

THE COEFFICIENTS OF VISCOSITY AND OF SLIP OF AIR
AND OF CARBON DIOXIDE BY THE ROTATING
CYLINDER METHOD.

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ABSTRACT.

Coefficients of viscosity of air and of CO₂, determined by the constant deflection method.—With the rotating cylinder apparatus designed by Millikan and used by Gilchrist, Harrington, Yen and Stacy in measurements of high precision, a new determination has been made of the coefficient of viscosity of dry air. The value obtained, $\eta_{23} = 1822.1 \times 10^{-7}$, is only 1/40 per cent less than the standard value of Harrington. The coefficient of viscosity of CO₂ obtained by the same method comes out $\eta_{23} = 1471.5 \times 10^{-7}$. The gas used was from c.p. NaHCO₃, and since, after purification by freezing, various samples gave concordant results, this value is thought to be correct to within 1/20 per cent. Comparison with the results of Breitenbach indicates that all his values, though relatively correct, are 1.5 per cent too high.

Coefficients of slip for rough and smooth surfaces in air and CO₂ were computed from values of the apparent coefficients of viscosity measured by this method for pressures of 0.5 to 0.1 mm. For an *old shellac surface*, the values came out in both air and CO₂ only 3 per cent greater than the theoretical lower limit computed by Millikan for a completely diffusing rough surface, in agreement with Stacy's result; while for a surface *coated with watch oil*, the coefficients in air and CO₂ were respectively 21 and 12 per cent higher, in good agreement with the corresponding values found by Millikan's oil drop method. For clean and scratched *brass surfaces* intermediate values were obtained.

Fatigue of a watch spring steel wire, twisted under load.—In five years the period decreased 0.09 per cent, showing a gradual stiffening. A twist of 8° for half an hour caused a temporary zero shift of 0.004°.

I. INTRODUCTORY.

THE constant deflection method of studying the viscosities of gases, and, in particular, the rotating cylinder apparatus designed by Professor Millikan has heretofore yielded several determinations of viscosity coefficients for which a high degree of precision has been claimed: the viscosity of air determined by Gilchrist,¹ and redetermined by Harrington,² and the viscosities of oxygen, nitrogen and hydrogen by Yen.³ It is one purpose of the experimental investigation herein described to *add the coefficient of viscosity of carbon dioxide to the above list of precisely known experimental magnitudes*. The main purpose, however, is to obtain

¹ Gilchrist, PHYS. REV., 1, 124, 1913.

² E. L. Harrington, PHYS. REV., 8, 738, 1916.

³ K. L. Yen, Phil. Mag., 38, 582, 1919.

further experimental evidence from the rotating cylinder method as to *how the external friction of a gas or the "coefficient of slip" depends upon the character of the bounding surface, and upon the nature of the gas in contact with it.* The results furnish convincing evidence for specular reflection of gas molecules against a bounding surface.

II. THE ROTATING CYLINDER METHOD.

In the rotating cylinder method the viscosity of a gas is obtained from the deflection of a suspended cylinder against a torsion fiber when a similar concentric cylinder is rotated at a constant speed. The deflection measures the viscous drag of one cylinder upon the other, and thus combines into a single measured effect both the internal friction of a layer of gas of known thickness and the external friction between the gas and the two bounding surfaces. The dimensions of the rotating cylinders in use are such that the viscous drag as measured by the deflection against the torsion fiber is sensibly independent of the pressure of the gas for pressures between atmospheric and ten centimeters of mercury. The falling off in deflection at ten centimeters of pressure is about one part in ten thousand (from the theory), at one to two centimeters pressure about 1 part in 1,000 (observable), at 1 or 2 millimeters of mercury about a per cent, while at pressures of one or two tenths of a millimeter the deflection is from ten to fifteen per cent less than its value at atmospheric pressure.

This falling off of the viscous drag through a gas at low pressures is interpreted by the kinetic theory not as any variation in the internal friction, but rather as resulting from a decrease in the friction at the bounding surface. Thus the kinetic theory holds η , the coefficient of viscosity, independent of pressure, and introduces from the hydrodynamical analog a coefficient of slip, ζ , defined as the ratio of η to the external friction.

