DETERMINATION OF VISCOSITIES AND OF THE STOKES-MILLIKAN LAW CONSTANT BY THE OIL-DROP METHOD

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Abstract.

Viscosities of nine gases, determined by the oil-drop method.—Millikan determined the value of e, the elementary charge, from measurements of the rate of fall of charged droplets in air, assuming the coefficient of viscosity to be $1,823 \times 10^{-7}$. Now that e is known, the method may also be used to determine coefficients of viscosity. Using carefully purified gases, tested spectroscopically and by density measurements, the results of long series of measurements in *argon, helium, hydrogen, methane, ethane, isobutane, nitrous oxide, and carbon dioxide*, when reduced to 23°, come out, respectively, 2,210, 1,981, 880, 1,079, 927, 755, 1,449, and 1,471, each times 10^{-7}. These agree with such other reliable determinations as are available for comparison, and are probably accurate to within 0.3 per cent. Isobutane is the first gas whose viscosity has been measured near its condensation point.

Coefficients of slip and of diffuse reflection for clock oil drops in the above nine gases.—As pointed out by Millikan, from hydrodynamic and kinetic theory, the constant A in the correction term for Stokes' Law, $(1 + Al/a)$, is equal to the coefficient of slip ζ divided by the mean free path l, and also to $0.7004(2 - f)/f$, where f is Maxwell's coefficient of diffuse reflection, hence from measurements of A both may be computed. The values of A for the nine gases were found to vary with the gas from 0.811 for hydrogen to 0.901 for helium, and they give corresponding values of f varying from 0.926 to 0.874. The results for air and CO_2 agree closely with those of Van Dyke.

Determination of the elementary charge by the droplet method.—The measurements in air give, incidentally, $(4.770 \pm .014) \times 10^{-10}$ e.s.u., in good agreement with Millikan's more accurate value, $4.774 \pm .005$.

Introduction.

The problem of a sphere moving through a viscous medium has received renewed attention in recent years in connection with various physical investigations, *e.g.*, the determination of the elementary charge (electron). Stokes[1] came to the conclusion from hydrodynamical considerations that a sphere of radius a moving at a steady speed v experiences a resisting force F given by

$$F = 6\pi\eta a v,$$

η being the viscosity of the medium. Millikan,[2] however, found in

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[1] Trans. Camb. Phil. Soc., Vol. IX., p. 8 (1850).

[2] Phys. Rev., XXXII., 1911, p. 366.

carrying out the oil-drop experiment that the formula is not exact if the sphere is so small that its radius is comparable with the mean free path of the molecules of the gaseous medium. A good deal of discussion [1] has centered round the correction necessary to bring Stokes' formula into agreement with experiment, and it is found practicable to denote it, generally, as a dimensionless correction factor, which multiplies the resisting force by $f(l/a)$, where l is the mean free path. Millikan gave to this function the form $(1 + A(l/a))$, and has carried out, with his pupils, a considerable number of experiments to determine whether or not A varies with the nature of the surface [2] and the nature of the gas.[3] The results have been altogether unambiguous in demonstrating such a variation with the nature of the surface. A variation with the nature of the gas was also indicated but with less certainty. At Professor Millikan's suggestion I have carried out with his apparatus the following experiments upon a considerable number of gases, paying especial attention to the monatomic gases helium and argon with which he anticipated the largest divergence from the behavior of ordinary gases.

Method of Calculation.

If a falling oil-drop [4] has a mass m and has reached a terminal velocity v_1, then by Stokes' Law we have

$$mg = 6\pi\eta a v_1.$$

This equation has however to be modified for very small drops by the above factor $f(l/a)$ to represent the various empirical or theoretical corrections advocated and we write

$$mgf\left(\frac{l}{a}\right) = 6\pi\eta a v_1. \tag{1}$$

If now the drop has attached to it an electron (charge e) in an electrostatic field E opposing gravitation and a terminal velocity v_2 is attained we have

$$(Ee - mg)f\left(\frac{l}{a}\right) = 6\pi\eta a v_2. \tag{2}$$

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[1] Cunningham, Proc. Ray Soc. (1), 83, p. 357 (1910); Knudsen, Ann. Phys., vol. 36, p. 981 (1911); Arnold, Phil. Mag., XXII., p. 755 (1911); Zerner, Phys. Zeit., XX., p. 546 (1919); Weysenhof, Ann. Phvs., vol. 62, p. 1 (1920).

