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Summary.

The amount of light given by the unstriated discharge and by the arc indicates that the rate at which ions recombine in these forms of discharge varies as the first power of the current, while the equations usually assumed for discharge through gases would lead us to expect that this rate varies as the square of the current. This is explained by assuming that approximately all of the current is carried by electrons and not by ions of molecular size, and that the great majority of the electrons combine first with molecules and afterwards with positive ions.

The fact that the electric force in this form of discharge is a linear function of the pressure of the gas is explained by assuming that the ionization is caused by the impact of the more rapidly moving electrons on the molecules, and that but few of the collisions between electrons and molecules result either in ionization or in recombination, the greater number resulting in no permanent change in either electrons or molecules.

The fact that the electric force decreases slightly when the current is increased, is explained by the added assumption that the potential difference through which an electron must go in order to ionize is smaller with larger currents than with small ones.

Colgate University,
October, 1913.

XXXII. *On the Relationship between the Viscosity, Density, and Temperature of Salt Solutions.* By W. J. WALKER, B.Sc., Carnegie Research Scholar, University College, Dundee*.

[Plate IV.]

THE following notes are derived from the results of experiments carried out at the suggestion of Professor A. H. Gibson in connexion with tests on the resistance to flow of brine solutions through pipes of different diameters. The solutions were of sodium chloride and calcium chloride. The primary object of the experiments was the determination of "the kinematic coefficient of viscosity," or the ratio viscosity/density. Absolute values of the viscosity were obtained by means of the apparatus shown in fig. 1.

Reservoir A was used to maintain a constant head of about

* Communicated by the Author.

18 cm. in vessel B. Discharge from the latter vessel took place through a glass tube C of small bore and 71.5 cm. in length. After the completion of the experiments, the diameter of the tube was ascertained by breaking it up into

Fig. 1.

pieces varying from 2 cm. to 3 cm. in length and measuring the diameters by means of a microscope furnished with micrometer eyepieces. The mean of these results gave .2590 cm. as the tube diameter. In calculating the viscosities the value $\frac{1.5V^2}{2g}$ was subtracted from the measured head.

The relationship between the percentage of salt in the solution and its density was measured by means of a Mohr specific gravity balance, with the following results in the case of sodium chloride :—

Temperature=60° F.	
Percentage Solution.	Specific Gravity.
0	1.000
6	1.042
12	1.088
18	1.134
24	1.165
28	1.198

NOTE.—Percentages reckoned as parts of salt in 100 parts of solution.

From these figures it appears that the specific gravity increases uniformly with the percentage of salt in the solution until this attains a value of about 20 per cent. After this point the rate of increase in specific gravity diminishes. This is probably due to the fact in the stronger brines, solution was not complete but that some of the material was held in suspension.

As a check on the accuracy of the viscosity apparatus, this was used to determine the viscosity of water at 62°·3 F. The mean value obtained was ·00002265 in F.P.S. units as against Poiseuille's value of ·0000227. This result gives an assurance that experiments have been carried out with a fair degree of accuracy. The results of one series of experiments on each solution are given below, the sodium chloride series being carried out at a temperature of 62°·5 F. and the calcium chloride series at a temperature of 63° F. An empirical formula was deduced for the sodium chloride series before the calcium chloride series was carried out and is given here:

$$\mu = \cdot 00002265 + \cdot 0000428(\rho - 1) + \cdot 000228(\rho - 1)^2.$$

This gives in F.P.S. units results practically identical with experimental values.

Sodium Chloride 62°·5 F.			Calcium Chloride 63° F.		
ρ .	μ .	$\frac{\mu}{\rho}$	ρ .	μ .	$\frac{\mu}{\rho}$
1·000	·00002265	1·000	1·000	·00002248	·993
1·008	·00002300	1·009	1·0188	·00002358	1·022
1·015	·00002335	1·016	1·054	·00002586	1·083
1·025	·00002380	1·025	1·063	·00002660	1·106
1·037	·00002445	1·041	1·084	·00002855	1·163
1·058	·00002548	1·063	1·1029	·00003020	1·210
1·065	·00002580	1·071	1·115	·00003170	1·256
1·078	·00002685	1·100	1·130	·00003318	1·295
1·095	·00002790	1·126	1·149	·00003555	1·365
1·115	·00003035	1·165	1·165	·00003800	1·425
1·142	·00003250	1·255	1·184	·00004180	1·523
1·170	·00003655	1·378	1·2078	·00005060	1·850

NOTE.— $\frac{\mu}{\rho}$ is here taken relative to water at 62°·5 F.