The theory of viscosity and of slip determinations with the rotating cylinder apparatus has been given in a preceding paper by Professor Millikan. The working equations as used are given for convenience of reference. They are:

$$\begin{aligned}
 (1) \quad & \eta = k'td, \\
 (2) \quad & \eta = k'td(1 + \zeta k), \\
 (3) \quad & \zeta = \left(\frac{\eta_1}{\eta_2} - 1 \right) \frac{1}{k}, \\
 (4) \quad & k' = \frac{I(b^2 - a^2)}{4a^2b^2lDT^2}, \\
 & k = 2 \left(\frac{b^3 + a^3}{ab^3 - a^3b} \right),
 \end{aligned}$$

where η in (1) is the coefficient of viscosity, whether real (within the limits of error) as measured at a pressure of 10 cms of mercury or above, or apparent when measured at some pressure so low that the slip term in (2), the equation for the true value of the coefficient of viscosity, becomes significant. In these equations k' is a constant of the apparatus in terms of the radii, a and b , of the inner and outer cylinders, I the moment of inertia of the suspended cylinder, T the complete period of oscillation of the suspended cylinder in vacuo, l the length of the inner cylinder, and D the radial distance between the mirror mounted at the base of the suspension fiber and the curved scale upon which the deflection, d , is read when the outer cylinder is rotated steadily at the rate of one revolution every t seconds.

The coefficient of slip, ζ_p , is computed from two determinations of the apparent viscosity, one, η_1 , at atmospheric pressure, and another, η_2 , after evacuation to a pressure p cms of mercury, by (3) above. This formula is obtained from (2) on the assumption that at the pressure at which η_1 is determined the second term can be neglected.

III. THE APPARATUS.

The apparatus is that used by the previous observers referred to and its constants have been given by Harrington. The adaptation of the apparatus for working at low pressures is described by Stacy in a preceding paper. It suffices to repeat that the entire cylinder system is covered by a large glass jar (about 35 liters capacity) and the whole sealed with mercury. The rotating cylinder is driven mechanically through a mercury seal. A pressure as low as 0.001 mm is attainable. The only changes which have been made in the apparatus in the present work are in the deflection observing system and in the pumps used in evacuation.

A scale, distant about two and a half meters from the apparatus, curved to an arc, of which the suspension fiber was the center, was used for reading the deflections of the inner cylinder. The scale was illuminated from behind and the deflection observed against the cross hairs of a telescope mounted at a new observer's position in front of the chronograph (see diagram in Harrington's paper) and focused through two fixed auxiliary mirrors on the image of the scale in the deflecting mirror. No accuracy of the reading of deflection was sacrificed by the change in the observer's position, while much was gained in convenience of manipulation of the driving apparatus and chronograph, and in the convenience of temperature observation and control.

The scale used in the experimental work represented in the data of the first three tables was a flexible transparent celluloid scale divided

into millimeters and calibrated from time to time against a standard B. and S. steel meter scale. The celluloid scale was discarded later when its calibration showed a sudden change with the advent of damp summer conditions in a basement room. The standard B. and S. steel meter scale was then substituted for the celluloid scale, the steel rule being clamped onto a brass frame cut in an arc of radius 236 cms, and firmly mounted at approximately this distance from the suspension fiber. The transparent feature of the celluloid scale had been so convenient that a transparent glass scale (10 cms long and divided into mms) was mounted as a slider on the steel scale, and in all later work was moved back and forth from the zero position on the scale to the position of deflection. The deflection thus involved the sum of two differences, one on the steel scale (60 cm) and one on the glass rider (usually but a few millimeters). In practice it was found convenient to let the deflection swing about its mean position during the period of observation, the usual amplitude of the swings being but one or two millimeters, and the position of the cross hair was read at equal intervals (about 30 readings) and the mean of these used in computing the deflection.

It will be recalled that in Harrington's absolute determination of the viscosity of air much time was devoted to the study of suspension fibers, uncoiled stock for watch hair springs being finally adopted as most satisfactory, no zero shift being found. Harrington's "F" suspension (see his table of data) is still in use, but presents some shift of the zero with every deflection. This shift is very small, of the order of three tenths of a millimeter on the scale (at a distance of 236 cms from the mirror) under the normal deflection of about 70 cms for half an hour. The return of this zero to its original reading before the deflection requires from two to three hours. In all of the work to be reported a zero reading is taken by the method of small oscillations in common use in reading the position of the beam of an analytical balance before it comes to rest. The zero position is read in this way both before deflection and again as soon as possible (about three minutes) after the deflection is released, and the mean of these two used in computing the deflection. The whole error in reading the deflection cannot be greater than 0.3 mm when all of the factors are allowed for.