[2] J. Y. Lee worked with shellac drops, Phys. Rev., Vol. IV., p. 420 (1914); O. Silvey and J. Derieux with Hg drops, Phys. Rev., Vol. VII., p. 87 (1916), Vol. XI., p. 203 (1918).

[3] Hydrogen was used by Millikan, W. H. Barber, and Ishida, Phys. Rev., Vol. V., p. 334 (1915), abstract, and J. Lassalle worked with CO_2 (Phys. Rev. **17**, 354, 1921).

[4] The oil used in this work was "Superfine" Clock Oil furnished by the Wm. Nye Co.

Equations (1) and (2) are insufficient to determine the unobserved quantities e and a since $f(l/a)$ is unknown. Following Millikan (loc. cit.), however, we may employ a process of successive approximations depending on the assumption[1] that $f(l/a)$ can be approximately represented by the expression $[1 + A(l/a)]$, *A being the constant which I have called the Stokes-Millikan Law Constant.*

If we write σ for the density of the oil and ρ that of the gas so that allowing for buoyancy

$$m = \frac{4}{3}\pi a^3(\sigma - \rho)$$

and introduce what Millikan calls the "apparent charge" e_1 given by

$$e_1^{2/3} = \left(\frac{4}{3}\pi\right)^{2/3}\left(\frac{9\eta}{2}\right)\frac{v_1^{1/3}(v_1 + v_2)^{2/3}}{E^{2/3}}, \tag{3}$$

then we may formally solve equations (1) and (2) and obtain

$$a^3 = \frac{3Ee}{4\pi(\sigma - \rho)}\frac{v_1}{(v_1 + v_2)}, \tag{4}$$

$$e_1^{2/3} = e^{2/3}\left(1 + A\frac{l}{a}\right). \tag{5}$$

We shall, further, following Millikan, make use of the fact (kinetic theory of gases) that the mean free path l is inversely proportional to the pressure so that

$$\left(1 + A\frac{l}{a}\right) = \left(1 + \frac{b}{pa}\right), \tag{6}$$

where b is a constant connected with A by

$$\frac{b}{p} = Al. \tag{7}$$

Equation (5) then becomes linear in $e_1^{2/3}$ and $1/pa$, viz.:

$$e_1^{2/3} = e^{2/3}\left(1 + \frac{b}{pa}\right), \tag{5'}$$

and we can plot the experimentally determined values of $e_1^{2/3}$ from (3) against the reciprocal of the corresponding products pa in which a is given by (4). This latter step is allowable since, although (4) involves the variable e supposed unknown, this quantity is in fact very closely given by Millikan's published work. The straight line thus obtained

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[1] Experiment showed that this first-order correction is insufficient when l/a becomes too large and the deviation, in the case of air, was investigated by Millikan (PHYS. REV., April, 1920 (abstract). In the present instance, however, we shall confine ourselves to the first-order term.

has $e^{2/3}$ for intercept and if this differs from the assumed value (Millikan's) we can resubstitute in (4) and obtain a still closer approximation. The slope of the final line thus obtained is then given by

$$\tan \theta = e^{2/3}b \tag{8}$$

so that b as well as e is now determined.

Now the determination of e_1 from (3) assumes that the viscosity has been previously determined. This was the case for air from which the value of e has hitherto been derived, but when we proceed to other gases, as in the present work, it is found that the values of the viscosities as given by various experimenters differ widely among each other. Accordingly it has been considered advisable to *use the oil-drop method to determine the viscosity indirectly* by assuming that e must be a constant for all gases. On this latter hypothesis all the various $e_1^{2/3}$, $1/pa$ lines must have the same intercept on the vertical axis, viz., $e^{2/3}$ and the procedure adopted was to assume at first that all the gases have the same viscosity given by $\eta = 10^{-4}$ gm/cm sec. This gives a set of lines of various slopes and intercepts as shown in Fig. 1. The ordinates of these lines are then multiplied by factors to make them all cut the vertical axis at the same point as shown in Fig. 2, and these factors give the values of the various

