

- (i) Frozen electrolytes at low temperatures are capable of acting as dielectrics even in the case of those substances which in the liquid state and in aqueous solutions have relatively a very high electrolytic conductivity.
- (ii) At temperatures not far removed below their freezing points, these electrolytes have dielectric constants of large value, and numerically of the order of that of ice or water at 0° C. or in some cases much larger.
- (iii) The majority of these high dielectric values so far as observed are reduced to very much lower values (near to 3) when the dielectrics are cooled to, and below the temperature of, liquid air.
- (iv) Certain aqueous solutions of potash retain their high dielectric values to nearly the liquid air temperature, but give indication of being reduced at lower temperatures to small values.
- (v) Frozen electrolytes at very low temperatures have very great insulating power, but recover sensible conductivity with great rapidity at temperatures far below their melting points.
- (vi) It appears probable that at the absolute zero of temperature all electrolytes become perfect non-conductors of electricity or have infinite resistivity, also that it is possible their dielectric constants may all be reduced to, and represented by, a number near to 2 or 3 at that temperature, that of a vacuum being taken as unity.

We are engaged in examining as many electrolytes as possible at low temperatures to test the validity of the above last inference. In conclusion, we have again to thank Mr. J. E. Petavel for much valuable assistance in the laborious work of taking these observations, a work which has necessitated frequently very considerable endurance, in consequence of the fact that such series of observations, when once begun, had to be continued often through the night without interruption until completed.

“On the Dielectric Constants of Pure Ice, Glycerine, Nitrobenzol, and Ethylene Dibromide at and above the Temperature of Liquid Air.” By J. A. FLEMING, M.A., D.Sc. F.R.S., Professor of Electrical Engineering in University College, London, and JAMES DEWAR, M.A., LL.D., F.R.S., Fullerman Professor of Chemistry in the Royal Institution, &c. Received May 6,--Read June 3, 1897.

In another communication we have described the instrumental appliances we are at present using in investigations on dielectric

constants at very low temperatures,* and there is, therefore, no need to repeat these descriptions.

In the present paper we give the results we have obtained for the variation of dielectric constants at low temperatures when using certain carefully purified bodies as dielectrics.

As pure water is a standard substance the electrical constants of which have been very carefully studied, we desired in the first place to repeat our former experiments on the dielectric constant of ice, using, however, very pure distilled water as the means of procuring it.

Dr. Scott very kindly prepared for us in the Davy-Faraday laboratory a sample of pure water distilled in a silver still, and the gilt cone condenser used was carefully washed out with this water. The condenser was then kept full of this water for ten days, the water being changed twice a day. During the day-time the condenser full of water was kept at a temperature of 90°C . Having thus very carefully purified the condenser it was again filled with the pure distilled water, and this water frozen into ice by the aid of liquid air. The whole mass of the condenser and the ice being reduced to -185°C . by immersing the cones in a large vacuum vessel full of two litres of liquid air, the condenser was then raised out of the liquid air into the equally cold gaseous air lying above it in the vacuum vessel, and was allowed to warm up very slowly, taking four hours thirty minutes to rise in temperature from -185°C . to 5°C .

During this rise of temperature the dielectric constant of the ice was measured at various temperatures by the arrangements already described, and also the resistance of the ice condenser.

The corrected galvanometer scale deflection, when the condenser as used was filled with gaseous air at the ordinary temperature of 15°C ., was 3.73 centimetres, using a charging voltage of 100 volts. This value is corrected for the capacity of the leads and for that of the vibrator. In the following table the temperature of the ice is given in platinum degrees in terms of our standard platinum thermometer P_1 .

* See Fleming and Dewar, "On the Dielectric Constants of some Frozen Electrolytes at and above the Temperature of Liquid Air," 'Roy. Soc. Proc.,' vol. 61, p. 299, 1897; also Dewar and Fleming, "Note on the Dielectric Constant of Ice and Ethylic Alcohol at very Low Temperatures," 'Roy. Soc. Proc.,' vol. 61, p. 2, 1897.

Dielectric Constants of Pure Ice.

