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COEFFICIENTS OF SLIP IN GASES AND THE LAW OF REFLECTION OF MOLECULES FROM THE SURFACES OF SOLIDS AND LIQUIDS.

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ABSTRACT.

First order correction term to Stokes Law of fall of droplets.—(1) *Empirical.* The experiments by which the value of the electronic charge was determined by the droplet method gave consistent results only when this law was modified by the factor $(1 + Al/a)$, where l/a is the ratio of mean free path to radius of droplet. (2) *Hydrodynamic theory* gives as a first approximation $(1 + \xi/a)$, where ξ is the coefficient of slip. (3) *Kinetic theory* gives $(1 + 0.7004l/a)$ in case all the molecules are diffusely reflected from the surface of the droplet, where l is defined by the relation $\eta = .3502\rho\bar{c}l$. If, however, the fraction reflected diffusely is f, the fraction $(1 - f)$ being specularly reflected, then the factor is $[1 + 0.7004(2/f - 1)(l/a)]$. The theory developed by Cunningham gave the numerical constant as 0.79, but this value is too high since experimental values of A nearly as low as 0.70 have actually been obtained.

Coefficient of slip between gases and solids.—(1) *Stokes' law method.* Since $\xi = Al$, ξ may be computed directly from A. (2) *Rotating cylinder method* of determining viscosity is also capable of giving values of ξ accurate to one per cent. If θ_0 is the limiting deflection for high pressures, and θ the deflection for a low pressure, then ξ for that low pressure is $(\theta_0 - \theta)/K$, where K is a geometrical constant of the apparatus. Values obtained by this method agree closely with those obtained by the first method. (3) *Capillary effusion method.* If the rate of flow of gas for unit pressure difference is T_0 for high pressures and T for a low pressure, then ξ for that low pressure is $R(T - T_0)/4T_0$, where R is the radius. (4) *Values of ξ/l vary with the surface,* for instance from 0.70 for air-mercury, and 0.87 for air-oil and air-glass, to 1.07 for air-fresh shellac. They also *vary with the gas,* for instance from 0.81 for hydrogen-oil and 0.82 for CO_2-oil to 0.86 for air-oil, and 0.90 for helium-oil.

Coefficient of diffuse reflection of gas molecules, determined from the relation $A = (2\eta/\rho\bar{c})(2/f - 1)$ gives values of f which *vary with the surface* from 0.79 for air-fresh shellac and 0.89 for air-glass to 1.00 for air-mercury. The values also *vary with the gas* from 0.87 for helium-oil and 0.895 for air-oil to 0.92 for CO_2-oil and hydrogen-oil. The values are for 23° C.

1. INTRODUCTION.

IN 1911[1] it was first shown that the so-called "oil-drop method" was capable of yielding not only a measurement of the electron, but also a determination of the "*coefficient of slip*" between a gas and the surface of a liquid or solid, which was of a sufficient degree of precision to justify the hope that it would be possible with its aid to settle definitely some of the interesting and important problems of the kinetic theory which had absorbed the attention of Maxwell, Kundt and Warburg and others half a century ago but which have been since then matters of dispute for the reason that the experimental technique of that day was insufficiently precise to permit of definitive conclusions. Since the results which have followed from a careful pursuit of these problems by the oil-drop method and by a new one quite as accurate which is presented herewith, are in some particulars at variance with a considerable amount of preceding work, some of it theoretical and some experimental, the theoretical considerations which are here involved will be quite fully restated for the sake of facilitating a critical analysis by others. An attempt will also be made to present the development of ideas in this field in its correct historical sequence.

2. THE OIL-DROP METHOD OF MEASURING SLIP.

If e_n is the charge on a spherical particle falling first with speed v_1 under the influence only of the gravitational pull mg and then rising against gravity with a speed of v_2 in a vertically directed electric field of strength F, the equation which is nothing more than the expression of the fact that the velocity of the particle is proportional to the acting force—a fact about which in the case of small enough drops there can not be the slightest uncertainty, since it has been rigorously and accurately proved both theoretically and experimentally—is

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \quad \text{or} \quad e_n = \frac{mg}{F}\frac{(v_1 + v_2)}{v_1}. \qquad \checkmark(1)$$

Equally certain may we be about the correctness of Stokes' hydrodynamical equation

$$X = 6\pi\eta a v, \tag{2}$$

provided it be assumed that the medium is homogeneous and that there is no slip between it and the surface of the sphere. Making this assumption, for the moment, and combining (2) with the equation expressing the relation between mass, density, and volume, viz.,

$$X = mg = \tfrac{4}{3}\pi a^3(\sigma - \rho)g, \tag{3}$$

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[1] PHYSICAL REVIEW, 32, 382, 1911.

there results at once the usual form of Stokes' law of fall, namely,

$$v = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho). \tag{4}$$

From 1, 3 and 4 there then follows at once

$$e_n = \frac{4}{3}\pi\left(\frac{9\eta}{2}\right)^{3/2}\left(\frac{\mathrm{I}}{g(\sigma - \rho)}\right)^{1/2}\frac{(v_1 + v_2)v_1^{1/2}}{F}, \tag{5}$$

which gives the charge upon the droplet in terms of the velocity $(v_1 + v_2)$ and otherwise accurately known quantities.

The most characteristic and most significant fact brought to light by the oil-drop method was that $(v_1 + v_2)$ could be made to take on a series of values constituting an arithmetical progression and having a greatest common divisor $(v_1 + v_2)_0$ which corresponds then to a charge of one electron upon the droplet, so that the equation

$$e_1 = \frac{4}{3}\pi\left(\frac{9\eta}{2}\right)^{3/2}\left(\frac{\mathrm{I}}{g(\sigma - \rho)}\right)^{1/2}\frac{(v \quad + v_2)_0}{F}v_1^{1/2} \tag{6}$$

is the value of the electronic charge provided only the assumptions made in (2) of homogeneity in the medium and no slip, are correct.