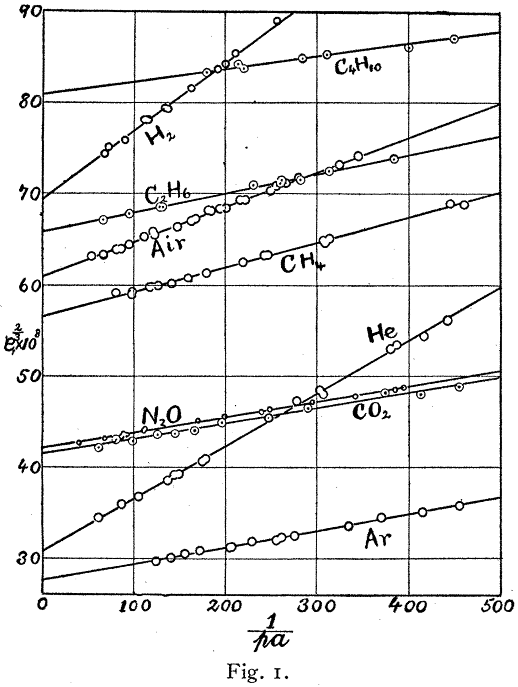

Fig. 1.

viscosities with air taken as standard. The data for these figures are given later.

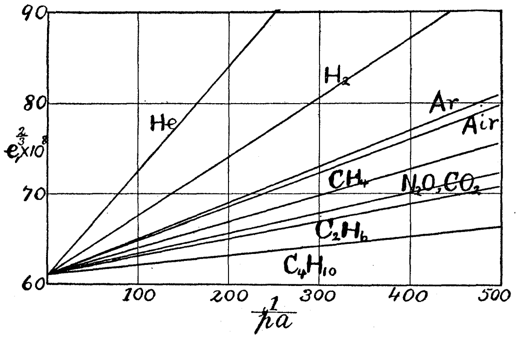

Fig. 2.

From Fig. 2 we may read off the slopes and determine the various values of the constant b by equation (8). The mean free path l is given by Boltzmann's equation [1]

$$l = \frac{\eta}{.3502\rho u\sqrt{\frac{8}{3\pi}}},$$

where

$$u = \sqrt{\frac{3p}{\rho}}.$$

Experimental Arrangement.

The experimental arrangement has been more than once described by Millikan and his pupils and we may refer to an earlier diagram.[2] Two modifications have been introduced: (*a*) all rubber tubing connections have been replaced by glass, and (*b*) in order to avoid contamination of the oil drops by stopcock grease and to prevent the oil in turn rendering the grease unable to maintain a vacuum, the aspirator apparatus shown in Fig. 3 was constructed to replace the corresponding part A, S, r of Millikan's diagram (loc. cit.). Thus the tube T is supposed to be continued into the tank. The bulb A (100 c.c.) containing the oil which is to be aspirated, and a drop of which is to be suspended between the charged plates, is kept at tank pressure by a communicating tube. The stopcock S is carefully ground at one operation into the two sockets B and C. The part C forms the neck of the bulb D which completely encloses B, the latter being the essential passage for the oil to the aspirator E. No grease is used at B, the oil itself serving as the seal. Oil leaks

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[1] Wiener Sitzungsber., LXXXIV., p. 45 (1881).

[2] Phil. Mag., XXXIV., p. 5 (July, 1917).

through the seal only slowly since by means of the spiral glass tube "shunt" *F* the interior of *D* is also at tank pressure. On the other hand, to withstand the possible difference of pressure between tank and atmosphere at *C*, good stopcock grease is employed, and, as is seen, the oil and grease are kept quite separate. The bulbs *G*, *H*, and *J* serve as "traps" for oil. To form a "cloud" of drops a small amount of oil is first admitted into the aspirator nozzle by opening the stopcock *S*, the oil being driven down by its own weight only. The heat of the hand applied to the bulb *J* will force any accidental excess out into the trap *H*. To aspirate, the stopcock *K* leading to a reservoir of the same gas under pressure is then momentarily opened. Exhaustion [1] of the tank is carried out through the stopcock *L* and trap *H* in parallel with the main exhaust so as to ensure that any oil which might come out of the aspirator is drawn into the trap and does not reach the tank. It is important to notice that the glass tubing connections, leading from the apparatus shown to more distant parts, as well as the connections of the main tank system, all contain a considerable length of tubing coiled into spiral form. This supplies that considerable "play" which is often required in adjustments. The completed apparatus was found capable of maintaining a vacuum (the vapor pressure of oil) over several weeks. The tank capacity was about 14 liters.