Frequency of contact maker 120.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant of ice.	Observations.
-206.0	9.45	2.43	Charging voltage 100.7 volts.
-199.8	9.40	2.42	
-197.2	9.39	2.42	
-183.7	9.39	2.42	
-175.0	9.46	2.43	
-164.3	10.05	2.59	Charging voltage 19.8 volts.
-156.0	11.42	2.96	
-149.0	13.2	3.43	
-144.7	2.97	3.94	
-136.0	3.76	5.02	
-128.0	4.45	5.95	
-120.0	5.50	7.38	
-114.0	7.15	9.60	
-111.0	8.08	10.8	
-106.2	10.3	13.9	
-97.8	14.65	19.8	Charging voltage 1.434 volts.
-93.7	17.3	23.4	
-89.4	20.5	27.6	
-87.2	1.55	29.0	
-82.3	1.80	33.5	
-77.7	2.0	37.3	
-72.4	2.24	41.8	
-63.8	2.57	46.8	
-54.8	2.99	55.8	
-49.0	3.05	57.2	
-39.2	3.14	58.9	
-35.2	3.13	58.5 ?	
-27.2	3.16	59.2	
-24.5	3.15	59.1	
-22.5	3.15	59.1	
-21.0	3.28	61.3	
-17.8	3.28	61.3 ?	
-15.0	3.50	65.4 ?	
-10.2	3.63	67.8 ?	
-7.5	2.78	70.8 ?	

In the case of the last four observations the discharge and charge currents of the condenser were no longer quite equal, thus showing that conductivity had begun to have influence prejudicial to the accuracy of the measurements of the dielectric constant.

The results of these observations are set out in the curve in fig. 1 marked *pure water*.

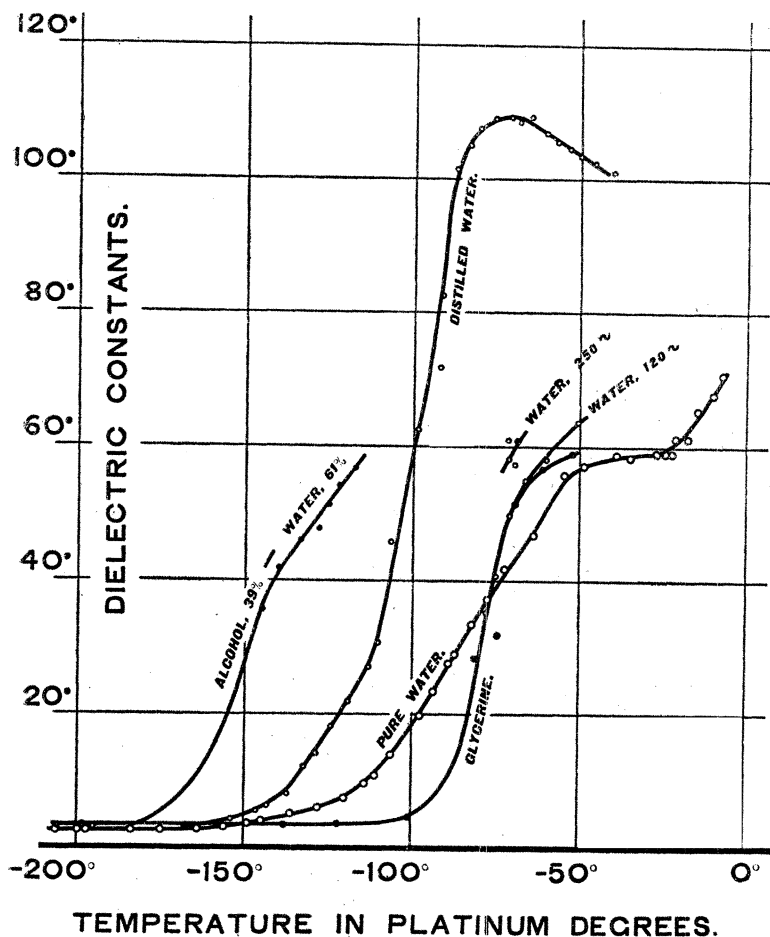


FIG. 1.—Curves showing the variation of dielectric constant of ice and frozen glycerine with temperature.

It will be seen from the form of this curve that the dielectric constant of the pure ice would be evidently represented by a number not far from 80 at the temperature of the melting-point of ice.

We determined also the electrical resistance of this ice condenser during the time it was very slowly warming up to the temperature of the room, a process which occupied about six hours.

