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THE GENERAL LAW OF FALL OF A SMALL SPHERICAL BODY THROUGH A GAS, AND ITS BEARING UPON THE NATURE OF MOLECULAR REFLECTION FROM SURFACES

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ABSTRACT

Law of fall of a small spherical body through a gas at any pressure.—(1) *Theoretical derivation.* When the ratio of free path to radius of droplet, l/a, is small, the resistance to motion is due entirely to viscosity and is proportional to a, while when l/a is large the resistance is due entirely to the inertia of the molecules hit and is proportional to a^2. The equation: $F=6\pi\eta av[1+A'l/a]^{-1}$ satisfies both these theoretical conditions. From Kinetic theory, however, it has been shown that A' is not constant but varies from a lower theoretical limit of .7004 (diffuse reflection) for l/a small, to 1.164 for l/a large. We therefore put $A'=A+B\epsilon^{-ca/l}$ and write the complete equation: $F=6\pi\eta av[1+(A+B\epsilon^{-ca/l})l/a]^{-1}$. (2) *Experimental verification.* By the oil drop method, values of A' have been determined for a wide range of values of l/a, from 0.5 to 134, for oil drops in air. These results are found to agree within the experimental error of ± 2 per cent or less with the theoretical equation, and give $A=.864$, $B=0.290$, $c=1.25$. A discussion of results obtained with other drops indicates that while A varies with the nature of the gas and even more with the material of the droplet, $(A+B)$ is within two or three per cent the same for most sorts of particles which might settle through the atmosphere. (3) *Differentiation between diffuse reflection, specular reflection, radial reflection, and condensation and re-evaporation of molecules.* Radial reflection is shown to be thermodynamically and dynamically impossible; condensation and re-evaporation to be inconsistent with the observed value of (A+B). This observed value is satisfied only by a combination of about 1/10 of specular reflection with 9/10 of diffuse reflection, this last being defined as a re-emission from each element of surface and in such directions as to satisfy the Maxwell distribution law, of all molecules which impinge upon that element. The agreement adds new evidence for the existence of specular reflection of molecules since 1/10 had also been indicated by the values of A previously obtained for oil-drops in air. (4) *Effects of mechanical roughness of the surface.* The apparent discrepancies between the author's results and those of Knudsen and Gaede, which seemed to indicate complete diffuse reflection, are explained by the effects of minute mechanical protuberances which are thought to have existed on the insides of these authors' capillary tubes.

1. Introduction

IT is well known that Stokes' law of motion of a sphere through a homogenous medium which does not slip at all at the surface of the sphere, namely,

$$F = 6\pi\eta av \tag{1}$$

is obtained by neglecting entirely the resistance which arises from the inertia of the medium, the "push resistance," and considering the force opposing the motion to be due solely to shear, the "drag resistance," and therefore to arise wholly from the viscosity of the medium.[1] It is also well known that this assumption is valid provided the velocity is small compared with $\eta/\rho a$,[1] or, referring to Arnold's accurate experiments,[2] provided a is less than 6/10 of the so-called critical radius $\bar{a}$ defined by $\bar{a} = \eta/\rho v$.

Stokes' law is then applicable to spheres falling under gravity, first, when they are so small that the foregoing condition is fulfilled, and, second, when the medium may still be regarded as homogeneous and therefore as non-slipping.

In liquids this last condition may be considered as fulfilled for spheres of radii greater than 10^{-6} cm, so that Stokes' law of fall is presumably rigidly applicable in liquids to spheres of radii between the wide limits 10^{-2} and 10^{-6} cm.[3] In gases at ordinary pressures, however, it has been shown[4] that the slip due to the molecular inhomogeneities causes the law to be slightly incorrect even for spheres of radii as large as 0.005 mm, and that Eq. (1) must then be replaced by an equation of the form

$$F = 6\pi\eta\ a\ v/(1 + Al/a) \tag{2}$$

in which A for different gases and different drop-substances was found to vary between the limits 0.7 and 1.0, and in which the lower theoretical limit for A was found from simple hydrodynamical considerations to be 0.7004[5] when l is defined by $\eta = .3502\rho\bar{c}l$.

Since the denominator in (2) is merely a small correction term to Stokes' law and has been developed by introducing into the hydrodynamical considerations underlying that law the single additional assumption of surface-slip due to molecular inhomogeneities, it is clear

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[1] C. G. Stokes, Cambr. Trans. 9, 1851, and Mathematical and Physical Papers, **3,** 59. See also Lamb's Hydrodynamics

[2] Arnold, Phil. Mag. **22,** 755, 1911

[3] Arne Westgren, Zeit. Phys. Chemie **89,** 63, 1914

[4] Millikan, Phys. Rev. **32,** 376, 1911

[5] Millikan, Phys. Rev. **21,** 217, March, 1923

that the *assumption of a resistance due to viscosity alone is inherent in the validity of Eq. (2)* as developed in the articles referred to. It should be noted, also, that the derivation of (2) is only valid for values of Al/a which are small in comparison with unity.