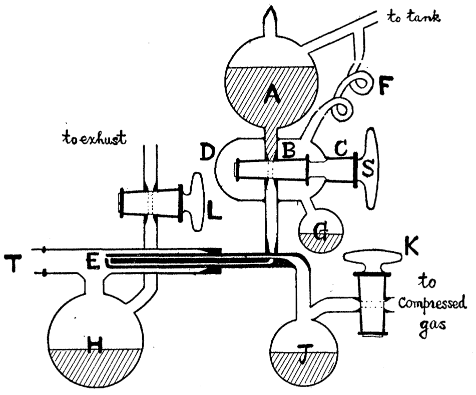

Fig. 3.

PREPARATION OF THE GASES.

The wide divergence in the viscosity results obtained by different experimenters for various gases has probably been partly due to the difficulty of obtaining very pure samples of gas. It was therefore thought

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[1] Diffusion pump assisted by the Gaede mercury pump was used for this work.

necessary to give the greatest possible attention to the elimination of impurities.

Argon.—Pure argon prepared by the calcium arc method,[1] was furnished by the General Electric research laboratory of Schenectady, N. Y., who also supplied a certain amount of 90 per cent pure gas. The tank was washed [2] several times for occluded gases beginning with the cheaper impure gas and finishing with the pure supply. Finally the pure gas was transferred from the reservoir to the tank by means of a Töpler pump through a tube of P_2O_5 and a trap cooled to $-135°$ C by "pasty" liguorn. The gas in the tube leading from the trap to the tank showed no traces of impurities under spectroscopic test for pressures less than a centimeter or so. Higher pressure showed H_α and Hg lines.

Helium.—The gas, 60 to 80 per cent pure, was supplied from the Texas source. All impurities except hydrogen and neon were easily got rid of by passing through charcoal cooled in liquid air. Liquid hydrogen, which would also have removed these, was not available, but fresh liquid air was used and the diffusion made very slow by passing the gas through 5 meters of small pyrex tubing (2 mm diam.) filled with charcoal grains. The spectrum of the purified helium showed no trace of neon (red line) below a pressure of 4 cms. Further increase of pressure brought out first the H and then Hg lines.

Hydrogen.—Hydrogen was generated electrolytically from platinum electrodes in dilute sulphuric acid, the interior of the generator being water-cooled to diminish the amount of water vapor going over. The gas was cooled with an ice-salt mixture and then passed in succession through P_2O_5, for water vapor, metallic sodium at 100° C for oxygen and cocoanut charcoal cooled in liquid air for other possible impurities such as N_2, CO_2 and the hydrocarbons. This final product was spectroscopically pure.

Nitrous Oxide (N_2O).—Nearly pure (99 per cent) gas was prepared by the White Dental Manufacturing Co., Philadelphia, the impurities being air and CO_2. The CO_2 was removed by bubbling through concentrated KOH solution, and the gas was then passed over P_2O_5 and frozen in a liguorn trap when the residual unfrozen gas (air) was pumped off.

Carbon Dioxide.—This was prepared by heating sodium bicarbonate in a thick-walled pyrex bulb and drying. To remove possible impurities, due to air, the gas was frozen in "pasty" liguorn, the residual gas (air) being pumped off.

Methane.—The gas was prepared by the reaction of methyl iodide on a

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[1] Fischer and Ilioici, Ber. Deut. Chem. Ges., 42, p. 527 (1909).

[2] This process is important for all gases including air.

mixture of methyl alcohol and water in which there was a zinc copper couple.

Ethane.—For the preparation of this gas the same scheme as for methane was used, substituting ethyl iodide and ethyl alcohol for the methyl compounds. To generate the gas the mixture was heated to 60° C.