Resistance of Condenser with Pure Ice as Dielectric.

Temperature in platinum degrees.	Resistance of the condenser in megohms.
-206.0	25,000
-152.1	2,500
-138.2	2,000
-92.0	1,200
-68.2	1,200
-47.0	410
-42.1	260
-33.2	250
-27.6	40
-26.1	15
-19.2	3
-10.2	1

It is seen from the above figures that our former observations on the resistance of ice from ordinary distilled water are confirmed. Above a certain temperature there is a relatively rapid increase in the conductivity of the ice, as it rises in temperature.

It was considered desirable to ascertain the difference made in these values by using the ordinary distilled water of the laboratory instead of this carefully purified distilled water, and therefore the same experiments were repeated, using ordinary water, with the following results:—

Dielectric Constant of Ice from ordinary Distilled Water.

Frequency of contact maker 120. Corrected galvanometer deflection with condenser having air at 15° C. as dielectric = 5.63 cm. for 100 volts.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
-205.8	17.30	2.88	Charging volts 104.0.
-205.8	3.59	2.90	Charging volts 20.2.
-199.9	17.22	2.88	Charging volts 103.7.
-195.0	17.24	2.91	
-154.0	24.7	4.16	
-146.3	6.2	5.37	Charging volts 20.3.
-143.2	7.15	6.18	
-137.2	9.15	7.97	
-132.2	13.9	12.1	
-128.6	16.2	14.1	Changing resistance in circuit from 91,500 to 1,500 ohms only altered deflection 1 mm.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
-124.2	20.8	18.1	Charging volts 1.434.
-119.2	1.77	21.8	
-113.0	2.2	27.1	
-110.2	2.5	30.7	
-106.5	3.7	45.8	
-98.8	5.05	62.5	
-92.3	5.8	71.7	
-91.7	6.65	82.5	
-87.8	8.2	101.5	
-83.7	8.59	105.0	
-80.8	8.7	107.5	
-76.4	8.83	109.0	
-71.5	8.85	109.2	
-69.0	8.78	108.5	
-65.6	8.7	109.2	
-61.0	6.62	106.8	
-57.7	8.53	105.5	
-53.9	8.45	104.5	
-50.3	8.33	103.4	
-46.2	8.28	102.4	
-40.7	8.18	101.0	

Beyond this last temperature (-40.7) the observations are not of much value. Sensible conductivity had begun to make its appearance, and the measurements no longer gave the true dielectric constant.

These results are plotted in a second curve in fig. 1, marked *distilled water*. It is clear that there is in this case a well marked maximum value for the dielectric constant at about -65° , and that above that temperature the dielectric constant falls again. We have already pointed out that in the case of the ice from ordinary distilled water, a very rapid increase of electric conductivity takes place at or about -90° , and the temperature somewhat precedes the temperature at which the dielectric constant is a maximum for the ice. Other observers who have studied the variation of the dielectric constant of water at temperatures above zero centigrade, agree that beyond a certain temperature the dielectric constant decreases with rise of temperature. Thus C. B. Thwing ('Zeitschrift für Physikalische Chemie,' vol. 14, 1894, p. 296) gives the following values for the dielectric constant for water using a rapidly oscillating electromotive force:—

Temperature, Centigrade.	Dielectric constant of water (Thwing).
0°	79·46
2	80·84
4	85·20
6	80·84
7	79·40
9	77·95
12	76·20
15	75·50
20	73·92
27	72·70
40	69·80
65	64·32
80	60·50
88	57·90

L. Drude ('Wied. Ann.,' vol. 59, pp. 17—68) using electric waves 74 cm. in wave-length, determined the electric refractive index of water for various temperatures. Also Heerwagen ('Wied. Ann.,' vol. 49, 1893, p. 278) made similar determinations, using, however, a slow speed method. The results of the two last observers are given for comparison in the following table:—

Temperature, Centigrade.	Dielectric constant of water.	
	(Drude.)	(Heerwagen.)
0·2°	87·3	86·96
4·1	86·02	85·55
7·9	84·49	84·17
11·6	83·41	82·83
11·9	81·20	80·90
25·8	77·99	77·70
37·9	73·44	72·67
45·4	71·28	70·60
49·8	70·01	69·00
54·8	68·60	67·21
59·7	67·17	66·02
66·0	66·02	63·14
70·1	64·83	61·66
72·8	63·68	60·66
76·3	62·82	59·41

Drude and Heerwagen do not agree with Thwing in making the dielectric constant of water a maximum at 4° C., but they all agree that an increase of temperature *decreases* the dielectric constant of water beyond that point. As we find an enormous decrease in the

constant in cooling ice from 0°C. to -185°C. , it follows that there is unquestionably *some temperature at which ice-water has a maximum value for its dielectric constant.* This temperature may, and probably does, vary with the presence of slight impurities in the water, and with the frequency of the electromotive force reversals.