But it is extremely interesting to know the *complete* law of motion of small bodies coming to the earth from great distances through very rarified atmospheres and reaching Stokes' law merely as a limit in the dense atmosphere near the earth's surface. The accurate experimental determination of this law is the first result of the present investigation. A second result is the interpretation of this law from the point of view of the theory of molecular reflection from liquid and solid surfaces.

It was in 1909 and 1910 that the first experiments[6] were performed which showed that the simple law of fall given in (1) had to be changed to the form given in (2) in order to account for observed rates of fall, and in these first experiments the value of A was given as .817. In 1911 McKeehan[7] verified these results by an independent, though perhaps somewhat less precise method, and wrote the law of fall of wax spheres through air in the same form, but with A having the value 1.00 instead of .817. During the same year, however, my own observations showed that it was impossible to represent the *complete* law of fall by an equation of the form of (2), and in 1912 the first direct determination of this complete law was published[8] very briefly and without comment in the form

$$F=6\pi\eta\, av/[1+l/a\ (A+B\epsilon^{-c\, a/l})] \tag{3}$$

The constant A was here given as .874, B as .35, and c as 1.7. Further, in 1911 Knudsen and Weber[9] had arrived by an *indirect* method, namely by observations on the damping in a vessel at very low pressures, of two glass spheres tortionally suspended in a horizontal plane at the ends of a thin rod, at a resistance equation of the same form but with different constants, which they wrote as follows:

$$F=6\pi\eta\ a\ v/[1+.68\,l/a+.35l/a\ \epsilon^{-1.85a/l}] \tag{4}$$

These purely empirical equations of Knudsen's and the author's, the likenesses and differences in which will be considered later, have up to the present time been given no theoretical interpretation whatever, but the reasoning which lead the author, at least, to adopt this particular form of empirical equation is as follows.

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[6] Millikan, Science, **32**, 436–443, 1910, and Phys. Zeit. **11**, 1097–1109, 1910; Phys. Rev. **32**, 351–397, 1911

[7] McKeehan, Phys. Rev. **32**, 341, 1911

[8] Millikan, British Association Reports, Dundee, 1912, p. 410

[9] Knudsen and Weber, Ann. der Phys. **36**, 982, 1911

2. THEORY

As indicated in the foregoing, the sole appreciable cause of resistance to the motion of a small sphere through a dense gas is the *viscosity* of the medium. In a very highly rarefied atmosphere, however, it is evident that this cause drops out entirely, and the sole appreciable cause of resistance is then the inertia of the molecules which are being *directly* encountered per second by the sphere. When, with decreasing pressure, this latter condition has been fully reached the resistance must be proportional to the number of molecules encountered per second, that is to the cross section of the sphere or to the square of the radius; whereas at the other extreme, i.e., at high pressures where viscosity is the sole appreciable element, the resistance is proportional, as indicated in (1), to the first power of the radius.

It will be seen at once that both of the foregoing conditions are realized by giving the correction term to Stokes' law, as was done in (2), the form $(1+Al/a)^{-1}$; for so long as $A\,l/a$ is small in comparison with unity, the denominator of (2) remains essentially unity and F is then proportional to a, but when l/a is so large that 1 is negligible in comparison with $A\,l/a$, F becomes proportional to a^2. In other words, *so far as form alone is concerned, (2) is adapted to express the necessary relations between* F *and* a, *both at high pressures where viscosity is the only essential factor in the resistance, and also at very low pressures where viscosity plays no appreciable role in the resistance.*

But there is no reason whatever for supposing that the necessary linear relation between F *and* a^2 *at low pressures, and the equally necessary linear relation between* F *and* a *at high pressures correspond to the same value of the constant* A, *for this constant appears for wholly different reasons in the two cases.* It has been shown, as indicated above, that for sufficiently high pressures, that is for small values of l/a, the lowest possible value of A, that corresponding to diffuse reflection or to condensation and evaporation, is 0.7004. At the other extreme, when l/a is very large in comparison with 1, it may also be shown theoretically (see below) that the lowest possible value of A is larger than 1. But throughout each of these two regions, first, that in which Stokes' law is just beginning to break down, and, second, that in which the gas is very rare, A must be a constant.

Now it has also been shown[10] that so long as A is a constant its value in an equation of the form of (2) may be easily and accurately determined experimentally by observing the slope of the necessary linear relation

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[10] Millikan, Phys. Rev. **32,** 378, 1911

between $e_1^{2/3}$ and l/a in the characteristic equation of the oil-drop method, namely $e_1^{2/3}=(1+A\ l/a)e^{2/3}$. Any generalized law of fall, then, which will connect the two resistances, the one close to where Stokes' law is valid, and the other corresponding to very low pressures where Stokes' law fails entirely and F is proportional to a^2, must contain a term of such form as to make the linear relation between $e_1^{2/3}$ and l/a corresponding to a *small* value of A (e.g., .700) pass over into another linear relation between $e_1^{2/3}$ and l/a corresponding to a larger value of A. Since, then, for the purposes of this complete law of fall, A must be considered a variable, I propose henceforth to call this variable A'. The form, then, which must be given to A' to make it execute such a shift as that just described from a low constant value to a higher constant value is clearly as follows

$$A'=A+B\epsilon^{-c\,a/l} \tag{5}$$

for when l/a is small the second member reduces to zero and A' to A, while when l/a is large the exponential term becomes unity and A' changes to $(A+B)$. The constant c may be given a value to correspond to any rapidity of shift.