These two hydrocarbons methane and ethane were fractionally distilled by means of liquid air and liguorn paste six to eight times after usual precautions had been taken for CO_2 and water vapor. Otherwise it is very difficult to get rid of the vapor of the iodine compounds. Long trains of zinc had been previously tried without material success.

Isobutane.—Impure gas prepared in the Kent Chemical Laboratory of the University of Chicago and it was only after many fractional distillations that a density of 2.608×10^{-3} was obtained which is near the accepted value.

As a rough check on all these gases except hydrogen and air their densities were fairly carefully determined, and the following table shows the agreement between the accepted values and the present ones after reduction to N. T. P.

	He.	Ar.	CH_4.	CO_2.	N_2O.	C_2H_6.	${}_4H_1C_0$(Iso).
Accepted value.......	.179[1] .178[2]	1.787[1] 1.781[2]	.716[3] .717[4]	1.965[5] 1.977[6]	1.966[3] 1.978[8]	1.357[7]	2.594[8]
Observed value.......	.180	1.780 1.784[9]	.719	1.974	1.971	1.363	2.608

Results of Experiments.

During the experiments the temperature was maintained as nearly as possible at 23° C for all gases except air and hydrogen. Temperature corrections for viscosity were made in the case of these two gases by Sutherland's formula, the constants being taken from Landolt and Bernstein's tables. For all other gases the simpler formula

$$\eta = \eta_{23}[1 + .003(t - 23)]$$

was used which is close enough for the small temperature deviations involved.

A summary of the results is shown in Table I. The intercepts and slopes of the lines given in Fig. 1 are contained in the first two columns of the table in the same units as in the diagram. The next column gives

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[1] Ramsay and Travers. [2] Watson. [3] Thomson. [4] Baume and Petit. [5] Raleigh and Leduc. [6] Guye and Pintza. [7] Baume and Parrot. [8] Frankland. [9] Measured by General Electric Co.

the deduced viscosities, *i.e.*, the multiplying factors for the ordinates of Fig. 1 required to bring all the intercepts into agreement as in Fig. 2 and explained above. These numbers are thus equal to the ratios of the intercept for air to the intercepts for the various gases. The following column gives the constants b which are the slopes of Fig. 2, and are thus equal to the ratios of slope to intercept of the first two columns. The density column is for the actual experimental condition (23° C) and the mean free paths of the succeeding column were calculated from these values (Boltzmann's formula above).

TABLE I.[1]

Gases.	Intercept $\times 10^8$.	$\tan\theta \times 10^3$.	$\eta \times 10^4$.	$b \times 10^4$.	$\rho \times 10^4$.	$l \times 10^5$.	A.	$\zeta \times 10^7$.	f.
C_4H_{10}(Iso)	80.82 ± .03	14.07 ± .01	.755	1.74	23.9	.275	.834	23.0	.91
C_2H_6	65.85 ± .01	20.84 ± .04	.927	3.16	12.5	.466	.891	41.5	.88
N_2O	42.13 ± .01	16.92 ± .04	1.449	4.02	18.2	.606	.873	53.0	.89
CO_2	41.50 ± .03	16.46 ± .08	1.471	3.97	18.2	.615	.849	52.2	.90
CH_4	56.58 ± .02	27.01 ± .05	1.079	4.77	6.6	.749	.838	62.8	.91
Air	*61.05* ± .01	*37.66* ± .04	*1.823*	6.17	11.9	.942	.862	81.1	.90
Ar	27.62 ± .01	18.09 ± .02	2.210	6.55	16.4	.972	.868	86.1	.88
H_2	69.37 ± .01	74.42 ± .12	.880	10.73	.83	1.741	.811	141.2	.92
He	30.82 ± .02	57.99 ± .07	1.981	18.82	1.65	2.75	.901	248	.87

The 8th column gives the various values of the constant A as calculated from equation (7).

The data of the various gases from which Fig. 2 is drawn will now be discussed (see Table II.). Measurements for air which, on account of its known viscosity, determine the value of e were repeated at various times throughout the work so as to ensure constancy of working conditions. This part constitutes of course a repetition and verification of Millikan's published work. The values of $e_1^{2/3}$ and $1/pa$ were calculated as explained above from equations (3) and (4), the known value 1.823×10^{-4} for the viscosity of air being used and the value 10^{-4} for all other gases. The corresponding straight lines of Fig. 1 were calculated by least squares.