Now the fact which was brought to light as soon as these experiments were tried, in the fall of 1909, was that e_1 did not come out a constant when droplets of different rates of fall and therefore of different radii were used in air at atmospheric pressure; but, instead, while perfect consistency was obtained in working on different droplets having the same rate of fall, the larger (more rapidly falling) drops gave consistently smaller values of e_1 than did the smaller drops. Indeed the apparent value of e_1 pushed up quite continuously about 10 per cent as the times of fall per cm increased from 5 to 50 seconds. This clearly meant that the smaller droplets fell more rapidly than in accordance with the requirements of Stokes' law because, as they diminished in size, they began to fall, so to speak, more and more nearly freely between the holes of the medium, *i.e.*, between the molecules of the air.

However, at the time at which these experiments were first performed (in the fall of 1909) there was available no theoretical work whatever as to the correct law of motion of a spherical droplet through a gaseous medium, with which (2) might be replaced. The procedure followed therefore was to seek to obtain wholly empirically a correction term to Stokes' law which should take into account the inhomogeneities in the gaseous medium. Since the size of the inhomogeneities had the linear dimensions of the mean free path l, while the corresponding linear dimension of the drop had to be proportional to its radius a, the correction which was to be applied to Stokes' law had evidently to be a function of the argument l/a, and in order to fit the experimental data, or for that matter to satisfy obvious theoretical considerations, it had to be applied in such a way as to cause the speed to increase as l/a increased. Therefore a corrected form of Stokes' law which would take into account any kind of increase in speed due to the gaseous inhomogeneities could clearly be written as follows:

$$X = 6\pi\eta a v \left\{ 1 + f\left(\frac{l}{a}\right) \right\}^{-1}, \tag{7}$$

for this simply adds to Stokes' law a correction term of unknown form in l/a but in such a way as to make v increase as l/a increases. In the absence of information as to the form of $f(l/a)$ we could evidently express it, as pointed out in earlier papers, in terms of the undetermined constants A, B and C, etc., by writing

$$f\left(\frac{l}{a}\right) = 1 + A\frac{l}{a} + B\frac{l^2}{a^2} + C\frac{l^3}{a^3}, \text{ etc.,}$$

and *so long as attention is confined to sufficiently small departures from Stokes' law* it is clearly legitimate to neglect second-order terms in l/a and therefore to write

$$X = 6\pi\eta a v \left\{ 1 + A\frac{l}{a} \right\}^{-1} \tag{8}$$

or

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\eta}\left\{ 1 + A\frac{l}{a} \right\}. \tag{9}$$

Using this form of equation to combine with (1) and denoting now by e the absolute value of the electron and by e_1, as above, the apparent value of this charge obtained from the use of (4) rather than of (9) there resulted at once

$$e\left(1 + A\frac{l}{a}\right)^{3/2} = e_1 \quad \text{or} \quad e^{2/3}\left(1 + A\frac{l}{a}\right) = e_1^{2/3}. \tag{10}$$

If then we knew a for all of our droplets, since l was known, we could obtain e_1 from (6) and then plot a curve connecting l/a and $e_1^{2/3}$. It is clear too from the form of (10) that this curve would necessarily be a straight line so long as the observational data were confined to a region in which the neglecting of the higher terms in the expansion of $f(l/a)$ was legitimate. *How far this would be true could only be determined by examining the curve itself.* The slope of that straight line would then clearly be A and the intercept of this line on the $e_1^{2/3}$ axis would be $e^{2/3}$.

In the preceding papers $e^{2/3}$ has been the sole object of concern, and the straightness of the line has been found to hold much farther than a most satisfactory determination of the value of the intercept demanded. In this paper, on the other hand, attention is directed solely to the constant A, to its accurate measurement and to its significance.

Since l itself is incapable of precise evaluation, but since with a given gas it is always inversely proportional to pressure, I have in later papers preferred to write (10) in the form

$$e^{2/3}\left(1 + \frac{b}{pa}\right) = e_1^{2/3} \tag{11}$$

and then to plot $e_1^{2/3}$ against $1/pa$, thus determining the constant b instead of A. With this procedure, by directly measuring $e_1^{2/3}$ for different drops at the same pressure, or for the same drop at different pressures, or both, and by plotting the different values of $e_1^{2/3}$ thus obtained against $1/pa$, it became possible to obtain b (or A, since $A = b/pl$) wholly empirically, and thus to find by direct experiment and with much precision the law of fall which must replace Stokes' law when the droplets become so small that the inhomogeneities in the gaseous medium begin to cause that law to fail. *There could be no uncertainty about the correctness of this procedure if a and p were known with enough accuracy, and if the observational data were confined to a region close enough to that in which Stokes' law was found valid.* It was by this empirical procedure that the first term of the proper correction to Stokes' law of fall of a droplet of oil through air was finally found to have the exact numerical value given in (12),

$$X = 6\pi\eta av\left(1 + .864\frac{l}{a}\right)^{-1}, \tag{12}$$

provided that l is defined by $\eta = .3502\rho\bar{c}l$. Also this law was found to be correct up to $l/a = .5$, at which point a second correction term to Stokes' law became necessary.

In the foregoing work in order to determine a with any required degree of precision, the method of successive approximations was used. Thus the rigorously correct equations 1 and 3 (when reduced by the evaluation of the greatest common divisor of the speeds, so as to correspond to a single charge upon the drop) were solved for a, thus giving

$$a = \sqrt{\frac{3Fe}{4\pi g(\sigma - \rho)}\frac{v_1}{(v_1 + v_2)_0}} \tag{13}$$

and an approximately correct value of e inserted in this equation. This gave, in view of the cube-root sign, a series of values of a containing errors of but one third that contained in the assumed value of e and with which therefore a value of e containing only a very minute error was obtained. With this new value of e in turn a new series of values of a containing only wholly inappreciable errors could be computed with the aid of (13) and the final value of e then obtained from the intercept.

I have thus far shown merely how the constants A and b in (10) and (11) were empirically determined. But it remains to show what is their significance from the standpoint of the hydrodynamical concept of slip. In hydrodynamical theory the modified form of Stokes' law which takes into account surface slip[1] is

$$X = 6\pi\eta av \left\{ \frac{1 + 2\gamma}{1 + 3\gamma} \right\} \tag{14}$$

or

$$v_1 = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho) \left\{ \frac{1 + 3\gamma}{1 + 2\gamma} \right\}, \tag{15}$$

in which γ is defined by the equation

$$\gamma = \frac{\eta}{a\epsilon} = \frac{\zeta}{a}, \tag{16}$$

ϵ being called *the coefficient of external friction*, and the ratio of the internal to the external coefficient of friction $\eta/\epsilon = \zeta$ being called *the coefficient of slip*.

