DETERMINATION OF N_e FOR HYDROGEN FROM MEASUREMENTS OF BROWNIAN MOVEMENTS.

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INTRODUCTION.

VALUES of N_e for gaseous ionization have been determined by Townsend,¹ Franck and Westphal,² Fletcher, and others. By means of the measurement of the Brownian movements of a small oil drop, Fletcher³ in 1911 made a direct determination of N_e for ionized air, and more recently⁴ determined by the same method the value of the Avogadro constant N for air. Working with the same apparatus the writer attempted a determination of N for hydrogen, but obtained results which seem to indicate that the ak factor of the law of fall for hydrogen is different from that obtained by Millikan⁵ for air. The determination of N_e was then undertaken since it does not involve the factor ak . The present article extends the Brownian movement method of Fletcher to the study of hydrogen with the view of testing the method in the case of gases other than air, and of determining directly the value of N_e for hydrogen.

§ I. EQUATIONS USED, APPARATUS, AND METHOD OF PROCEDURE.

The formula deduced by Fletcher⁶ for the Avogadro constant N is

$$(1) \quad N = \frac{RTz^2}{6\pi\mu akV_g^2t_g},$$

where R is the gas constant, T the absolute temperature, a the radius of the oil drop, μ the coefficient of viscosity of the gas through which it moves, t_g its time of fall under gravity, V_g its average velocity of fall, k a factor of the law of fall that depends on the radius of the drop and the mean free path of the gaseous molecules, and z a term, defined by equation (4) below, that comes from the solution of the integral that involves the Brownian movements of the oil drop.

¹ Proc. Roy. Soc., A, Vol. LXXX., p. 209, 1908.

² Verh. D. Phys. Ges., Juli 2, 1909.

³ PHYS. REV., Vol. XXXIII., No. 2, Aug., 1911.

⁴ PHYS. REV., Vol. IV., s. series, No. 5, Nov., 1914.

⁵ PHYS. REV., Vol. I., s. series, p. 219, 1913.

⁶ PHYS. REV., Vol. IV., s. series, No. 5, p. 442, Nov., 1914.

The motion of a sphere of charge e in an electrostatic field of intensity X is determined by

$$(2) \quad Xe = 6\pi\mu ak \frac{V_1 + V_2}{2},$$

where V_1 is the velocity of fall and V_2 the velocity of rise against gravity.

Combining equations (1) and (2), the equation used for the determination of N_e is

$$(3) \quad Ne = \frac{RTz^2}{V_g^2 t_g X} \cdot \frac{V_1 + V_2}{2}.$$

All the quantities of the right hand member of this equation can be measured by experiment.

The apparatus, consisting of the lighting system, the observing system, the timing system, and the vessel containing hydrogen and suspended oil drops, is that described in detail by Fletcher,¹ with the addition of a hydrogen generating system and a slightly modified arrangement for blowing the oil drops. The hydrogen was generated from good chemicals, and was passed through potassium permanganate solution to remove impurities, and concentrated sulphuric acid and calcium chloride to remove moisture. The vessel was filled with hydrogen to the desired pressure, and the oil drops were blown by hydrogen from the atomizer into the vessel and between the condenser plates. Every precaution was taken to keep air from the chamber.

The method used to determine the quantities given in equation (3) by use of this apparatus has been described in detail by Fletcher,² and consists first of observing the Brownian movements of a very small oil drop (liquid vaseline) as it falls under the influence of gravity between two uncharged condenser plates, and then of observing its time of fall and rise under an electrostatic field of known intensity. The drop responds to the electric field when it contains one or more charges which it has caught from the ionized hydrogen. The ionization is produced by X-rays.

A scale of fifty divisions of known length is mounted in the eye piece of the observing telescope, and in observing the Brownian movements, the time is recorded as the drop crosses each division. When the full scale has been covered, the drop is raised by means of the electrostatic field, and observations are again taken. By a repetition of this process, as many as 1,666 observations were taken for a single drop (Table III., below). The average of all these times of fall is taken as t_g , and V_g is obtained from t_g and the length of the scale division b . The factor z of equation (3) is defined by the equation

¹ *L. c.*, p. 443.

² *L. c.*, p. 446.

$$(4) \quad z = \frac{2t_g}{\sqrt{\pi\tau}} \left(1 + \frac{1}{2z^2} + \frac{1}{4z^4} + \frac{3}{8z^6} + \cdots \right),$$

where

$$\tau = \frac{t_a^+ - \bar{t}_a^-}{2},$$

t_a^+ being the average of all times of fall greater than t_g , and $\bar{t}_a^-$ being the average of all times of fall less than t_g .¹ The factor z which thus involves the Brownian movements of the oil drop, can be calculated to any desired degree of accuracy from equation (4).

The gas constant R is taken as 83.15×10^6 . The electrostatic field X is determined by finding the difference of potential between the condenser plates by a Kelvin multicellular electrometer. The plate distance is 1.605 cm.

§ II. THE DATA.