In the case of air we obtain an intercept of $(61.048 \pm .008) \times 10^{-8}$ as against Millikan's final 1917 intercept of 61.086 and from this on making allowance for the systematic errors[2] which in a larger sense are also probable errors, since they, too, are distributed haphazard, the

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[1] The values for the coefficient of slip $\zeta = A/l$ and for the coefficient of diffuse reflection $f = 1.4/(A + 0.7004)$ have been added by the editor for comparison with the results given by Millikan, Van Dyke and others in preceding papers.

[2] Errors of this type will be discussed later.

derived value of the elementary charge is

$$e = (4.770 \pm .014) \times 10^{-10},$$

agreeing with Millikan's value 4.774 ± .005 well within the limits of my experimental errors which, as indicated, are somewhat larger than those involved in Millikan's determination.

TABLE II.

	$e_1^{2/3} \times 10^8$.	1/*pa*.	*w*.		$e_1^{2/3} \times 10^8$.	1/*pa*.	*w*.
Air	63.20	53.5	2	C_2H_6	67.62	85.7	1
Ranges { temp. 22.5 – 26.8° C press. 26.7 – 75.2 cm Hg voltage 3,330 – 5,330 volts	63.48	66.5	1	Ranges { temp. 23.0 –23.15° C press. 23.5 –57.8 cm Hg voltage 1,350 –4,730 volts	67.75	95.4	2
	63.98	81.0	2		68.52	128.1	2
	64.13	86.4	1		68.57	131.4	2
	64.51	94.7	2		70.85	229.5	2
	65.33	111.2	2		71.18	260.1	1
	65.87	121.0	1		71.37	261.3	1
	65.61	122.5	2		71.55	281.6	1
	66.49	147.0	2		72.50	312.8	1
	67.07	162.1	2		73.82	383.7	1
	67.33	167.3	2		76.41	510.7	1
	68.20	181.4	2		76.98	534.2	2
	68.05	183.9	2				
	68.36	193.4	2	C_4H_{10}(Iso)	83.31	179.5	
	68.42	200.1	2	Ranges { temp. 23.0 –23.1° C press. 16.7 –25.2 cm Hg voltage 1,990 – 2,660 volts	84.20	214.4	
	69.26	214.6	2		83.77	221.4	
	69.38	221.6	1		84.83	284.2	
	69.93	237.4	2		85.25	310.9	
	70.27	249.2	2		85.76	373.0	
	71.03	256.3	1		87.13	449.5	
	71.13	266.3	2		88.01	520.3	
	71.39	280.4	2		88.81	563.5	
	73.21	324.4	2		89.80	617.2	
	74.52	355.4	2		89.74	642.6	
Ar	29.79	124.1	2	H_2	74.26	67.9	2
Ranges { temp. 22.9 –23.7° C press. 21.0 –40.0 cm Hg voltage 1,300 –2,000 volts	30.13	139.5	1	Ranges { temp. 22.8 –27.0° C press. 30.7 –74.7 cm Hg voltage 2,000 –3,340 volts	75.15	72.4	1
	30.48	153.7	1		75.75	90.1	2
	30.85	172.0	2		78.01	111.5	2
	31.29	204.4	2		78.01	113.8	1
	31.31	206.1	2		78.11	117.5	2
	31.82	227.7	2		79.37	134.1	2
	32.08	255.1	1		79.32	136.9	1
	32.34	261.0	2		81.50	163.2	2
	32.54	274.9	2		83.65	192.4	1
	33.62	333.7	2		84.30	200.5	2
	34.43	369.7	2		84.81	210.9	1
	35.09	414.1	1		88.89	257.0	1
	35.81	455.4	2		96.33	363.2	2

TABLE II. (*Cont.*).