If the last factor in (16) is expanded in powers of γ into

$$1 + \gamma + 2\gamma^2 + 4\gamma^3, \text{ etc.},$$

then we may neglect powers of γ higher than the first, provided γ is kept sufficiently small. But γ can be kept as small as we please so long as we confine attention to the region which has been under consideration in all which has preceded, namely the region in which Stokes' law is just beginning to break down because the medium is just beginning to be sufficiently inhomogeneous so that the phenomenon of slip is just beginning to appear. Then (15) becomes

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\eta}(1 + \gamma), \tag{17}$$

which is identical with the empirical equation (9). It is thus seen that $\gamma = \zeta/a = Al/a$, that is, that

$$\zeta = Al. \tag{18}$$

In other words the oil-drop method of determining e, which consists in plotting a series of values of $e_1^{2/3}$ taken on different droplets at different

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[1] See Basset's Hydrodynamics, Vol. II., p. 271.

pressures against $1/pa$, and finding the intercept on the $e_1^{2/3}$ axis, *i.e.*, finding the limit toward which $e_1^{2/3}$ tends as pa becomes infinite, is simply equivalent to graphically reducing the medium to a condition of infinite pressure in which the holes (inhomogeneities) are all squeezed out, and in which therefore Stokes' hydrodynamical equation is rigorously valid. This removes all uncertainty from all of the equations upon which the determination of e depends. It is of course assumed in the foregoing that the sole cause of slip in gases is found in molecular inhomogeneities, but if this were not true Stokes' unmodified law would not hold accurately in dense media *as it is found experimentally to do.*

Similarly the slope of the $e_1^{2/3}$, $1/pa$ *line close to the intercept, where the* γ *of* (17) *is just as small as we please, must correspond to a region in which the hydrodynamical theory underlying Basset's equation is rigorously applicable and therefore where it is rigorously correct to identify* γ *with* Al/a *or* ζ *with* Al.

From the hydrodynamical theory of slip alone we should not expect an equation of the form of (17) to remain valid through a large range of values of $1/pa$, *i.e.*, far from the region in which Stokes' law is valid. But in the case of gases this theory is applicable only to very small values of $1/pa$ so that we need not be concerned because the $e_1^{2/3}$, $1/pa$ line is actually found to remain straight, and an equation of the form of (17) to hold for a surprisingly long range of values of $1/pa$. This is merely a fortunate circumstance which makes it possible to determine coefficients of slip between gases and liquids and gases and solids with much certainty and precision by the oil-drop method. Without this fortunate circumstance the precision of this method of measuring slip would be greatly impaired. The slope of the $e_1^{2/3}$, $1/pa$ line is indeed theoretically identifiable with slip only very close to the intercept with the $e_1^{2/3}$ axis, but since that slope is *in fact* constant up to very appreciable values of $1/pa$ we are not concerned, when determining slip by the oil-drop method, with whether the hydrodynamical theory of slip accounts for the length of this straight line or not; for we are well aware that the physical conditions underlying this hydrodynamical theory of slip are no longer satisfied near the upper end of this line.

To recapitulate then, we have proved that since the coefficient of slip ζ is equal to Al and since from (12) A for oil and air is .864 and l at 23° and 76 cm for air is computed from $\eta = .3502\rho\bar{c}l$ to have the value .000009417 cm, the coefficient of slip between air at 23° C, 76 cm and oil is

$$\zeta_{\text{air } 23^\circ,\, 76 \text{ cm}} = .864 \times .000009417 = 0.000008136. \tag{19}$$

For drops of radii from .0001 cm up to .0006 cm which is about the range with which we are practically concerned $\gamma = \zeta/a$ would have a value varying from 1/12 to 1/70, so that the complete justification for dropping higher powers of γ than the first will be evident.

The foregoing procedure may then be used with entire confidence for finding the coefficient of slip between any gas and a liquid or solid to which the oil-drop method of experimentation is applicable.

3. THE KINETIC THEORY OF SLIP IN GASES.

But there is an altogether general relation between the coefficient of slip and the law of reflection of gaseous molecules which may be obtained as follows.

To begin with the simplest possible case, assume a gas streaming slowly through a tube and let it be assumed at first that the gaseous molecules impinging upon the surface of the tube are "diffusely reflected," *i.e.*, are wholly absorbed and later reëmitted so that the direction of exit of a molecule from the surface bears no relation whatever to its direction of impact upon the surface. Familiar kinetic-theory considerations show that the number n of molecules impinging per second upon 1 square centimeter of surface in a gas at rest is given by

$$n = \tfrac{1}{4}n\bar{c}, \tag{20}$$

in which n is the number of molecules per c.c. and $\bar{c}$ is their average velocity of agitation. This is a perfectly general relation quite independent of the validity of any particular law of distribution of molecular velocities, and the error due to slow streaming motion is negligible.

If now the impinging molecules be assumed to have an average or mass motion parallel to the surface of velocity v (which is exceedingly small compared to $\bar{c}$), then obviously the tangential momentum communicated to the wall per second by the impact of the $\frac{1}{4}n\bar{c}$ molecules upon it is

$$\tfrac{1}{4}n\bar{c}mv, \tag{21}$$

but if the *impinging* molecules have the average tangential velocity v, since the *layer of the gas* which is next to the surface is made up half of molecules entering that surface with the tangential velocity v, and half of molecules leaving that surface with the average tangential velocity which, according to our assumption, is zero, the *average* tangential velocity v_0 of the layer of gas next the wall is given by $v_0 = v/2$ and the expression for the tangential momentum given to the wall per second per square centimeter in terms of this mean velocity of the surface layer of gas is $\frac{1}{2}nm\bar{c}v_0$. But this expression, which is equal to the tangential force in dynes acting on each square centimeter, when it has been divided by v_0, is, by definition, the coefficient of external friction ϵ so that we have