The curves for these solutions showing the relation between viscosity and density are given in fig. 2 (Pl. IV.).

It was intended at first to deduce an empirical formula for

the calcium chloride series, but on plotting the curves as shown, their appearance suggested an inquiry which led to the following interesting discovery of a relation between viscosity and density which does not appear hitherto to have been noticed.

In the Phil. Mag.* Ramsay and Young published a law connecting temperatures at which different saturated vapours have the same vapour pressure. Porter, in the same magazine †, showed that if $\frac{T}{T_0}$ be plotted against T where T and T_0 are temperatures of two liquids having the same vapour pressure or the same viscosity at these temperatures, then a straight line will be obtained. From this he deduced that Ramsay and Young's law is accurately true if

$$f(p) = A - \frac{B}{T}$$

or $F(\mu) = a - \frac{b}{T}.$

Porter showed the latter law to hold for two such dissimilar substances as mercury and water. Now in the cases given of sodium and calcium chloride it was found that if $\frac{\mu}{\mu_0}$ be plotted against μ where μ and μ_0 are viscosities at similar densities, an approximate straight line was obtained, indicating the relationship

$$F(\rho) = A - \frac{B}{\mu} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In order to eliminate one of these constants this was thrown into the form

$$F'(\rho-1) = A - \frac{B}{\mu} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

When $\rho=1$ we get $B = \mu'A,$

where μ' is the viscosity of water at temperature considered. (2) then becomes

$$F'(\rho-1) = A \left(1 - \frac{\mu'}{\mu} \right).$$

* Jan. 1886.

† June 1907 and June 1912.

Tentatively, it was found that $F'(\rho-1)$ was of the form $(\rho-1)^n$ where " n " lay between 1 and 2 for both solutions.

On plotting $\log(\rho-1)$ against $\log\left(1 - \frac{\mu'}{\mu}\right)$ practically straight lines are obtained in each case, as shown in fig. 3.

The values for " n " for these two lines as drawn are 1.038 and 1.055 for sodium and calcium chloride respectively.

In the Smithsonian Tables (1908) figures are given showing the relation between viscosity and density at temperatures 10° , 30° , and 50° C. for sodium and calcium chloride solutions. It was thought desirable to find how " n " and " A " varied with temperature, so experiments were carried out at temperatures ranging from 0° to 100° C. on the sodium chloride solutions. The intermediate figures agreed well with the Smithsonian figures, except that at 30° C. the Smithsonian figures were slightly higher. In the case of the calcium solutions the experiments were only carried out at the lowest temperature. The apparatus was the same as used by Reynolds* in his viscosity experiments and is shown in fig. 4. Its reliability was proved by the good results it gave

Fig. 4.

for water. The low temperatures in the experiments were obtained by means of a freezing-mixture of ice and sodium chloride. At the same time figures were obtained to show the variation of density with temperature of several solutions of different strengths. These figures are not given, but they were used to obtain for sodium chloride the curves shown in

* Scientific Papers, vol. ii. p. 239.

figs. 5 & 6 (Pl. IV.), giving the relation between viscosity and temperature, and viscosity and density. The three upper curves in fig. 5 were for solutions of densities 1.188, 1.146, and 1.101 at a temperature of 18° C. The lowest curve is for water. In fig. 6 the curves shown are for temperatures 0°, 10°, 30°, 50°, and 100° C. Figs. 7 and 8 give the same curves for calcium chloride. Straight lines were obtained for the logarithmic values plotted as in fig. 3 for each of the above temperatures. The values of “*n*” for sodium chloride were found to be, when

T = 0° C.,	<i>n</i> = 1.48,
T = 10°,	<i>n</i> = 1.35,
T = 30°,	<i>n</i> = 1.10,
T = 50°,	<i>n</i> = 1.09,
T = 100°,	<i>n</i> = 1.075.