	$e_1^{2/3} \times 10^8$.	$1/pa$.	w.
CO_2 Ranges { temp. 22.9 −23.12° C press. 18.9 −50.2 cm Hg voltage 1,970 −3,340 volts	42.22	63.7	
	43.09	80.3	
	43.40	98.0	
	43.27	104.9	
	43.73	144.7	
	44.04	165.8	
	44.92	195.7	
	46.56	290.5	
	48.17	373.9	
	48.03	412.1	
	48.82	454.8	
	50.86	569.9	
	51.57	588.4	
CH_4 Ranges { temp. 22.85 − 23.13° C press. 22.6 − 43.3 cm Hg voltage 1,940 − 3,310 volts	59.19	80.0	
	59.05	97.5	
	59.26	98.9	
	59.60	117.5	
	59.95	126.3	
	60.23	141.3	
	60.82	158.8	
	61.37	178.5	
	62.52	219.0	
	63.28	242.2	
	63.29	245.5	
	63.59	261.2	
	64.90	306.6	
	64.67	308.4	
	65.08	313.2	
	68.85	445.9	
	68.76	460.9	
	71.70	543.0	
	74.29	665.2	

	$e_1^{2/3} \times 10^8$.	$1/pa$.	w.
N_2O Ranges { temp. 22.9 − 23.15° C press. 24.7 −71.0 cm Hg voltage 2,600 −3,980 volts	42.74	39.9	
	43.21	67.7	
	43.44	85.9	
	43.67	88.4	
	43.58	92.2	
	44.06	110.5	
	44.24	112.8	
	45.08	169.9	
	45.58	198.8	
	46.16	238.4	
	46.56	258.9	
	47.21	294.9	
	47.88	341.4	
	48.51	384.4	
	48.79	393.7	
He Ranges { temp. 22.8 − 23.2° C (except one 23.9) press. 23.1 −67.2 cm Hg voltage 680 −1,340 volts	34.45	61.2	1
	36.46	96.2	2
	36.81	104.6	1
	38.59	135.6	2
	39.18	144.1	2
	39.32	148.7	1
	40.77	174.8	2
	41.05	178.4	1
	45.43	247.3	1
	47.29	277.4	2
	48.43	302.5	1
	48.15	307.0	1
	53.11	380.6	2
	53.48	387.2	2
	54.40	416.5	1
	56.31	442.3	2

w is the weight of each obs.
Empty space indicates uniform weight.

The following table gives a comparison of the viscosity values here obtained and those of some other workers for 23° C. The latter were

TABLE III.

$\eta_{23} \times 10^7$ ($\eta_{23} \times 10^7$ for air taken 1,823).

	He.	H_2.	Ar.	CH_4.	CO_2.	N_2O.	C_2H_6.	C_4H_{10} (Iso).
Other workers' values	2,005[1] 1,988 } [2] (1,979)[8] }	890[3] 882[4]	2,258[1] 2,249 } [2] (2,238)[9] }	(1,226)[5]	1,471.5[7] 1,500[3] (1,629)[5]	1,488[6]		
Obtained values	1,981	880	2,210	1,079	1,471	1,449	927	755

[1] Schultze. [2] Rankine. [3] Breitenbach. [4] Yen: Phil. Mag., XXXVIII., p. 582 (1919). [5] Grahm. [6] Tisher. [9] Rankine, Proc. Roy. Soc., 83, p. 265, 516 (1910). [7] Van Dyke, Phys. Rev., **21,** 250, 1923. [8] Rankine, Proc. Roy. Soc., 84, p. 181 (1910).

computed from the values at 0° C by means of the Sutherland formula. Those in brackets were computed by a linear formula.

The values here obtained are estimated to be correct within .3 per cent. It will be noticed that in this table most other workers come consistently higher, but this is thought to be due to the fact pointed out before by Millikan that air has generally been given a value about 1.5 per cent too high and other gases have been referred to it. The following table showing the ratios $\eta_{\text{air}}/\eta_{\text{gas}}$ gives excellent agreement whenever these ratios have been accurately determined in preceding work.

TABLE IV.

Values of $\frac{\eta_{\text{gas}}}{\eta_{\text{air}}}$ *at 23° C.*

	He.	H_2.	Ar.	CH_4.	CO_2.	N_2O.
Other observers	1.082 (Rankine) 1.086 (Schultze for 15°)	.482 (Breitenbach) .484 (Yen)	1.224 (Rankine)	.632 (Graham for 20°)	.808 (Van Dyke) .812 (Breitenbach) .841 (Graham for 20°)	.841 (Graham for 20°)
Our values.....	1.087	.483	1.212	.592	.808	.795

GENERAL ACCURACY.