$$\tfrac{1}{2}nm\bar{c} = \epsilon. \tag{22}$$

Therefore the coefficient of slip is given by

$$\zeta = \frac{\eta}{\epsilon} = \frac{.3502nm\bar{c}l}{.5nm\bar{c}} = .7004l,^{1} \tag{23}$$

or since l when computed from the equation used above, namely $\eta = .3502nm\bar{c}l$, is at 23° C, 76 cm .00009417, *the numerical value of the coefficient of slip between air at 23°, 76 cm and a surface which reflects its molecules wholly "diffusely" is given by*

$$\xi_{(\text{air } 23°,\ 76)} = .7004 \times .00009417 = .000006595. \tag{24}$$

The fact that this is considerably less than the observed value of the slip found in (19) *can only mean that the assumption of diffuse reflection is incorrect in the case in hand: namely air and oil. This result furnishes the complete justification for Maxwell's introduction of the coefficient* f which he defined as the fraction of the total number of impinging molecules which are "absorbed and afterwards evaporated,"[2] the fraction $(1 - f)$ being then taken as the portion which is specularly reflected. The existence of this fraction f merely means that there is a measurable tendency for molecules which impinge at a given angle upon the surface in question to be reflected so as to make the angle of incidence equal to the angle of reflection, and that the actual distribution of reflected molecules, all of which are incident at a given angle, can be *reproduced* by mixing a fraction f of diffusely reflected molecules with a fraction $1 - f$ of specularly reflected molecules. The theoretical evaluation of Maxwell's f from the measured coefficient of slip may be made, in accordance with the mode of approach used above, as follows.

If only the fraction f of the *impinging* molecules is absorbed, the momentum communicated to the wall, in terms of f and the average tangential velocity v of all the impinging molecules, is

$$\tfrac{1}{4}mn\bar{c}fv. \tag{25}$$

But the average tangential velocity v_0 of the *surface* layer of molecules, since it is made up of $\frac{1}{4}n\bar{c}$ impinging molecules of tangential velocity v, and of $\frac{1}{4}n\bar{c}(1 - f)$ returning molecules, also of tangential velocity v, and of $\frac{1}{4}n\bar{c}f$ returning molecules of tangential velocity zero, and since the total number of molecules in this layer is the sum of those going in

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[1] This is precisely the result obtained by Kundt and Warburg (Pogg. Ann., 155, p. 547, and 159, p. 401, 1876), and by Maxwell, Scientific Papers, Vol. II., p. 709, save that these authors used slightly different value of the constant .3502. This, however, does not change the numerical value of the slip, if only the same constant is used as, of course, it should be in the evaluation of l.

[2] Maxwell, Scientific Papers, Vol. II., p. 705.

and those coming out, namely $\frac{1}{2}n\bar{c}$, is given by

$$v_0 = \frac{\{\frac{1}{4}n\bar{c} + \frac{1}{4}n\bar{c}(1 - f)\}v + \frac{1}{4}n\bar{c}f \times 0}{\frac{1}{2}n\bar{c}};$$

$$\therefore \quad v_0 = \left(1 - \frac{f}{2}\right)v \qquad \text{or} \qquad v = \frac{v_0}{\left(1 - \frac{f}{2}\right)} \tag{26}$$

Substituting this value of v in (25) and then writing the definition of ϵ, namely

$$\tfrac{1}{4}mn\bar{c}f \frac{v_0}{\left(1 - \frac{f}{2}\right)} = \epsilon v_0, \tag{27}$$

there results

$$\zeta = \frac{\eta}{\epsilon} = \frac{.3502mn\bar{c}l}{\frac{1}{4}mn\bar{c}\left(\frac{f}{1 - \frac{f}{2}}\right)} = .7004l\left(\frac{2}{f} - 1\right)^{[1]} \tag{28}$$

or since

$$\zeta = Al, \qquad f = \frac{1.4008}{A + .7004} \tag{29}$$

Inserting in (29) the observed value of A for air and oil at 23° C, 76 cm, viz., .864, we obtain

$$f = .895.$$

Therefore, when the molecules of air impinge upon oil at a given angle, $89\frac{1}{2}$ *per cent of the impinging molecules are diffusely reflected (absorbed and reëmitted) and* $10\frac{1}{2}$ *per cent are specularly reflected.* The foregoing method of finding f should be altogether valid so long as $2/f$ is not very large in comparison with unity. As f approaches zero, however, ζ becomes large and the procedure used in reducing (15) to (17) becomes invalid.

4. SIGNIFICANCE OF VARIATIONS IN A WITH THE NATURE OF THE GAS.

Although equations (28) and (29) appear to involve the assumption that the constant k of the viscosity formula $\eta = k\rho\bar{c}l$ has the value .3502, the value of f obtained from the use of (28) is quite independent of any assumption whatever as to the value of k provided only that in the computation of A from

$$\zeta = \frac{b}{p} = Al$$

the value of l used is obtained from $\eta = .3502\rho\bar{c}l$ as it should be. That

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[1] This form again is the same as that found by Maxwell, see Scientific Papers, Vol. II., p. 709, save for the use of 1/3 by him in place of .3502.

this is true may be seen by writing (23) and (28) in the forms

$$\zeta_0 = \frac{\eta}{\epsilon} = \frac{2\eta}{\rho\bar{c}} = \frac{2k\rho\bar{c}l}{\rho\bar{c}} = 2kl \tag{30}$$

and

$$\zeta_f = 2kl\left\{\frac{2}{f} - 1\right\}. \tag{31}$$

From which

$$\zeta_f = \zeta_0\left\{\frac{2}{f} - 1\right\}$$

or

$$f = \frac{2\zeta_0}{\zeta_f + \zeta_0}, \tag{32}$$

in which ζ_0 is seen from (30) to have the value $2\eta/\rho\bar{c}$, an expression quite independent of k and all of whose terms are accurately known. This shows that if we have any means whatever of measuring ζ_f we may substitute the measured value in (32) and solve for f.