The tables contain the average values which were computed from the observations on seven drops. Over 10,000 observations of the Brownian movements were made under good experimental conditions. Part I. of the tables contains the velocities of the drop in the electrostatic field. The quantities $V_1', V_1'', V_1''', \dots; V_2', V_2'', V_2''', \dots$ are the velocities of fall and rise respectively in the electrostatic field when the drop has 1, 2, 3, etc., charges. The values $V_1^{(n)} + V_2^{(n)}$, from which n is clearly determined, are divided by n to reduce to the condition of a single charge, and the average of all such values is used in equation (3). In Part II. of the tables, column 1 gives the constant distance over which time of fall under gravity was taken, column 8 gives the value of Ne calculated from equation 3, column 9 gives the number of observations, and the other columns give the average values computed from the Brownian movements of the drop.

TABLE I.

Drop 1.								
Temperature 21.1° C.				Pressure 30.12 cm.				
Part I.								
Volts = 993.1.			$V_1' = .0378.$		$V_1' + V_2' = .0678$ per charge.			
$X = 2.062.$			$V_2' = .0300.$					
Part II.								
b	t_g	V_g	t_a	$\bar{t}_a$	τ	z	Ne	No. Obs.
.00922	2.079	.00444	2.552	1.693	.429	5.46	2.99×10^{14}	235
.01844	4.158	.00444	4.785	3.529	.628	7.46	2.79×10^{14}	167

¹ See Fletcher, *l. c.*, p. 441, for the values of t_a^+ and $\bar{t}_a^-$ as deduced from the Brownian movement theory.

TABLE II.

<i>Temperature 20.8° C.</i>		<i>Drop 2.</i>	<i>Pressure 30.39 cm.</i>
Part I.			
Volts = 290.6.	$V_1'' = .0232.$	$V_1'' + V_2'' = .0361.$	
$X = .604.$	$V_2'' = .0129.$	$\therefore V_1' + V_2' = .0180$ per charge	
Part II.			

δ	t_g	V_g	$\bar{t}_a$	$\bar{l}_a$	τ	z	Ne	No. Obs.
.00922	1.863	.00495	2.220	1.531	.344	6.18	3.05×10^{14}	1019
.01844	3.724	.00495	4.240	3.284	.478	8.83	3.08×10^{14}	509
.02766	5.586	.00495	6.196	5.011	.592	10.70	3.05×10^{14}	337
.03688	7.448	.00495	8.191	6.790	.700	12.04	2.91×10^{14}	254

TABLE III.

<i>Temperature 20.5° C.</i>		<i>Drop 3.</i>	<i>Pressure 16.41 cm.</i>
Part I.			
Volts = 1,414.7.		$V_1'' = .0832.$	$V_1' = .0449.$
$X = 2.938.$		$V_2'' = .0718.$	$V_2' = .0329.$
	$V_1'' + V_2'' = .1551.$		$V_1' + V_2' = .0778.$
	$\therefore V_1' + V_2' = .0777$ per charge.		

δ	t_g	V_g	$\bar{t}_a$	$\bar{l}_a$	τ	z	Ne	No. Obs.
.0118	1.963	.00601	2.254	1.672	.278	8.04	2.94×10^{14}	1666
.0236	3.926	.00601	4.370	3.542	.414	10.78	2.65×10^{14}	831
.0354	5.889	.00601	6.372	5.393	.489	13.66	2.84×10^{14}	550
.0472	7.852	.00601	8.389	7.277	.556	16.00	2.92×10^{14}	410
.0590	9.815	.00601	10.479	9.227	.626	17.85	2.91×10^{14}	315

TABLE IV.

<i>Temperature 21.0° C.</i>		<i>Drop 4.</i>		<i>Pressure 52.39 cm.</i>	
Part I.					
Volts = 1,074.1.	$V_1' = .0165.$	$V_1'' = .0308.$	$V_1''' = .0447.$		
$X = 1.233.$	$V_2' = .0113.$	$V_2'' = .0251.$	$V_2''' = .0396.$		
	$V_1' + V_2' = .0278.$	$V_1'' + V_2'' = .0559.$	$V_1''' + V_2''' = .0843.$		
		$V_{1IV} = .0575.$			
		$V_{2IV} = .0527.$			
		$V_{1IV} + V_{2IV} = .1102.$			
		$V_1' + V_2' = .0278$ av. per charge.			

δ	t_g	V_g	$\bar{t}_a$	$\bar{l}_a$	τ	z	Ne	No. Obs.
.00937	3.640	.00254	4.320	3.069	.625	6.65	2.87×10^{14}	846
.01874	7.280	.00254	8.180	6.477	.851	9.85	3.15×10^{14}	421
.02811	10.920	.00254	12.024	9.913	1.055	11.75	2.99×10^{14}	278

TABLE V.

Drop 5.

Temperature 21.2° C. Pressure 52.78 cm.

Part I.