In view of the fact that the viscosities and other quantities given above were indirectly derived, it is important to form an estimate of their probable errors. In calculating the slopes and intercepts of the lines of Fig. 1, the observational data were divided into two classes. Where the same drop was kept under observation during many consecutive falls through the telescopic field for, say, an hour or so, the result was given double the weight given to periods of half this time or less. There were a few cases that had to be discarded, the results being for some unexplained reasons 10 to 50 per cent out. The probable errors in slope ($e^{2/3}b$) and intercept ($e^{2/3}$) were derived in the usual way[1] and are recorded in Table I.

Besides these "probable" accidental errors there remains the possibility of systematic errors, *i.e.*, errors remaining constant and of one sign throughout the experiments. For experimental reasons, which need not be discussed at present, we know that such systematic errors can only have entered as approximately *constant percentage* errors into the

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[1] See, *e.g.*, Johnson's The Theory of Errors and Method of Least Squares, pp. 108.

data for the ordinates and abscissæ of Fig. 1. The results would therefore be a shearing effect on the diagram not affecting the linearity of the observational points. The errors would enter into the ordinates $e_1^{2/3}$ through the factors (equation (3)): distance of fall, time of fall and voltage, and the maximum possible systematic error is estimated at .3 per cent. Since the viscosities are essentially ratios of ordinates (intercepts) they are independent of this possible error provided the experimental conditions are identical.

When looked at from the practical point of view of agreement with other dependable determinations, the intercepts, *i.e.*, the viscosities, entirely justify the estimate of an uncertainty not greater than about 0.3 per cent. For the viscosities of H_2 and CO_2 have recently been determined with an accuracy of about 0.1 per cent by Yen and Van Dyke by the constant deflection method—a method far transcending in accuracy those previously used—and the present determinations are seen from Table III. to show no deviation from their values greater than a fourth of a per cent. Further the ratio of the viscosities of helium and hydrogen with respect to air have been previously accurately determined and Table IV. shows that these ratios also are practically identical with those here found. The divergence of the present determinations of the viscosities of CH_4 and N_2O from Graham's values is without significance in view of the early date of Graham's work.

It is worthy of remark that the method here used, unlike the usual methods, is just as applicable to vapors near their condensation points as to permanent gases, and that *the viscosity of one such vapor C_4H_{10} has for the first time been accurately determined.*

I estimate the practical uncertainties in the slopes, however, *i.e.*, in the values of A as very much greater than the uncertainties in the viscosities. Indeed Millikan estimates that when his value of e (intercept) is determined with an uncertainty of not more than 0.1 per cent his slope may be in error by as much as 1 per cent. In this work, in which smaller numbers of drops in a given gas were taken, the uncertainty in A may well in some cases be as much as 2 per cent. Nevertheless the excellent agreement between my values of A in both air and hydrogen with the values taken some years earlier by Millikan in the same gases, viz., .861 in air against his .864 and .811 in H_2 against his .815, speaks well for the duplicability of results by different observers under different conditions. It is not so satisfactory to compare my value of A for CO_2, viz., .849 with that obtained by Lassalle, viz., .825, but the slope for CO_2 is the least reliable of any for the observations were made rather hurriedly.

Nevertheless no consideration of experimental errors appears to be able to account for the variations in A found in Table I. where the lowest value (hydrogen) is .811 and the highest (helium) .901.

I look upon this data then as furnishing good evidence that the A in the Stokes-Millikan formula varies with the nature of the surrounding gas. It is interesting that the monatomic gases He and Ar both show very high values of A, but the variation of A with the nature of the gas is apparently not large enough in comparison with the precision of my results to bring to light the exact law of dependence of A upon other molecular characteristics.

The author takes this opportunity of expressing his great indebtedness to Professor Millikan for initiating him into this work, and for much assistance and encouragement during its progress. He also wishes to heartily thank I. G. Barber, E. S. Akeley, I. S. Bowen, and Miss O. L. Risk for assistance with the observations.

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