Now the oil-drop slope b/p is a direct measure of ζ_f since we had $\zeta_f = b/p = Al$. Also since $\zeta_0 = A_0l$, ζ_0 being assumed to be measured with the same gas on a perfectly diffusing surface, it will be seen from (30) and (32) that

$$f = \frac{2\zeta_0}{\zeta_f + \zeta_0} = \frac{2A_0}{A + A_0} = \frac{4k}{A + 2k}. \tag{33}$$

But since A is obtained from the slope b/p by means of

$$A = \frac{b}{pl} = \frac{b}{p}\frac{k\rho\bar{c}}{\eta} \tag{34}$$

we have

$$f = \frac{4k}{A + 2k} = \frac{4k}{\dfrac{bk}{p}\dfrac{\rho c}{\eta} + 2k} = \frac{4}{\dfrac{b}{p}\dfrac{\rho\bar{c}}{\eta} + 2}. \tag{35}$$

Thus f is a constant for different gases if $(b/p)(\rho\bar{c}/\eta)$ is a constant; also if $(b/p)(\rho\bar{c}/\eta)$ is constant, then this expression multiplied by any quantity whatever which is *assumed* to be the same for all gases (as was the $k = .3502$ used above) is also a constant.

Hence if A in (9) and (10) is found to come out a constant for different gases f is also the same for the different gases, and if A varies from gas to gas f also varies. *In other words the present experiments throw no new light whatever upon the proper value of the kinetic theory constant k but they are altogether unambiguous in their significance as to f.*

5. THE CORRECT FORM OF THE FIRST ORDER CORRECTION TERM TO STOKES' LAW OF FALL.

We are now in position to obtain the general form of the first order correction term to Stokes' law. For since (17) rests upon an unimpeachable hydrodynamical basis so long as ζ/a is small and since in (17) we have proved that for this case

$$\gamma = \frac{\zeta}{a} = \frac{Al}{a}$$

and also that in general

$$\zeta = .7004l\left(\frac{2}{f} - 1\right), \tag{36}$$

it follows that the correct numerical form of the equation which should replace Stokes' law when l/a becomes so large that this law just begins to fail is

$$X\left\{1 + .7004\left(\frac{2}{f} - 1\right)\frac{l}{a}\right\} = 6\pi\eta a v$$

or

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\eta}\left\{1 + .7002\left(\frac{2}{f} - 1\right)\frac{l}{a}\right\}. \tag{37}$$

It is interesting to compare this equation with that deduced from purely theoretical considerations by Cunningham[1] in 1910, in which the correction term to Stokes' law takes the form[2]

$$1 + \frac{1.63\frac{l}{a}}{1 + f} \tag{38}$$

It is not at all surprising that this does not agree with (37) when $f = 0$, for, as indicated above, (37) could not hold for that case anyway—a case of no practical interest since nothing like it occurs in nature. But it *is* significant that for the case of diffuse reflection ($f = 1$) Cunningham's numerical coefficient is .815 when (36) indicates that it should be .7004. The discrepancy is not quite so bad when Cunningham's equation is freed from a slight error which, as I pointed out in a footnote in PHYSICAL REVIEW, 32, 380, 1911, crept into it because of a confusion of $\bar{c}$ with $\sqrt{\bar{c}^2}$. When this error is eliminated and when l is obtained, as in all the foregoing from $\eta = .3502p\bar{c}l$, the numerical coefficient in that equation becomes .788 instead of .815. But even this is more than 10 per cent higher than it should be if (37) is valid.

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[1] Cunningham, Proc. Roy. Soc., Series A, Vol. 83, p. 360, 1910.

[2] The notation used by Cunningham in his paper is the reverse of that introduced by Maxwell, f and $1 - f$ being interchanged. The form in (38) is Cunningham's when reduced to Maxwell's notation.

It was because of this discrepancy that I undertook two rather elaborate series of experiments designed to test in wholly independent and different ways the validity of equation (37) and the interpretation which has been placed upon the divergence between the numerical constants in (19) and (24).

6. Oil-Drop Tests of Equation (37).

The first definite experimental evidence which was found in favor of the correctness of (37) came when the nature of the droplet was changed without changing the nature of the gas. Thus, the curves labelled I., III. and IV. in Fig. 1 represent measurements made in air upon droplets of oil, mercury and shellac respectively. The values of A for these three lines are .842, .708, and 1.078 respectively and the corresponding values of $\zeta_{23°,76}$ are .00000793, .00000667, and .0000101.

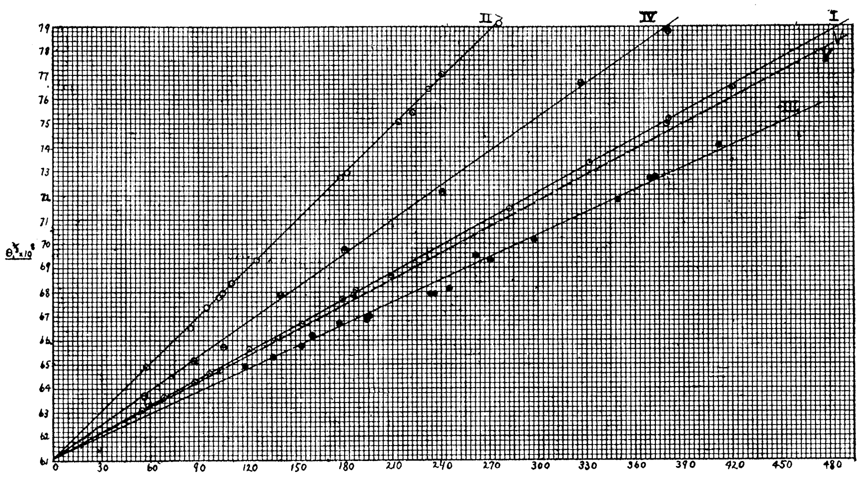

Fig. 1. $e_1^{2/3}$ x10^8 as a function of $1/pa$.