From these figures it appears that “*n*” decreases proportionally to temperature from 0° to 30° C, but from there the relative diminution becomes much less up to 100° C. Values of μ were calculated from these values of *n* and were found to agree exceedingly well with the experimental values. It was desirable, however, to have a formula which would involve the three quantities μ , ρ , and T. The above values of “*n*” do not provide this, but it was found that, on assuming “*n*” to vary regularly in values from 1.4 to 1.0 between the limits 0° and 100° C., a quite accurate formula was obtained in the form

$$(\rho - 1)^{1.4 - .004T} = A \left(1 - \frac{\mu'}{\mu} \right).$$

The same procedure was gone through with the calcium chloride results. The values of “*n*” here varied regularly from .95 to .85 as the temperature varied from 0° to 50° C. This gives as the best formula between these limits

$$(\rho - 1)^{.95 - .002T} = A \left(1 - \frac{\mu'}{\mu} \right).$$

To obtain the value of A it is best to use the point at which the solution has its highest density. Otherwise, if A be obtained from a low density point the liability to error in calculating the viscosities at higher densities is appreciable.

The variation of A with T was next noticed. The figures below give the actual values in each case for log. A.

Sodium Chloride.

Actual values.

At	0° C.		—·6795
	10°		—·6455
	30°		—·5670
	50°		—·4924
	100°		—·3016

Calcium Chloride.

Actual values.

At	0° C.		—·3583
	10°		—·3511
	30°		—·3449
	50°		—·3333

By readjusting these values so that $\log A$ may be regarded as a linear function of T , formulæ were obtained for each of the solutions which gave a fairly accurate relation between ρ , μ , and T . The readjusted values are:—

Sodium Chloride.

Readjusted values.

At	0° C.		—·6790	} $\log A = -\cdot6790$ +·00374 T .
	10°		—·6416	
	30°		—·5716	
	50°		—·4920	
	100°		—·3050	

Calcium Chloride.

Readjusted values.

At	0° C.		—·3580	} $\log A = -\cdot3580$ +·0005 T .
	10°		—·3530	
	30°		—·3430	
	50°		—·3330	

The tables below give a comparison between the experimental and calculated values of μ , according to the given formulæ

I. $(\rho-1)^{1.4-.004 T} = A\left(1-\frac{\mu'}{\mu}\right)$ for sodium chloride.

II. $(\rho-1)^{.95-.002 T} = A\left(1-\frac{\mu'}{\mu}\right)$ for calcium chloride.

I. Sodium Chloride.

T = 0°. $n = 1.4.$			T = 10°. $n = 1.36.$			T = 30°. $n = 1.28.$		
$\rho.$	$\mu_e.$	$\mu_c.$	$\rho.$	$\mu_e.$	$\mu_c.$	$\rho.$	$\mu_e.$	$\mu_c.$
1.19	187.0	187.0	1.18	128.5	127.6	1.172	74.5	73.8
1.15	150.0	150.5	1.15	111.0	110.3	1.15	68.0	67.1
1.10	122.0	123.3	1.10	91.5	91.3	1.10	57.0	56.2
1.05	107.0	107.6	1.05	79.1	79.2	1.05	50.0	48.9

T = 50°. $n = 1.2.$			T = 100°. $n = 1.0.$		
$\rho.$	$\mu_e.$	$\mu_c.$	$\rho.$	$\mu_e.$	$\mu_c.$
1.16	47.8	47.5	1.15	21.5	21.5
1.15	45.0	45.0	1.10	18.7	18.75
1.10	37.9	38.4	1.05	16.6	16.65
1.05	34.0	34.0			

II. Calcium Chloride.

T = 0°. $n = .95.$			T = 10°. $n = .93.$		
$\rho.$	$\mu_e.$	$\mu_c.$	$\rho.$	$\mu_e.$	$\mu_c.$
1.277	310.0	308.0	1.30	273.0	277
1.200	200.0	198.0	1.20	145.5	148.0
1.10	136.0	134.5	1.10	99.0	99.8
1.05	116.0	115.5	1.05	84.0	85.2
T = 30°. $n = .89.$			T = 50°. $n = .85.$		
1.293	177.0	172.5	1.30	137.0	137.0
1.20	96.4	94.8	1.20	69.0	68.7
1.10	63.0	62.8	1.10	45.0	44.7
1.05	53.0	53.2	1.05	37.5	37.4

Here μ_e = experimental value of μ . μ_c = calculated value of μ .