The pumps used in evacuating the apparatus between the high and low pressure viscosity determinations proved an important factor in the consistency of the results obtained for the coefficient of slip. For the determinations listed in Table III. the pumping system consisted of a large May-Nelson pump (oil) and a Gaede rotary mercury pump. The aim was to evacuate as rapidly as possible so that a determination of the

viscosity at the low pressure could be made before the effects of the release of occluded gases became serious, an effect which Stacy found troublesome. With this pumping system the total time of evacuation was more than two hours, and consistent results in slip coefficients were obtained only after some twenty or thirty attempts which were very inconsistent.

In all later slip work a mercury diffusion pump backed by the May-Nelson pump was used. This combination permitted a determination of the apparent viscosity at 0.1 mm to be made within an hour after that made at atmospheric pressure. No further trouble was had from varying values of slip on the surfaces listed following the installation of the diffusion pump.

IV. APPARATUS CONSTANTS AND EXPERIMENTAL CONDITIONS.

The constants of the cylinder, which should have shown no change since they were carefully determined by Gilchrist and again by Harrington, were not redetermined. They were taken from the latter's paper.

$$a = 5.3412 \text{ cm}, \quad b = 6.0632 \text{ cm}, \quad l = 24.88 \text{ cm}, \quad I = 7,617.3.$$

The period of the suspended system was determined from time to time in vacuo and the constancy of the suspension fiber watched in this way. It is interesting to note that the period of the suspended system is very closely the same as with previous observers, but that there is evidence of a gradual stiffening of the steel wire under continued strain. (In terms of the period, Harrington—175.58 seconds; Stacy—175.48; November, 1920—175.45; June, 1921—175.42 seconds.) This is but an instance of the known tendency of solids to harden when standing under strain.

The distance between mirror and scale was slightly increased over that used by previous observers, and was measured with a combination of meter sticks fastened together, and this in turn calibrated with the B. and S. steel meter.

$$D, 235.81 \text{ cms, when using celluloid scale,}$$

$$D, 236.36 \text{ cms, when using steel scale.}$$

Pressure readings were made on a McLeod gauge reading to 0.0001 mm. Errors in observing the pressure were considerably less than the rise in pressure over the interval required for a complete determination. This was usually two or three thousandths of a millimeter. Pressure readings were taken before and after each determination, and in many cases it was found possible to take several observations of pressure during the determination. The mean pressure was used in the computation of the coefficient of slip.

Temperatures were read every few minutes on a Beckman thermometer within the apparatus, and in most cases showed but two or three hundredths of a degree change during the fifteen minutes during which the observations were being taken. A high-grade thermometer hung beside the Beckman and its reading was also recorded at least once during the run. Both of these thermometers were calibrated against a standard Baudin Thermometer which had been calibrated at the Bureau International des Poids et Mesures in Paris. In general the temperature was held fairly close to 23° C and the value of η obtained corrected to 23° C by the linear formula

$$\eta_{23} = \eta_0 + k(23 - \theta),$$

where the coefficient for air is 4.93×10^{-7} as used by Millikan,¹ and for CO₂ is 4.77×10^{-7} , this latter being computed by the substitution of Breitenbach's constants for CO₂ in the Sutherland equation.² For the small temperature differences involved the error introduced in the reduction is insignificant.

V. DETERMINATION OF THE VISCOSITY OF AIR.

A complete absolute determination of the viscosity of dry air was made for the purpose of ascertaining how closely the value obtained by Harrington could be duplicated with the apparatus as set up. The apparatus was not dismantled, but left as found. Harrington's values of the dimensions of the cylinders were used but the period of the suspended system was redetermined. Table I. gives the observed data and the computed viscosities. It is not the intention to present an absolute determination, but rather to illustrate the type of consistency to be expected in repeating determinations with the apparatus. Also the mean η_{23} of Table I. is taken as a calibration of the apparatus and to be used in making relative to Harrington's value for air the determination of the viscosity of carbon dioxide next described.

TABLE I.

Viscosity of Dry Air.

$T = 175.45$ sec., $D = 235.81$ cm, $k' = 8.2789 \times 10^{-7}$.

d (cm).	t (sec.).	θ (° C).	$\eta_0 \times 10^7$.	$\eta_{23} \times 10^7$.
71.12.....	30.951	23.13	1822.3	1821.7
71.44.....	30.805	23.12	1821.9	1821.3
71.36.....	30.865	23.24	1823.5	1822.3
71.42.....	30.858	23.27	1824.6	1823.3
71.27.....	30.904	23.27	1823.4	1822.1
Mean $\eta_{23} = 0.00018221$.				
Harrington's Mean $\eta_{23} = 0.00018226$.				