Although, under the conditions prevailing at the time these experiments were made, the error in the slopes may possibly be as much as 3 per cent (indeed the value of A for air-oil is here 2.5 per cent lower than my most reliable determination, Phil. Mag., Vol. XXIX., p. 12, 1917, which reduced the probable error in A to about 1 per cent) yet the differences between these slopes are so large as to leave open no escape from the conclusion *that the nature of the surface exerts a very important influence upon A and therefore upon the tendency of the molecules to be specularly reflected.*

It is very interesting, too, to observe that the value of A for air-mercury, namely .708, has practically reached the lowest limit permitted by (37) which in the case of diffuse reflection ($f = 1$) is seen to be .7004. This observed value is more than 10 per cent lower than the lowest possible value permitted by Cunningham's equation.

I am disposed to connect the attainment of diffuse reflection in the case of droplets of mercury with the powerful molecular (cohesive) field possessed by this substance. This would result in the condensation and reëvaporation of the surrounding gas—a condition which is equivalent to diffuse reflection as the latter term is used by Maxwell.

The organic substances oil and shellac might be expected to have very much weaker molecular fields and to condense the gas much less completely than mercury, as they are in fact here seen to do. It is possible, however, that the cause of the low value of A for mercury is to be found rather in the roughening of the surface by oxidation than in the high value of the molecular constant. I have found no substance which shows a higher value of A than does fresh shellac.

But again Fig. 1 also shows that the nature of the gaseous molecule as well as the nature of the reflecting surface may exert an influence upon the tendency to specular reflection. For curve II (Fig. 1) represents a series of experiments which I made on oil drops in hydrogen. This slope, when divided by the ratio of the mean free paths of the molecules of hydrogen and air, namely 1.845, is shown in the dotted line labelled V. It is 3.3 per cent lower than the value of the slope for the air-oil line, *i.e.*, it gives for hydrogen-oil $A = .815$ against .842 found in this experiment for air-oil and .864 which I regard as the correct value for this combination. The difference is considerably larger than the estimated observational error. The evidence is then fairly good that *hydrogen shows a slightly larger tendency to specular reflection on oil than does air.* Also according to the best measurement on CO_2 and oil, the value of A for this combination is close to .82. Three different observers, working with my apparatus, have found it about 4 per cent lower than A for air-oil.

7. COEFFICIENTS OF SLIP BY THE ROTATING CYLINDER METHOD.

In view of the importance of checking the foregoing results by a wholly independent method a new series of slip-determinations was planned by the constant deflection method. So far as I know, this method has not been used heretofore for slip-determinations, but it is, I think, the most accurate method which is available. The theory of the method is as follows.

In the constant deflection method of measuring the viscosity of a gas, if the inner torsionally suspended cylinder has a radius a (Fig. 2) and a length L and the outer rotating cylinder a radius b, and if ω is the constant angular velocity of the layer of gas at any radius between a and b, then the torsional moment $\overline{Fr}$ due to the viscous drag acting on the cylindrical surface of gas of radius r is given by

$$\overline{Fr} = 2\pi r^3 L\eta \frac{\partial\omega}{\partial r} \cdot \qquad (39)$$

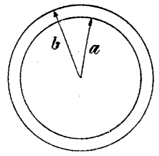

Fig. 2.

If now we assume *no slip* at either of the surfaces a or b and therefore integrate ω between the limits 0 and the angular velocity of the external cylinder ω_2 we obtain, since in the steady state $\overline{Fr}$ is not dependent on r,

$$\overline{Fr}\int_a^b \frac{\partial r}{r^3} = 2\pi L\eta \int_0^{\omega_1} \partial\omega \qquad (40)$$

or

$$\overline{Fr} = 4\pi L\eta \frac{a^2b^2}{b^2 - a^2}\omega_1. \qquad (41)$$

Replacing $\overline{Fr}$ by $\pi^2 I\theta/t^2$, where θ is the constant angular deflection of the inner cylinder, I its moment of inertia and t its half period in vacuo, we obtain the well-known characteristic formula of the constant deflection method, viz.:

$$\eta = \frac{\pi I\theta(b - a)(b + a)}{4t^2 La^2b^2\omega_1} \cdot \qquad (42)$$

In order now to modify this analysis so as to take account of slip between the surface of the gas and that of each cylinder a and b we must integrate the $\partial\omega$ in (39) and (40) not between 0 and ω_1, but rather between ω_a and ω_b, these symbols representing the angular velocities of the layers of gas in contact with a and b respectively. We thus obtain, instead of (41),

$$\overline{Fr} = 4\pi L\eta \frac{a^2b^2}{b^2 - a^2}[\omega_b - \omega_a]. \qquad (43)$$

But now, by definition of the coefficient ϵ of external friction, if f is the tangential force acting between the surface of the inner cylinder and v_0 the difference in linear velocity between the surface of the cylinder a and the layer of gas in contact with it, then

$$f = 2\pi aL\epsilon v_0' \qquad (44)$$

$$fa = \overline{Fr} = 2\pi a^2 L\epsilon v_0; \qquad (45)$$

substituting in this equation the value of v_0 obtained from $\omega_a = v_0/a$

we obtain

$$\omega_a = \frac{\overline{Fr}}{2\pi a^3 L\epsilon} \cdot \tag{46}$$

Precisely similarly, if f' is the tangential force on b and v_0' the difference in linear velocity between the surface of b and the gas in contact with it, we have

$$f'b = \overline{Fr} = 2\pi b^2 L\epsilon v_0' \tag{47}$$

and

$$\omega_b = \omega_1 - \frac{v_0'}{b} = \omega_1 - \frac{\overline{Fr}}{2\pi b^3 L\epsilon} \cdot \tag{48}$$

The substitution of (46) and (48) in (43) gives, after the insertion of

$$\overline{Fr} = \frac{\pi^2 I\theta}{t^2}$$

and also of the definition $\eta/\epsilon = \zeta$,

$$\eta = \frac{\pi I(b-a)(b+a)\theta}{4t^2 La^2b^2\omega_1}\left[1 + 2\zeta\frac{a^3+b^3}{ab(b^2-a^2)}\right] \cdot \tag{49}$$