On examining the curves for perfectly pure water and for ordinary distilled water, it will be seen that minute impurities, as well as change of frequency, evidently have a considerable effect upon the dielectric constant at any given temperature.

This was additionally shown as follows:—

Being desirous of trying the effect of varying the frequency of the contact breaker, two sets of experiments were made with the carefully purified distilled water, the condenser being reduced in temperature to -79°C. by the aid of solid carbonic acid and alcohol.

The following values were obtained:—

Dielectric Constant of Ice from Pure Distilled Water.

Frequency of contact maker 120. Charging volts 1.43.

Temperature in platinum degrees.	Dielectric constant.
—78.0	35.3
—75.1	40.7
—71.1	49.8
—66.5	55.0
—60.2	58.2
—50.7	63.8

It will be seen that the dielectric values are all higher than those given in the former table for the corresponding temperatures.

We are disposed to attribute the differences between the values obtained in the last set of observations and the first set to the fact that the water became slightly contaminated with alcohol during the process of freezing down the condenser in the carbonic acid and alcohol. This view was confirmed by the observations taken with a mixture of alcohol and water, which showed that such a mixture rises in dielectric value as temperature increases more rapidly than does the pure distilled water.

Similar observations were taken with a double frequency of 250 and a charging voltage of 1.434.

Temperature in platinum degrees.	Dielectric constant.
—71.8	61.0
—71.5	53.2
—69.8	57.4
—69.0	61.0
—68.7	61.4

These last two sets of observations are delineated in the short curves marked *water 250-* and *water 120-* given in Fig. 1.

The following observations were then taken with a mixture of water and ethyl alcohol.

Dielectric Constant of Alcohol and Water.

(39 per cent. alcohol.)

Frequency of contact maker 120. Deflection of galvanometer with air as dielectric of condenser = 3.44 cm. for 100 volts.

Temperature in platinum degrees.	Galvanometer deflection in centimetres.	Dielectric constant.	Observations.
-198.5	10.82	3.06	Charging voltage 100.
-145.0	25.00	36.6	
-140.2	2.07	41.8	Charging voltage 19.8. 1000 ohms in series with the galvanometer.
-133.7	2.27	46.0	
-128.2	2.35	47.7	
-125.2	2.52	51.2	
-122.0	2.67	54.1	
-117.3	2.80	56.7	

The dielectric constant is seen to rise with great rapidity very soon above the temperature of -190° . This is clearly connected with the temperature at which the alcoholic mixture becomes plastic previous to fusion.

We attempted to obtain the dielectric curve of pure ethylic alcohol, to compare it with that of water, but were stopped by the fact that at a temperature very little above -200° the ethylic alcohol, although still apparently in a solid condition, becomes possessed of such an amount of conductivity that our method is no longer able to give us the true dielectric constant.

In contrast to this we have taken the dielectric constant of pure glycerine (a triatomic alcohol), with the following results:—

Dielectric Constant of Glycerine.

Frequency of contact maker 120. Galvanometer deflection with air as dielectric in the condenser = 2.43 cm. for 100 volts.

Temperature in platinum degrees.	Galvanometer deflection in centimetres.	Dielectric constant.	Observations.
-198.2	8.4	3.21	Charging voltage 100.8
-138.2	8.84	3.40	
-122.0	9.27	3.56	
-100.8	11.80	4.62	

Temperature in platinum degrees.	Galvanometer deflection in centimetres.	Dielectric constant.	Observations.
-81.3	13.9	28.4	Charging voltage 20.0
-74.7	15.65	31.9	
-69.5	1.8	51.5	Charging voltage 1.43
-61.5	1.98	56.8	
-52.5	2.05	59.0	

The glycerine, like the other electrolytes examined, fell rapidly in resistance as the temperature rose, as shown in the following table:—

Resistance of Glycerine Condenser.