¹ R. A. Millikan, *Ann. der Phys.*, 41, 759, 1913.

² P. Breitenbach, *Ann. der Phys.*, 5, 166, 1901.

VI. DETERMINATION OF VISCOSITY OF CARBON DIOXIDE.

Carbon dioxide was prepared by heating NaHCO_3 in a closed glass system. The gas formed was passed through two tubes containing P_2O_5 and collected in a five-liter jar, from which it was removed from time to time during the preparation and frozen under liquid air for storage in quantity. Several different lots of carbon dioxide were made in this way, and from two different samples of the carbonate. One was Merck's "Highest Purity," and the other, Baker's "Analyzed." The carbon dioxide as stored under liquid air was exposed to the Gaede pump for a considerable time, and then as the pumping continued the liquid air was replaced by a thick paste of alcohol at a temperature of about -120°C . The carbon dioxide gradually evaporated from this as the alcohol rose in temperature, and was allowed to enter the apparatus after the first two or three samples were pumped off. The last portions of the solid carbon dioxide were always discarded.

The viscosity determinations are listed in Table II. They were made

TABLE II.

Viscosity of CO_2 .

$$T = 175.42 \text{ secs.}, D = 235.81 \text{ cms}, K' = 8.2815 \times 10^{-7}.$$

d (cm).	t (cm).	p (cm).	θ ($^\circ\text{C}$).	$\eta_\theta \times 10^7$.	$\eta_{23,p}$.	η_{23} .
57.48....	30.918	67	22.97	1471.7	1471.8	1471.8
57.44....	30.931	67	23.03	1471.3	1471.2	1471.2
57.47....	30.918	35	23.16	1471.7	1470.9	1470.9
57.66....	30.816	35	23.22	1471.7	1470.7	1470.7
57.52....	30.845	10	22.88	1469.4	1470.0	1470.2
57.50....	30.886	10	23.01	1470.9	1470.9	1471.1
57.77....	30.746	6	22.95	1471.1	1471.3	1471.6
57.70....	30.760	2.1	23.03	1470.0	1469.9	1470.7
57.68....	30.772	2.1	23.07	1470.1	1469.8	1470.4
57.77....	30.772	2.5	23.16	1472.3	1471.5	1471.9
57.73....	30.793	2.5	23.21	1472.3	1471.3	1471.7

Mean $\eta_{23} = 1471.1$.
Mean $\eta_{23}(\text{CO}_2)$ relative to Harrington's $\eta_{23}(\text{air}) = 1471.5$.

upon four different samples of the gas. The last of these samples was subdivided for the different determinations listed into three fractions after the first determination of its viscosity as a whole was made. This division was made in the following way in an attempt to obtain some indication of the homogeneity of the sample. A liquid-air trap was opened to the apparatus after the determination was made, and carbon dioxide slowly drawn back to the trap and there solidified. As the

pressure fell the first trap was closed off and a second one exposed, this taking the second portion of the gas. The viscosity of the last third was then determined, and in succession the other two. Their viscosity determinations are all in agreement to within the limits of error in these determinations. It will be noted that in this table a number of the determinations were made at pressures (p) far below atmospheric. The individual values determined, η_p , are corrected to the true viscosity, η , in the last column by the addition of a small slip correction easily approximated from the slip determinations to be described.

When the mean for the values for CO_2 is made relative to Harrington's η_{23} for air by correction in the proper ratio, η_{23} for CO_2 becomes $1,471.5 \times 10^{-7}$. Relative to air this is probably correct to a part in several thousand.

Determinations of the viscosity of CO_2 by other methods have given rather varying values. Lassalle¹ and Ishida² have obtained values $1,490 \times 10^{-7}$ and $1,471 \times 10^{-7}$ respectively, both from oil drop experiments and both relative to the same η_{23} for air, namely $1,823 \times 10^{-7}$. Ishida's value is in excellent agreement with the present determination. As pointed out by Lassalle, Breitenbach's value obtained from the capillary method when corrected to 23°C by the Sutherland formula and made relative to Harrington's value for air in the same ratio as his own value for air is higher than Harrington's becomes $1,474 \times 10^{-7}$. It is felt, however, that the precision obtained from the constant deflection method is of a different order entirely from that given by the other methods, and that the value given is probably correct to at least one part in 2,000. It speaks well for the correctness of the *relative* values of viscosities usually quoted, viz., those of Breitenbach,³ that there is but 0.2 per cent of difference between the absolute value for CO_2 of η_{23} as found herewith, viz., $1,471.5 \times 10^{-7}$, and the value computed by multiplying Harrington's value for air by Breitenbach's ratio of η_{23} (air) and η_{23} (CO_2). All of Breitenbach's absolute values, however, must be considered as 1.5 per cent too high.