If now we denote by η_a the *apparent* value of the viscosity obtained by the use of (42) and by η the real value obtained by the use of (49) and if for brevity we write

$$\frac{2(a^3+b^3)}{ab(b^2-a^2)} = K \tag{50}$$

we obtain from (42) and (49)

$$\zeta = \left(\frac{\eta}{\eta_a} - 1\right)\frac{1}{K} \cdot \tag{51}$$

For the practical application of this formula it is of course only necessary, if the speed of rotation of the outer cylinder is always kept constant, to measure the deflection θ at a relatively high pressure where ζ $(= .7004l)$ is so small that the second term in (49) is wholly negligible, and then to reduce the pressure until θ has attained a measurably smaller value θ'. The slip coefficient for this lower pressure is then given very simply by

$$\zeta = \left(\frac{\theta}{\theta'} - 1\right)\frac{1}{K} \cdot \tag{52}$$

The accuracy with which, under the best attainable experimental conditions, θ can be determined by this method being about one part in two thousand, it should be possible to have a difference between θ and θ' of but 5 per cent and still to secure an accuracy in the determination of ζ of about 1 per cent. *This makes the determination of coefficients of slip* *a matter of real precision* and permits the definite settlement of questions left altogether unsettled by the cruder methods of the earlier observers. Under the somewhat imperfect working conditions used below the uncertainty in ζ is however from two to three per cent for air, and somewhat more for CO_2.

8. THE COMPARISON OF RESULTS BY THE TWO METHODS.

The following papers by Messrs. Stacy and Van Dyke will show not only how satisfactorily the foregoing results, both theoretical and experimental, are checked by the application of this method, but also how well the personal equation has now been eliminated by the agreement between the results of different observers working at different times and under somewhat different conditions.

The final results obtained to date by the constant deflection method may be briefly summarized as follows:

I. When the surfaces of the cylinders had just been machined so that, when looked at from the eyes of a molecule, they were essentially rough surfaces, capable only of throwing back the molecules diffusely, the coefficient of slip between this surface and air, reduced to 23°, 76 cm, was found by Mr. Stacy to be $\zeta = .000006615$ as against my limiting theoretical value (see 24) $\zeta = .000006595$. *In other words the value of A for this surface had practically the theoretical limit $A = .7004$ demanded by* (37).

II. When the cylinder surfaces were then covered with shellac and dried the value of the slip, reduced to 23°, 76 cm, at once increased to .0000097 which corresponds, since $\zeta = Al$, to $A = 1.03$. This, in view of the inconstancy in A for shellac, to be immediately considered, is in altogether satisfactory agreement with the value shown in Fig. 1, IV which, it will be remembered, was $A = 1.07$.

III. When the shellaced surfaces were allowed to stand for several days they showed a continually diminishing value of A (due, I think, to slow oxidation) which according to Mr. Stacy's observations reached in two months the figure $\zeta = .00000677$, only $2\frac{1}{2}$ per cent higher than the theoretical limit corresponding to diffuse reflection. Precisely the same sort of a slow change in A with shellac has been found as detailed in Mr. Stacy's paper by an independent observer Mr. Harrington.

IV. The observations on Mr. Stacy's old shellac surface, interrupted in 1918 by his and by the author's participation in the war, were taken up again two years later by Mr. Van Dyke who obtained a mean value $\zeta = .0000068$ in complete agreement with Mr. Stacy.

V. Mr. Van Dyke did not find it possible, by cleaning off the shellac from the cylinders, to restore completely their original diffusely reflecting quality, the mean value of ζ for the cleaned brass surface remaining at .0000075. By scratching the surface with sandpaper ζ was reduced to .00000728. The inability to restore completely the surface to the condition of perfect roughness, after the treatment it had received, is not surprising. Had the observed change been in the other direction the result would have been disturbing for the theory, for *only by making the surface so rough that molecular mountain peaks, so to speak, project far up into the streaming gas, and thus rendering the consideration of anything like a surface layer of gas altogether impossible, could the drag be made larger than that corresponding to diffuse reflection.* This condition could probably be realized with a granular surface like that produced by smoke or by an electrolytic deposit.

VI. I asked Mr. Van Dyke next to coat the cylindrical surfaces with the same clock-oil with which I had obtained the value $A = .864$ or the slip $\zeta = .00000814$. The slip at once rose to the mean value .00000818 *in excellent agreement with results of the oil-drop method.*

VII. Mr. Van Dyke then used CO_2 gas with his oiled cylinders and got a value of A distinctly lower than for air, viz., .813, also in complete agreement with the results of the oil-drop method, which had yielded in CO_2 $A = .82$, *thus fortifying the validity of the conclusion that the nature of the gaseous molecule as well as the nature of the surface has a measurable influence upon the tendency to specular reflection (Maxwell's f).*

9. *A* AND THE COEFFICIENT OF SLIP FOR GLASS AND AIR.

I have made no measurements upon the coefficient of slip between glass and air; but there is evidence that it has a value exceedingly close to that between oil and air. Thus Warburg[1] by reducing the pressure, in viscosity determinations with glass capillaries, until slip began to be observable, obtained, from his only recorded measurement with his capillary No. I., $\zeta_{15°,\ 3.38\ \text{mm}} = .00017$ which reduces to

$$\zeta_{15°,\ 76\ \text{cm}} = .0000076.$$

From his recorded measurements with capillary No. II. he obtained

$$\zeta_{15°,\ 3.9\ \text{cm}} = .00016 \quad \text{and} \quad \zeta_{15°,\ 3.38\ \text{cm}} = .00018.$$

These measurements reduce to

$$\zeta_{15°,\ 76\ \text{cm}} = .0000082 \quad \text{and} \quad \zeta_{15°,\ 76\ \text{cm}} = .0000080.$$

Giving all these three determinations equal weight we obtain

$$\zeta_{15°,\ 76\ \text{cm}} = .00000793,$$

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[1] Pogg. Ann., 159, p. 401, 1876.

which reduces when the temperature correction is made to

$$\zeta_{23^\circ,\,76\text{ cm}} = .00000822.$$

This is quite close to the value for oil and air given in (19), namely ζ 23°, 76 cm = .00000814.

The only other careful work by the capillary tube method from which I have been able to compute ζ for air and glass is that by Knudsen.[1] According to the following analysis of this data it yields a value of ζ for glass and air very close to the value found by Warburg.