Temperature in platinum degrees.		Resistance of condenser in megohms.
-200	greater than	25,000
-129	about	25,000
-90	„	800
-44	„	9

It is seen that the glycerine acts as do all the other electrolytes so far examined, its resistance falls as its dielectric constant increases.

In order to examine and compare the behaviour of water and glycerine with some non-electrolytic dielectrics, we selected for examination nitrobenzol and ethylene dibromide. Of these bodies, one, viz., mononitrobenzol, has, at the ordinary temperature and in the liquid state, a somewhat high dielectric value. The following are the results for ethylene dibromide:—

Dielectric Constant of Ethylene Dibromide.

Frequency of contact maker 120. Galvanometer deflection with air as dielectric in the condenser = 3.26 cm. for 100 volts.

Temperature in platinum degrees.	Galvanometer deflection in centimetres.	Dielectric constant.	Observations.
-201.7	9.45	2.72	Charging voltage 100.8
-197.8	9.32	2.68	
-177.6	9.35	2.69	
-145.5	9.40	2.71	
-102.2	9.50	2.77	
-78.0	10.00	2.79	
-60.6	10.20	2.95	90,000 ohms cut out of
-48.0	10.25	2.97	galvanometer circuit,
-30.8	10.30	2.98	no change in deflection.

Ethylene dibromide, therefore, presents a remarkable contrast to water or glycerine. Its dielectric constant at ordinary temperature, 15°C. , has a value of about 5.

It falls, on freezing, to nearly 3, and it continues, as seen by the above table, nearly constant down to the lowest temperature reached, at which it becomes 2.7.

Its resistance also remains, when cooled down after freezing, exceedingly high and constant, the condenser resistance being over 10,000 megohms between -200° and -30° .

From a consideration of the values which have been found for the dielectric constants of various bodies, it appears that the presence in a molecule of certain radicles such as *hydroxyl* and *nitryl* always cause high values of the dielectric constant in the liquid state. Hence we have examined one well-known nitro-substitution compound, nitrobenzol, to determine how this value is altered by very low temperatures. The dielectric constant of mononitrobenzol is given by C. B. Thwing as 32.19, presumably at 15°C. Our values for its dielectric constant at low temperatures and when solidified are as follows:—

Dielectric Constant of Nitro-benzol.

Frequency of contact maker 120. Galvanometer deflection with air as dielectric in condenser = 4.15 cm. for 100 volts.

Temperature in platinum degrees.	Galvanometer deflection in centimetres.	Dielectric constant.	Observations.
-205.2	11.45	2.61	Charging voltage 101.0
-205.0	11.55	2.64	
-191.2	11.15	2.54	
-175.9	11.15	2.54	
-157.5	11.25	2.57	
-141.3	11.25	2.57	
-124.5	11.38	2.59	
-103.3	11.5	2.63	Charging voltage 20.0
-93.8	11.6	2.65	
-84.0	2.4	2.97	
-38.8	2.73	3.16	
-21.5	2.92	3.40	

The values of the dielectric constant of glycerine, ethylene dibromide, and nitrobenzol are plotted with some other substances as curves in fig. 2, and it will be seen that those of the ethylene dibromide and nitrobenzol values are practically constant over a wide range of temperature, and very nearly equal to that of ice at -200° .