As a further check on the accuracy of the relative value obtained in the foregoing work the apparatus was twice dismantled and reassembled without, however, any change in the suspension. The relative deflections due to the successive insertion into the apparatus of air and CO_2 give, in terms of Harrington's value for air, $1,471.9 \times 10^{-7}$ and $1,472.2 \times 10^{-7}$ as against $1,471.5 \times 10^{-7}$ reported above.

¹ L. J. Lassalle, *PHYS. REV.*, 17, 354, 1921.

² Y. I. Ishida, *PHYS. REV.*, April, 1923.

³ P. Breitenbach, *Wied. Ann.*, 67, 803, 1899.

VII. SLIP DETERMINATIONS.

The experimental procedure in the determination of the coefficient of slip was much the same as that described by Stacy.¹ A viscosity run was first made upon the gas in the apparatus either at atmospheric pressure or at some pressure equivalent to it for viscosity determinations. In order to avoid the temperature disturbances which occurred within the apparatus when it was rapidly evacuated from atmospheric pressure the viscosity determinations were often made at a pressure of from 2 to 10 cms, and the slight slip correction involved in the viscosity at these pressures added. The apparatus was then evacuated as rapidly as possible to some pressure in the range of 0.1 mm to 0.4 mm and as soon as pressure conditions had become steady a second run was taken.

TABLE III.

Slip with Old Shellac Surfaces.

$$\begin{aligned} \eta_{23\text{air}} &= 1822.1, & T &= 175.42 \text{ sec.}, & D &= 235.81 \text{ cms}, \\ \eta_{23\text{CO}_2} &= 1471.1, & K' &= 8.2815 \times 10^{-7}, & k &= 2.815. \end{aligned}$$

Air.

p (mm).	d (cm).	t (sec.).	θ ($^{\circ}$ C).	$\eta_p \times 10^{-7}$.	ζ_p .	$\zeta_{76} \times 10^7$.
.173.....	65.43	30.945	23.05	1675.8	.0309	70.0
.250.....	67.25	30.881	23.02	1718.7	.0212	69.5
.397.....	68.81	30.888	23.46	1759.2	.01295	67.7
.425.....	68.95	30.906	23.11	1763.8	.01160	65.0

Mean ζ_{76} (air) = 68.0×10^{-7} .
 Millikan's theoretical value for a rough surface = 65.9×10^{-7} .
 Difference, + 3 per cent.

CO₂

.460.....	56.42	30.832	22.71	1440.5	.0715	43.2
.459.....	56.59	30.739	23.07	1440.5	.0753	45.4
.260.....	55.60	30.774	23.04	1416.9	.137	46.8
.250.....	55.69	30.789	23.04	1419.9	.129	42.5
.228.....	55.46	30.775	23.03	1413.4	.1425	42.8
.183.....	54.80	30.802	22.95	1397.8	.1860	44.8
.176.....	54.82	30.791	23.20	1397.8	.1880	43.5
.146.....	54.04	30.822	23.30	1379.4	.241	46.3
.142.....	54.16	30.782	23.19	1380.6	.236	44.2
.135.....	53.74	30.795	23.01	1370.5	.2605	46.5
.130.....	53.75	30.775	23.00	1369.9	.2618	44.7
.103.....	52.70	30.943	23.06	1350.5	.318	43.0
.095.....	52.18	30.854	23.03	1333.3	.3665	45.7

Mean ζ_{76} (CO₂) = 44.57×10^{-7} .
 Millikan's theoretical value for a rough surface = 43.2×10^{-7} .
 Difference, + 3 per cent.

¹ Stacy, preceding paper.