Knudsen writes Poiseuille's equation, uncorrected for slip, in the form

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p,$$

in which T is the quantity of gas, measured by the product of pressure and volume, which is driven per second through a capillary of length L and radius R by a pressure-difference of 1 dyne per sq. cm and p is the average pressure at the two ends, *i.e.*, $(p_1 + p_2)/2 = p$. Poiseuille's law, corrected for slip, then becomes

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}\left(1 + \frac{4\zeta}{R}\right)\cdot$$

Knudsen further measures the outflow through capillary tubes for a great range of mean pressures down to very low ones and represents all his results by the empirical formula

$$T = ap + \beta\frac{1 + c_1p}{1 + c_2p}$$

and evaluates the constants a, b, c_1, c_2 by means of his experimental data.

For such values of c_1p and c_2p as we are here concerned with 1 is negligible in comparison with this product and Knudsen's empirical equation becomes

$$T = ap + b\frac{c_1}{c_2}\cdot$$

For sufficiently large values of the pressure this reduces, as it should, to $T = ap$ and from Poiseuille's equation we see that

$$a = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}\cdot$$

If now, as in the case of Warburg's experiments, we let T' represent the apparent value of T if there were no slip, while T represents the real

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[1] Knudsen, Ann. der Physik, 28, p. 117, 1909.

value, we have

$$\frac{T}{T'} = \left\{ 1 + \frac{4\zeta}{R} \right\}.$$

Hence

$$\frac{4\zeta}{R} = \frac{b\frac{c_1}{c_2}}{ap}$$

and

$$\zeta = \frac{Rb\frac{c_1}{c_2}}{4ap}.$$

We are therefore in position to compute the value of ζ_{76} from the values of R, b, c_1/c_2 and a given by Knudsen for any of the tubes and gases which he uses. The results are of course quite independent of his theory and dependent only upon the ability of his constants R, b, c_1/c_2 and a to reproduce the experimental T, p curve, in the region of pressures with which we are here interested, which is limited to the region in which Poiseuille's law is just beginning to break down because of the appearance of the phenomenon of surface-slip. This is the only region in which we are here concerned with Knudsen's experimental data.

Knudsen does not make experiments upon glass and air, but since ζ for different gases is proportional to l save as the nature of the gas modifies Maxwell's f, and since this last effect is only just measurable at best we may compute ζ for air and glass from his data taken with H_2, O_2, and CO_2 by multiplying by the ratio of mean free paths.

Utilizing in this way all the data taken by Knudsen (see Table II., p. 116, l.c.) except that on H_2 with tube No. 1., which I discard because Knudsen himself calls it unreliable, and all the data with tube No. 4, which I discard because it was a bundle of 24 tubes but 2 cm long and .00333 cm radius for which ζ comes out about 20 per cent higher than for any of the other tubes, presumably because the dimensions of such exceedingly minute capillaries can be determined with but little certainty, we obtain the following set of values of ζ for air at 25°, 76 cm.

Tube No. 1 (using O_2), air	.00000816
" " 1 (" CO_2), air	.00000784
" " 2 (" H_2), air	.00000855
" " 3 (" CO_2), air	.00000876
Mean	.00000828

When reduced to temperature 23° C this gives

$$\zeta_{23°, 76} = .00000821,$$

which is seen to be identical with Warburg's value, although the uncertainty in both these determinations is doubtless as much as 5 per cent.

The foregoing analysis appears to show then that ζ and A for glass and air are practically identical with ζ and A for oil and air for which my values are

$$\zeta_{23^\circ, 76} = .0000082,$$
$$A = .864.$$

10. Numerical Values of Maxwell's f.

A condensed summary of the whole of this work may be made by computing with the aid of equation (29) and observed values of ζ, or of A, the values of Maxwell's f for the different gases and surfaces with which we have experimented.

For air and oil all observers and both methods are in excellent agreement, my value using oil drops being $A = .864$, Ishida's independent determination with my apparatus yielding $A = .862$ and Van Dyke's observations with the rotating cylinder giving $\zeta = 81.8 \times 10^{-7}$, which when combined with the value of l, viz., 94.17×10^{-7}, with the aid of $\zeta = Al$ gives $A = .868$. The mean of the three determinations is $A = .8647$ and this value is taken for the computation of f from (29.)

For CO_2 and oil the different observers are in less satisfactory agreement probably because of the difficulty of duplicating exactly conditions as to purity of the gas. Dr. LaSalle obtained with my oil-drop apparatus $A = .825$. Mr. Eglin in very recent and very careful experiments with CO_2 has obtained $A = .820$. Dr. Ishida[1] with the same apparatus obtained .840 and Mr. Van Dyke's $\zeta = 50.0 \times 10^7$ by the rotating cylinder method reduces, since for CO_2 $l = 61.5 \times 10^7$, to $A = .813$. The mean of all these determinations, giving Van Dyke's and Eglin's data double the weight of the others since they ought to be the more precise, is $A = .823$ which is probably not in error by more than a per cent.

For hydrogen-oil my value of A is .815 while Dr. Ishida's value obtained with my oil-drop apparatus is .811. The mean of the two, viz., $A = .813$, has been taken for the computation of f.

The monatomic gas helium shows according to Dr. Ishida's determination a higher value of A than any other gas used with oil. There is as yet no other observation with which to compare it and f is therefore computed from Ishida's $A = .901$.

All of the observations made with oil drops in different gases show that, as was to have been expected, the character of the gas has but little influence upon the character of the reflection, though the observed differ-

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[1] Ishida regards his accuracy in the case of CO_2 as less than in the case of any other gas as he worked hastily and used but ten drops.

ences in A are apparently considerably greater than the observational error.

TABLE.

Values of Maxwell's f for Different Surfaces and Gases.

	A.	f = Per Cent Diffuse Reflection at 23° C.	$1 - f$ = Per Cent Specular Reflection at 23° C.
Air CO_2 } machined brass surface or old shellac surface	.70	100	0
Air-mercury	.70	100	0
Air-oil	.864	89.5	10.5
CO_2-oil	.823	92	8
Hydrogen-oil	.813	92.5	7.5
Air-glass (Warburg-Knudsen)	.872	89	11
Helium-oil	.901	87.4	12.6
Air-fresh shellac	1.07	79	21

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