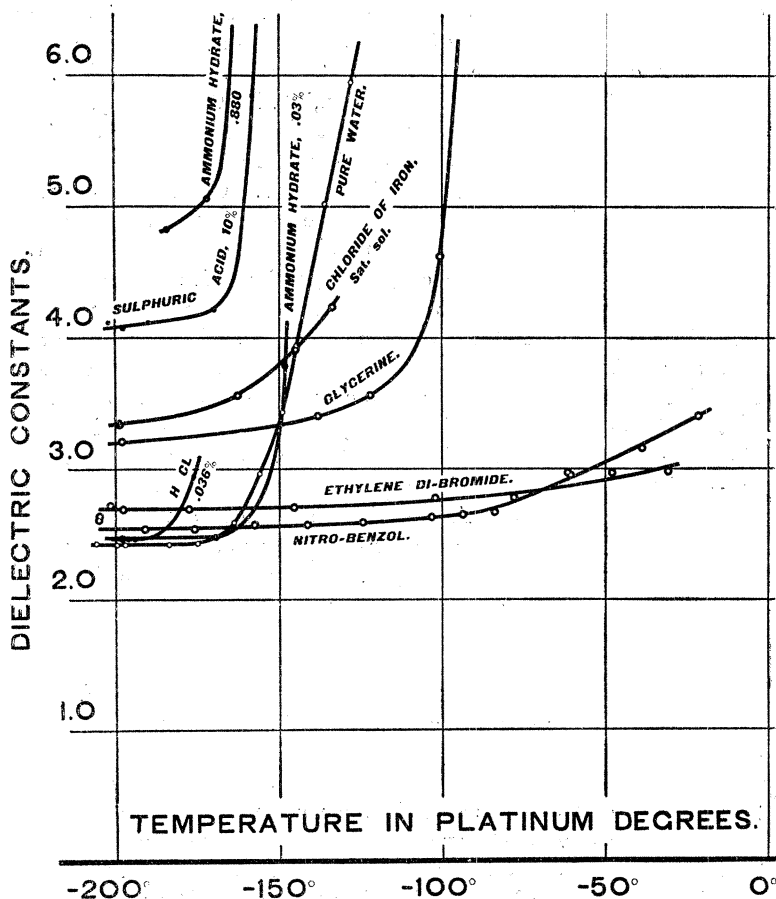


FIG. 2.—Curves showing the variation of dielectric constant of ethylene dibromide and nitro-benzol with temperature.

The dielectric constant of the mononitro-benzol value falls on solidifying at 3° C. from the high value of 32 to a low value of between 3 and 4 somewhat rapidly, and ultimately reaches 2.61 at -185° C.

In the case of these non-electrolytes, nitro-benzol and ethylene dibromide, the electrical resistance remains practically constant and exceedingly high during the rise of temperature from -200° upwards, being thus in contrast with the behaviour of the frozen electrolytes which, as shown, rise up very rapidly in conductivity at a certain temperature.

It should also be noted with regard to glycerine that other

observers who have examined the dielectric constant of this substance at temperatures above 0° C. have found for glycerine a negative coefficient of temperature variation. Thus W. Cassie ('Roy. Soc. Proc.,' vol. 46, 1889; also 'Phil. Trans.,' A, 1890, vol. 181) finds for glycerine between 18° C. and 41° C., a negative temperature coefficient equal to -0.006 . Hence within this range, increase of temperature decreases the dielectric constant of glycerine. C. B. Thwing ('Zeit. für Phys. Chem.,' vol. 14, p. 293) gives the value 56.2 for the dielectric constant of glycerine at ordinary temperatures. Since at low temperatures we find a positive coefficient, and much smaller values, it is clear that glycerine, like water, must have a maximum value for its dielectric constant at a certain temperature. It is very important that this point should be examined more fully. Up to the present time electrical theory has offered no complete explanation of how it is that change of temperature has such profound effect in modifying the dielectric quality of certain kinds of matter. Ice, for instance, taken at -200° has about 2.4 times the dielectric power of the electromagnetic medium alone. At -60° from 50 to 100 times the power. At the absolute zero of temperature perhaps about twice the power. On the other hand, we may carry such a body as ethylene dibromide over the same range of temperature, without making any very sensible change in the degree to which the substance affects the electrical qualities of the space in which it exists.

It is evidently, however, very closely a chemical question. Comparing the variation of many other physical qualities, such as density, refractive index, thermal conductivity, &c., with dielectric constants, we see that the variations which occur in the latter by changes of temperature and changes of substance are much more akin to the wide differences which occur between bodies in chemical activity. The presence of certain chemical radicles, such as OH, CO, COH, NO₂, has been shown by C. B. Thwing ('Zeit. für Phys. Chem.,' vol. 14) to be a most potent factor in determining high values for the dielectric constant at ordinary temperature, but the remarkable behaviour of an aqueous 5 per cent. solution of caustic potash has shown us that questions of concentration and the nature of the solvent have to be considered as well, whilst the behaviour of all electrolytes at the very low temperature indicates that decrease in temperature destroys the influence of the radicle in this respect.

