59.3
	107.3	6.30×10^{-4}	67.5
90.2	1.016	5.00×10^{-2}	50.8
	9.083	6.15×10^{-3}	55.9
	82.10	7.73×10^{-4}	63.2
100	0.995	4.51×10^{-2}	44.8
	11.1	5.11×10^{-3}	56.3
	123.0	6.12×10^{-4}	63.0

The following results were obtained for acetic acid at 0°.

TABLE V

CONDUCTIVITY OF ACETIC ACID IN AQUEOUS HYDROGEN PEROXIDE SOLUTIONS AT 0°

H_2O_2, %	Dilution in liters	Spec. cond.	Mol. cond.
22.26	0.486	6.44×10^{-4}	0.315
	1.200	5.01×10^{-4}	.757
	12.00	1.74×10^{-4}	2.090
	60.00	7.34×10^{-5}	4.40
	120.0	5.12×10^{-5}	6.14
	600.0	2.09×10^{-5}	12.5
	1200.0	1.69×10^{-5}	20.3
90.2	0.901	2.22×10^{-5}	0.020
	5.64	1.01×10^{-5}	.057
	273.0	6.1×10^{-6}	1.66

Probably the most satisfactory method of discussing the conductivities of potassium chloride and acetic acid in aqueous solutions of hydrogen peroxide is to compare them with those of water. For this purpose a series of curves is included to show the relation between the molecular conductivity and dilution for potassium chloride. The curves for water and 22.26, 35.48, 90.2 and 100% H_2O_2 are all of the same type as water. Further, as the percentage of H_2O_2 increases, the molecular conductivity for any one dilution decreases regularly. It might have been expected that the 35.47% H_2O_2 solution would show abnormalities comparable with the dielectric constant. Such, however, does not appear to be the case. From the fact also that the dielectric constant of all the solutions is higher than in the case of water, it would be anticipated that all of the solutions would show a higher value than water with respect to specific or molecular conductivity.

The ionizing power, however, with which the value of the dielectric constant is presumably most directly connected, is best investigated by determining the ratio of the molecular conductivity at any dilution with that at infinite dilution. To calculate accurately by extrapolation methods the molecular conductivity at infinite dilution necessitates the specific conductivities of solutions of from $N/1000$ to $N/10{,}000$. Such data are not available from the present measurements. In order to approximate this value for the various solutions, the following method was resorted to. The molecular conductivities were plotted against percentage of peroxide for dilutions of 10, 20, 40 and 100.

The value of the molecular conductivity of potassium chloride in water was taken as 81.5 at infinite dilution and 0° and the curve was drawn, by proportionality considerations, to those obtained at dilutions of 10, 20, 40 and 100. In this way then an approximation to the conductivities at infinite dilution was made, and was for 100% H_2O_2, 65.5; 90% H_2O_2, 66.0; 35.5% H_2O_2, 71.5; 22.2% H_2O_2, 75.8. A comparison can now be made for the apparent dissociation of potassium chloride in water and in the peroxide solutions.

TABLE VI

COMPARISON OF POTASSIUM CHLORIDE DISSOCIATION IN WATER AND IN HYDROGEN PEROXIDE SOLUTIONS AT VARIOUS DILUTIONS

H_2O_2, %	Dissociation	H_2O_2, %	Dissociation	H_2O_2, %	Dissociation
Dilution 10		Dilution 50		Dilution 100	
100	0.848	100	0.945	100	0.957
90	.856	90	.952	90	.962
35.5	.830	35.5	.928	35.5	.942
22.2	.868	22.2	.941	22.2	.971
Water	.877	Water	.932	Water	.955

The approximate ionizing power so calculated leads one to the conclusion that the degree of dissociation of strong electrolytes is about the same as in water. This point of view is fully substantiated by the lowering of the freezing point of salts dissolved in pure hydrogen peroxide.

Certainly there is no evidence to show that the higher dielectric constant of the peroxide solutions markedly increases the ionizing power. In point of fact it is to be noted that in all three cases, *i. e.*, for dilutions 10, 50 and 100, if anything a minimum value for the ionizing power is obtained for the 35% solution whose dielectric constant is higher. Due however to the approximate character of the data definite statements cannot be made until more accurate values are obtainable. The only conclusion which appears justifiable, until more data are available, is that, due to the abnormally high values of the dielectric constant of water, hydrogen peroxide and its aqueous solutions, the ionizing power of these solvents is high and of a comparable magnitude.

The conductivity of the acetic acid in peroxide solutions is astonishingly small in the higher concentrations of peroxide and will be investigated more thoroughly before any comments are made.

Hydrogen peroxide shows a great similarity to water in many of its physical properties. Hence it will be of interest to make a thorough investigation of the conductivities of electrolytes in hydrogen peroxide as a medium.

Acknowledgment is made to the National Research Council of Canada for a bursary and studentship awarded to one of us, during the tenure of which the work was carried out.

Summary

The dielectric constants of hydrogen peroxide and its aqueous solutions were measured. It was shown that a maximum occurs at a concentration of 35% of H_2O_2.

The refractive indices of hydrogen peroxide solutions were measured over the whole range of concentration and at three wave lengths. The molecular refractive power and dispersive power indicate that the structure cannot be represented by two hydroxyl oxygens. It is suggested that the coördinate oxygen linkage which is given by Sugden's parachor has a definite atomic refractive power.

The polarizability as calculated from the refractive indices was shown to increase continuously with increased concentration of peroxide.

A method was described for measuring electric conductivities in hydrogen peroxide and its solutions.

Potassium chloride solutions were measured and the amount of dissociation was shown to be nearly the same as in water.

Acetic acid solutions were found to have far smaller conductivities than the corresponding solutions in water.

The specific conductivity of pure hydrogen peroxide was shown to be less than 2×10^{-6} and consequently it can be only very slightly dissociated.

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