Volts = 1,044.8. $V_1' = .0138.$ $V_1''' = .0337.$ $V_1^{IV} = .0422.$
 $X = 2.170.$ $V_2' = .0060.$ $V_2''' = .0257.$ $V_2^{IV} = .0346.$
 $V_1' + V_2' = .0198.$ $V_1''' + V_2''' = .0594.$ $V_1^{IV} + V_2^{IV} = .0768.$
 $V_1^V = .0537.$ $V_1^{VII} = .0734.$
 $V_2^V = .0462.$ $V_2^{VII} = .0651.$
 $V_1^V + V_2^V = .0999.$ $V_1^{VII} + V_2^{VII} = .1385.$
 $V_1' + V_2' = .0198$ av. per charge.

Part II.

b	t_g	V_g	$\bar{t}_a^+$	$\bar{t}_a^-$	τ	z	Ne	No. Obs.
.01874	4.770	.00393	5.198	4.335	.431	12.54	2.39×10^{14}	551
.03748	9.540	.00393	10.068	8.993	.537	19.90	3.01×10^{14}	276
.05622	14.310	.00393	15.076	13.631	.722	22.40	2.54×10^{14}	178

TABLE VI.

Drop 6.

Temperature 20.8° C. Pressure 55.30 cm.

Part I.

Volts = 1,118.1. $V_1' = .0243.$ $V_1'' = .0440.$ $V_1''' = .0625.$
 $X = 2.320.$ $V_2' = .0140.$ $V_2'' = .0337.$ $V_2''' = .0526.$
 $V_1' + V_2' = .0383.$ $V_1'' + V_2'' = .0777.$ $V_1''' + V_2''' = .1153.$
 $\therefore V_1' + V_2' = .0385$ av. per charge, and $\frac{V_1' + V_2'}{X} = .0166.$

Volts = 1,123.8. $V_1' = .0233.$ $V_1'' = .0426.$ $V_1''' = .0611.$
 $X = 2.338.$ $V_2' = .0154.$ $V_2'' = .0345.$ $V_2''' = .0543.$
 $V_1' + V_2' = .0387.$ $V_1'' + V_2'' = .0781.$ $V_1''' + V_2''' = .1154.$
 $\therefore V_1' + V_2' = .0388$ av. per charge and $\frac{V_1 + V_2}{X} = .0166.$

$\therefore \frac{V_1 + V_2}{X} = .0166$ av.

Part II.

b	t_g	V_g	$\bar{t}_a^+$	$\bar{t}_a^-$	τ	z	Ne	No. Obs.
.01674	4.679	.0040	5.191	4.155	.518	10.27	2.83×10^{14}	446
.03748	9.358	.0040	10.145	8.667	.739	14.33	2.75×10^{14}	221

TABLE VII.

Drop 7.

Temperature 20.8° C. Pressure 55.30 cm.

Part I.

Volts = 1,123.8. $V_1' = .0233.$ $V_1'' = .0426.$ $V_1''' = .0611.$
 $X = 2.338.$ $V_2' = .0154.$ $V_2'' = .0345.$ $V_2''' = .0543.$
 $V_1' + V_2' = .0387.$ $V_1'' + V_2'' = .0781.$ $V_1''' + V_2''' = .1154.$
 $V_1' + V_2' = .0388$ av. per charge. $\frac{V_1' + V_2'}{X} = .0166.$

$$\begin{aligned}
 \text{Volts} &= 1,121.4. & V_1'' &= .0421. & V_1'' + V_2'' &= .0773. \\
 X &= 2.330. & V_2'' &= .0352. & V_1' + V_2' &= .0386 \text{ per charge.} \\
 & & \frac{V_1 + V_2}{X} &= .01658. & \therefore \frac{V_1 + V_2}{X} &= .01659 \text{ av.}
 \end{aligned}$$

Part II.

b	t_g	V_g	$\frac{+}{t_a}$	$\bar{t}_a$	τ	$\mathcal{B}$	Ne	No. Obs.
.01874	5.143	.00365	5.762	4.570	.596	9.78	2.83×10^{14}	379
.03748	10.286	.00365	11.156	9.475	.840	13.88	2.85×10^{14}	188

TABLE VIII.

A Summary of the Values of Ne and the Corresponding Number of Observations.

Drop.	Ne $\div 10^{14}$	No. of Obs.	Drop.	Ne $\div 10^{14}$	No. of Obs.
1	2.99	235	4	2.87	846
	2.77	167		3.15	421
				2.99	278
2	3.05	1019	5	2.39	551
	3.08	509		3.01	276
	3.05	337		2.54	178
	2.91	254			
3	2.94	1666	6	2.83	446
	2.65	831		2.75	221
	2.84	550	7		
	2.92	410		2.83	379
	2.91	315		2.85	188

Assigning weights to the values of Ne according to the number of observations, the average value

$$\text{Ne} = 2.880 \times 10^{14}$$

is obtained. The value of Ne obtained from electrolysis is 2.896×10^{14} . The average value differs from this by .5 per cent.

The results of this investigation lead, therefore, to the conclusion that the Brownian movement method holds for gases other than air, and that the molecules of ionized hydrogen carry the same charge as the hydrogen ions of electrolysis.

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