One of the most interesting points is the evidence which now exists that water, glycerine, ethyl alcohol, and no doubt many other bodies, have a maximum value for their dielectric constants at certain temperatures.

Thus W. Cassie ('Phil. Trans.,' A., 1890, vol. 181, p. 16) has shown that the curves representing the variation of the dielectric constant of glycerine, carbon disulphide, olive oil, benzol and tur-

pentine all have such a direction as to show that their dielectric constants *decrease* with rise of temperature between $+10^{\circ}$ C. and $+80^{\circ}$ C. We find that the constant for glycerine *increases* from -185° C. to -100° C., and hence it follows that it has a maximum value for a certain temperature.

This fact makes it necessary to be very cautious in drawing conclusions as to the complete form of the dielectric curve from observations made over a limited range of temperature. A somewhat hasty generalisation of this kind has been made by R. Abegg (see Wiedemann's 'Annalen,' 1897, No. 1, p. 59). He measured by Nernst's method the dielectric constants of water, alcohol, and other bodies from $+10^{\circ}$ C. down to -80° C. with such results as follows:—

Water.

Temperature.	Dielectric constant (Abegg).
$+10\cdot0^{\circ}$	83·8
$+20\cdot0$	101·0
$-40\cdot0$	112·0
$-60\cdot0$	127·0
$-80\cdot0$	137·0

Ethyl Alcohol.

$+14\cdot0$	26·4
$-33\cdot0$	33·9
$-61\cdot6$	38·8
$-86\cdot6$	44·3

He concludes that the dielectric constant of water would be 372 at the absolute zero of temperature, and that of alcohol would be 80 at -196° . As a matter of fact, both these constants have a value not far removed from 3·0 at the temperature of liquid air, and it is highly improbable that they increase again on further cooling.

Thus at 15° C. and at -185° C. we have the following dielectric constants for four definite compounds containing molecular groups OH and NO_2 .

	Dielectric constants.	
	At 15° C.	At -185° C.
Water, $\text{H}(\text{OH})$	80	2·4 to 2·9
Ethyl alcohol, $\text{C}_2\text{H}_5(\text{OH})$	25	3·1
Glycerine, $\text{C}_2\text{H}_3(\text{OH})_3$	56	3·2
Mononitrobenzol, $\text{C}_6\text{H}_5(\text{NO}_2)$	32	2·6

It remains to be seen whether in all cases cooling to very low temperatures destroys the power of these radicles to bestow high dielectric values on compounds containing them when at temperatures near or above their melting points.

In conclusion, we have again to thank Mr. Petavel for valuable help in taking the above described observations, and reducing the results.

Note added June 1.

In their paper "On Capacity and Residual Charge of Dielectrics as affected by Temperature and Time,"* Dr. J. Hopkinson and Mr. Wilson give measurements of the dielectric constant of glycerine for high and low frequencies at ordinary temperatures. The value they obtain is 60 for high frequency and 50 to 60 for low frequency. They also say that glycerine has no residual charge. We obtain an almost identical value for a frequency of 120 at -50° , but below that temperature the dielectric curve of glycerine, we find, runs almost parallel to that of ice. It is difficult to understand why residual charge (which in ice, the above-named authors say, is considerable) should be the cause of high dielectric value at ordinary temperatures in the case of one substance and not in the case of the other.

"The Sensitiveness of the Retina to Light and Colour." By Captain W. DE W. ABNEY, C.B., D.C.L., F.R.S. Received May 10,—Read June 3, 1897.

(Abstract.)

The author treats first of the extinction of the sensation of light on the centre of the retina. He made his reduction of the intensity of the light falling on the illuminated spot with a new piece of apparatus, which consisted of a gelatine wedge bent so as to make an annulus. He describes this wedge and its graduation, showing how its readings can be utilised, they being proportional to the logarithm of the intensity of light passing through it.

It is found that the smaller the spot of illuminated surface the less reduction in intensity of the light is required, and that the amount of reduction of the light falling on the spot which just produces no sensation of light is connected with the size of the spot by a simple formula, $I = x^m$, where I is the intensity and x the diameter of the spot. Further, he finds that it is the smallest diameter which governs the necessary reduction in intensity and not the area of the

* 'Phil. Trans.,' A, vol. 189, 1897, p. 134.