In the data given in Table III. the practice was to take two or three runs following each evacuation. Only the first of these is given in the table on air as the rise in the coefficient which occurred on standing at the low pressure was so rapid as to seriously distort the consistency obtained by taking the run as soon as possible after the evacuation. This rise was of the order of 3 per cent an hour in the coefficient of slip, and is attributed as in Stacy's work to the release of occluded gases of lower viscosity from the walls of the vessel and apparatus. A definite rise in pressure at the rate of about 0.001 mm per hour after the first hour was also noticeable.

In the case of the determinations made on carbon dioxide, less trouble was experienced from this effect, and in the data listed in the table the two determinations made after evacuation are listed.

In slip work done with the apparatus before the present investigation was started, the brass surfaces had been treated with a thin coat of shellac. The data in Table III. are for this old shellac surface.

VIII. SLIP DETERMINATIONS ON DIFFERENT SURFACES.

Clean Brass.

The apparatus was completely dismantled and the cylinders washed with alcohol and ether, until the brass surfaces appeared fairly bright

TABLE IV.

Slip with Brass Surfaces—Air Only.
 $k = 2.815.$

p (mm).	d (cm).	d' (cm).	t (sec.).	θ ($^{\circ}$ C).	ζ_p .	$\zeta_{76} \times 10^7$.
.519.....	69.484	71.73	30.800	22.53	.1147	78.3
.511.....	69.531	71.82	30.745	22.34	.1168	78.6
.356.....	68.519	71.675	30.834	22.73	.1638	76.6
.232.....	66.446	71.545	30.918	22.94	.2405	73.6
.175.....	65.859	71.91	30.830	23.81	.326	75.0
.1743.....	65.35	71.49	30.95	22.95	.334	76.6
.163.....	64.994	71.46	30.955	22.70	.354	75.8
.109.....	62.548	71.81	30.864	22.31	.527	75.6
.105.....	62.394	72.10	30.804	23.24	.543	74.9
.0915.....	61.194	71.93	30.774	22.99	.623	74.9
.086.....	60.896	71.98	30.746	22.93	.647	73.2
.0813.....	60.614	72.01	30.724	22.78	.678	71.4

Mean ζ_{76} (air) = 75.4×10^{-7} .

and clean. The coefficient of slip for this clean brass surface was then determined as before. (See Table IV., air only.) The new pumping system and the steel scale described above were used during this and later slip work, and the occluded gas effect was very little noticed in the values obtained for ζ_{76} . In the tables for this later slip work, Tables IV. to VI., the column d' gives the deflection obtained in cms for the gas in the apparatus taken at the equivalent of atmospheric pressure for viscosity immediately before evacuating and reduced to the temperature of the slip run and to the same driving speed as the slip run. The difference in the deflections, which is the measure of slip, is thus evident in each case.

Watch Oil.

The cylinders were then coated with watch oil such as is used in Millikan's oil drop experiments. The oil was applied with a camel's

TABLE V.

Slip with Oil Surfaces.

$k = 2.807$.

Air.

p (mm).	d (cm).	d' (cm).	t (sec.).	θ ($^{\circ}$ C).	ζ_p .	$\zeta_{76} \times 10^7$.
.574.....	69.816	72.02	30.742	22.80	.1131	84.4
.290.....	67.729	72.00	30.693	22.27	.226	85.1
.163.....	65.001	71.98	30.717	23.44	.3877	81.5
.157.....	64.889	72.14	30.710	22.97	.3975	81.1
.129.....	63.344	71.99	30.752	22.70	.490	82.1
.1258....	63.409	72.18	30.724	22.94	.492	80.2
.118.....	62.860	72.10	30.720	22.87	.528	80.9
.107.....	61.995	71.95	30.738	22.59	.577	80.0
.075.....	58.747	72.00	30.729	22.72	.809	78.8

Mean $\zeta_{76} = 81.8 \times 10^{-7}$,
 Millikan's value from oil drop data = 81.36×10^{-7} .

CO₂.

.2219....	55.595	58.20	30.739	22.91	.1722	50.2
.2015....	55.269	58.24	30.694	22.66	.1917	50.6
.1068....	53.015	58.25	30.716	22.98	.352	49.5
.0936....	52.328	58.26	30.705	22.78	.403	49.6

Mean $\zeta_{76} = 50.0 \times 10^{-7}$.
 Lassalle's value from oil drop data = 50.7×10^{-7} .

hair brush in as thick a coat as would hold to a vertical surface and then allowed to run down the vertical cylindrical surfaces over night. Drops collecting at the bottom were then removed and the apparatus assembled. In assembling the outer cylinder was not allowed to come into contact with the inner one in any way for fear of causing some of the oil to bridge the gap between the inner suspended cylinder and its guard rings. During the course of the four following days the determinations of slip given in Table V. were made. During this time there was no indication of any oil bridging the gap in question. This would have been immediately evident in the period of oscillation of the suspended cylinder and in the consistency with which the inner cylinder took up its zero position or its deflection position after displacement. These indications were very carefully watched for and no case of suspected sticking was found.