From these tables it appears that the greatest difference between experimental and calculated values occurs at about 30° C., but the differences (a little over 2 per cent. being the greatest) are not great when one considers the experimental difficulties involved in the measurement of viscosity.

Several other figures for different salts were taken from the Smithsonian Tables and the log. graphs plotted, and in no case was there any great deviation from the straight line. Unfortunately, however, in the majority of cases only three points are obtainable from the given figures, so that the comparison with these other solutions is not so rigid as is desirable. Again, some of the solutions actually diminish in viscosity as salt is added until a certain minimum viscosity is attained, after which the viscosity increases regularly with an increase of density as in the majority of solutions. One of the most noteworthy examples of this behaviour is found in ammonium nitrate, the density-viscosity curve of which is shown in fig. 9 (Pl. IV.). It might be thought that such a case would form a departure from the above law. It is found, however, that on giving the formula the form

$$\pm(\rho - x)^n = A \left(1 - \frac{\mu'}{\mu}\right),$$

where μ' is the minimum viscosity, and where the negative sign is used when x is greater than ρ , x being the density at the minimum viscosity point, then the law does hold very approximately. Five points are given in the case of ammonium nitrate, and on plotting the log. graph for these, they were found to lie very sensibly on a straight line as shown in fig. 10. The same thing is shown in fig. 10 for manganese chloride for which four points are given in the tables, the log. graph of these also being practically a straight line. Manganese chloride, however, does not have a minimum viscosity point but behaves like the majority of salts.

The reason for the difference in the value of " n " for sodium chloride as found in the two experiments* lies, of course, in the different conditions under which these were carried out, the solutions in the first set of experiments being unfiltered.

If this law holds generally for all salt solutions, as seems probable, the best method of obtaining the formula for each salt would be to make three accurate determinations (at the same temperature) of the viscosity and density at points as far apart as possible and deduce the value of " $\log A$ " and

* Pp. 292 & 293.

" n " therefrom. This may be repeated for say another two temperatures, and thus the variation of " $\log A$ " and " n " with temperature can be ascertained. The formula may then be completed.

One reason for the diminution of " n " with temperature may be stated as follows. At the higher temperatures the fluidity of the solvent is increased. Now the behaviour of the solute is found to be in many ways analogous to that of a gas. This analogy would apparently become more pronounced the higher the temperature, *i. e.* the greater the fluidity of the solvent, for then the particles of solute could move about with greater freedom. The viscosity of a gas is known to be independent of density, and on glancing at figs. 6 and 8 we see that the higher the temperature the less pronounced becomes the increase of viscosity due to the increase of density. This is specially evident in the case of sodium chloride at 100° C.

It may be of interest to note here that the same method of plotting was used to determine if $F(\mu)$ in the formula

$$F(\mu) = a - \frac{b}{T}$$

was of the form $(\mu)^n$ in the cases of water and mercury. It was found not to be so, so that some other form must be ascribed to this function in the case of these two substances at least.

In conclusion, I desire to express my thanks to Professor Gibson for the encouragement he gave me during the course of the work.

XXXIII. *The Electrification at Liquid-Gas Surfaces.* By H. A. McTAGGART, M.A. Toronto; Research Student of Gonville and Caius College, Cambridge*.

WHEN a liquid in the form of drops falls through a gas and splashes against an obstacle it is found to be electrified. At the same time the gas acquires a charge of the opposite sign. This charge found on the liquid varies with the liquid, the gas through which it falls, the nature of the obstacle on which it strikes, and the force of the impact. To account for this electrification it is usually supposed that at the surface of separation between the liquid and the gas, a double layer is formed, the two surfaces of which are

* Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S.

Fig. 2.

Fig. 3.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.