Scratched Brass.

The watch oil was then removed with benzine and the cylinders carefully washed with alcohol and ether, and an attempt made to roughen the surfaces with a medium grain emery paper (Barton No. 2). Upon this roughened brass surface the determinations of slip listed in Table VI. were made.

TABLE VI.

Slip with Scratched Brass.

$$k = 2.815.$$

Air.

p (mm).	d (cm).	d' (cm).	t (sec.).	θ ($^{\circ}$ C).	ζ_p .	$\zeta_{76} \times 10^7$.
.394.....	68.884	71.66	30.744	22.15	.143	74.0
.321.....	69.053	72.41	30.735	22.67	.173	73.0
.2822....	68.087	71.95	30.749	22.51	.2015	74.7
.277.....	67.902	71.67	30.757	22.31	.195	71.8
.141.....	64.514	71.45	30.855	22.36	.382	70.9
.135.....	63.254	71.91	30.722	22.51	.485	72.5

$$\text{Mean } \zeta_{76} (\text{air}) = 72.8 \times 10^{-7}.$$

CO₂.

.359.....	56.561	57.91	30.762	22.40	.0845	40.0
.316.....	56.241	57.91	30.758	22.43	.105	43.7
.107.....	53.424	57.93	30.742	22.42	.300	42.2
.0895....	52.678	57.88	30.780	22.43	.350	41.3

$$\text{Mean } \zeta_{76} (\text{CO}_2) = 41.8 \times 10^{-7}.$$

In the slip constant of the instrument,

$$k = 2 \frac{b^3 + a^3}{ab^3 - a^3b},$$

the thickness of the oil layer on the cylinders must be allowed for as changing the effective radii of the cylinders. It is evident from the formula that the oil layers are effective through the factor $(b - a)$ in the denominator to the extent that each added surface layer 0.01 mm thick increases k by about 3 parts in 2,000. It is also evident that the viscosity constant of the apparatus

$$K = \frac{b^2 - a^2}{a^2b^2l}$$

is decreased in the same ratio. From this latter effect on the viscosity (using air) an estimate of the probable thickness of the oil layer was obtained. A change of three tenths of a per cent was found as due to the oil layer, which is about the effect that would result from a coat of oil on each surface 0.01 mm thick. In the results given in the table on oil surfaces this change has been allowed for.

IX. DISCUSSION OF RESULTS.

The error involved in any single determination of the coefficient of slip is that of determining a difference between two apparent viscosities, and as such is dependent on the accuracy with which each of the two viscosity determinations can be made. The agreement shown in Tables I. and II. is evidence that even where the gas content of the apparatus is changed between determinations and the individual values involve temperature, angular speed of rotation and deflection, the individual values differ less than one part in two thousand from a mean. On the basis of this maximum error in both of the viscosity determinations used to compute a single value of slip, this value may be in error as much as 3.0 per cent if the slip run is in air at 0.4 mm pressure, 1.5 per cent if at 0.25 mm pressure, and 1.0 per cent if at 0.15 mm pressure. For carbon dioxide the errors possible at these pressures are twice those for air. The values of the coefficient of slip obtained show an agreement among themselves well within this allowance. It is noticeable in the tables that at the higher pressures the values computed are considerably further from a mean than at the lower.

On the above consideration it might seem justifiable to weight each individual value according to the size of the difference from which it was obtained. This discrimination in favor of the lower pressures is thought

not altogether justified, for the idea of this coefficient of slip is, as taken over from hydrodynamics, merely a first approximation valid only as the decreasing external friction begins to be a factor. It is also to be noted that for a pressure of 0.1 mm the distance between the two cylindrical surfaces amounts to but ten mean free paths of air, and that when carbon dioxide is used, ten mean free paths correspond to a pressure of about 0.07 mm.

The justification of the reduction of the coefficient of slip to the coefficient at atmospheric pressure lies in the individual values of ζ_{76} thus obtained being independent of the pressure from which they were obtained. Upon the consideration of the errors incident to the determinations at the higher pressures used, which have just been given, it will be seen that the range of values of ζ_{76} obtained in any one of the tables does not constitute evidence of the dependence of ζ_{76} on pressure. In Table III. the values of ζ_{76} are least as obtained from higher pressures, the widest departures coming at the highest pressures where the errors must be greatest. The direction of these departures is seen to be the reverse in this table from that found in Table V., for example. In general, however, it will be seen that the higher pressures are not consistent in indicating any particular direction of departure from the mean value of ζ_{76} , and the departures all fall within the limits of the errors expected at the particular pressure used. For pressures below 0.1 mm this is not true, for there seems to be a tendency of the values of ζ_{76} to fall off as the pressures are made lower than about this value. In view of the possible changes in the character of the gas at the extremely low pressures and the fact that the distance between the cylinders and the mean free path become comparable at the lower pressures, it has been somewhat arbitrarily decided to draw the lower limit of the region from which the value of the coefficient of slip is here obtained at about 0.1 mm for air and about 0.08 mm for CO_2 . Accordingly the means of the values of slip obtained in this region are listed together in Table VII. and presented as the values of the coefficients of slip of air and of carbon dioxide for the surfaces used.

The results shown in Table VI. may seem at first somewhat inconsistent since the mean value of ζ_{CO_2} for the scratched brass is there given as 41.8×10^{-7} while the lower theoretical limit is 43.2×10^{-7} . However, as indicated above, the experimental error with CO_2 is such that both the value found for the old-shellac surface, viz., 44.6×10^{-7} , and that for the scratched brass are, within that error, identical with that corresponding to a rough body, viz., 43.2×10^{-7} . That the same scratched surface was not quite rough with respect to *air* shows again the dependence of the character of the reflection upon *the nature of the gas*.

The definite variation of external friction with the character of the surface shows with great conclusiveness that the law which governs the return of gas molecules from the surface against which they strike must be different for different surfaces. If diffuse reflection were a general phenomenon there would be no possibility of a variation of ζ with the character of the surface. There must then be some relation between the direction of the molecules to and away from the surface. Maxwell explained the possible differences in external friction of a gas as due to the diffuse reflection of a part of the molecules from the walls of the containing vessel, and to the specular reflection of the remainder, the coefficient of slip taking higher values as the fraction reflected specularly is greater. From this it would be concluded that the oil surface presents a "smoother" surface to both air and carbon dioxide than does either of the other surfaces used. Furthermore, from a computation of the factor $(2 - f)/f$ which appears in the formula for the external friction following Maxwell (where f is the per cent of total incident molecules reflected diffusely) using only the ratios of the slip coefficients listed in Table VII., the watch oil surface is seen to be from four to seven per cent more specular to air than to carbon dioxide, the scratched brass surface from eight to fifteen per cent more, and the old-shellac surface about equally specular to the two gases.

X. COMPARISON WITH THE SLIP RESULTS OF OTHER OBSERVERS.

As shown in the tables, from his oil drop experiments Millikan¹ has obtained for the value of ζ_{76} for this same oil and air 81.4×10^{-7} , in place of my value 81.8, while Lassalle's² work with the oil and CO₂ yielded 50.7×10^{-7} in place of my 50.0. Both of these are then in remarkable agreement with the present values. Also Ishida³ obtained for oil and air 81.2×10^{-7} also in close agreement, but for the CO₂ and oil, his value, namely 52.3×10^{-7} , is slightly higher than mine. These comparisons are

TABLE VII.

Mean $\zeta_{76} \times 10^7$.

	Air.	CO ₂ .
Theoretical lower limit	65.9	43.2
Old shellac	68.0	44.6
Clean brass	75.4	
Scratched brass	72.8	41.8
Watch oil	81.8	50.0

¹ Millikan, *PHYS. REV.*, 2, 139, 1913.

² Lassalle, *loc. cit.*

³ Ishida, *loc. cit.*

made with the oil drop work by reducing the constant "A" in that work to ζ_{76} by multiplication by the value of l as computed from the equation $\eta = 0.3502nm\bar{c}l$. The same general discrimination of the oil surface between the molecules of air and carbon dioxide is seen in the above values from the oil drop as from the present work.

In conclusion the author wishes to acknowledge his indebtedness to the staff of Ryerson Laboratory, and in particular to Professor Millikan under whose direction the problem was undertaken, for constant and helpful interest and advice during the progress of the work.

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September 22, 1922.¹

¹The work described above was completed in August, 1921.