In the oil-drop method of determining the complete law of fall then, the exponential term is merely a convenient device for causing one linear relation between $e_1^{2/3}$ and l/a to shift over into a second linear relation of larger slope, the cause of that shift being a transfer from a viscous resistance which is proportional to a, to a direct impact resistance which is proportional to a^2.

3. THE EXPERIMENTAL DETERMINATION OF THE CONSTANTS $(A+B)$ AND c

Because of the very great significance, to be presently pointed out, of the constants A and $(A+B)$ for the theory of reflection of molecules, a great deal of attention has been devoted to their accurate evaluation for different gases and different surfaces. So far as A alone is concerned, this work has already been fully reported.[5] The work from which had been derived the values of A, B, and c, published in 1912, had been carried carried only up to a value of $l/a=12$, which was insufficient to determine these constants with accuracy. Since then, however, I have taken very long series of elaborate observations by the oil-drop method for the sake of determining A, B, and c with much greater precision.[11] In this work oil drops have been observed at pressures ranging from 760 mm down to 1.6 mm, and at values of l/a from .1 to 134, i.e., over a range of

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[11] See Phys. Rev. **15**, 545, 1920, for first publication of corrected form of complete law of fall.

TABLE I

Observations on Three Drops

	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$
(1)	(2)	(3)	(4)	(5)	(6)
Drop No. 10					
37.77	29.58			7	.008765
37.90	29.06				
37.96	39.06			6	.008676
		2	.008652		
37.69	120.50			4	.008682
38.03	121.41				
		2	.008546		
37.82	39.48			6	.008625
38.09	39.58				
		1	.008831		
37.77	60.85			5	.008575
		1	.008361		
38.37	40.33				
37.35	40.72			6	.008520
37.67	40.56				
		1	.008801		
37.68	63.08			5	.008462
37.35					
Mean 37.80			.008636		.008615
Drop No. 23					
50.42	64.34				
51.01	64.80			1	.035264(2)
49.77	66.79				
50.27	65.28				
50.33		1	.033159	2	.034212(1)
49.42	20.46				
49.67	20.79				
Mean 50.13					.034913
Drop No. 47					
8.9	12.4				
8.7	12.5				
10.0	12.5				
9.0	12.9			8	02316
9.3	13.4				
9.9	13.0				
10.2	13.2				
9.9	12.8				
		1	.02263		
9.2	18.2				
9.2	18.0				
9.0	17.7			7	.02347
9.4	17.7				
9.0	17.5				
9.3	16.5				
9.0	17.4				
		1	.02453		
9.0	28.7				
9.1	29.4			6	.02363
	26.7				
Mean 9.31			.02358		.02346

values varying 1300 fold. Out of 50 oil drops whose values of l/a are scattered somewhat uniformly over this whole region, three have been selected for presentation in Tables I and II. These are merely typical drops which will indicate to the reader the kind of precision obtained. As shown in Table II, for the three drops selected, the pressures were 5.33, 2.33, and 0.237 cm and the values of l/a, 1.2806, 6.459 and 105.08. The pressures were observed accurately with a very sensitive McLeod gauge. The notation used in recording these drops is the same as that which has been generally adopted; i.e., the column headed t_g represents the time in seconds which the drop required to fall the distance between cross-hairs, a distance which varies somewhat in some of these experiments, but was generally about a centimeter, its accurate value being always obtainable from the value of the velocity v_1 (Table II) and the value of the time t_g. The second column gives the time required for the drop to rise against gravity between the same cross-hairs when the voltage given in Table II under the heading V_i and V_f (initial and final) was applied between the plates. The third column gives the number of electrons by which the charge on the drop was changed when the value of t_F changed as indicated in the second column. The fourth column gives the value of the electronic charge in terms of a velocity as computed from each individual change in charge. The fifth column gives the total number of free electrons in the charge of the drop corresponding to various values of t_F. The sixth column gives the value of the electronic charge in terms of a velocity as computed from t_g and t_F.

TABLE II

	Drop No. 10	Drop No. 23	Drop No. 47	Units
V_i	1336.1	670.3	20.3	volts
V_f	1336.1	668.8	20.3	volts
t	22.98	22.99	21.8	°C
p	5.33	2.329	0.2372	cm Hg
v_1	.02704	.02039	.10966	cm/sec
a	10.50	4.77	2.905	10^{-5}cm
$1/pa$	1789.3	9024.8	14,683	
l/a	1.2806	6.459	105.08	
$e_1^{2/3}$, observed	136.88	501.6	7383	10^{-8}
calculated	137.3	496.6	7449	10^{-8}
A', observed	.968	1.118	1.151	
calculated	.973	1.103	1.144	

The accuracy of the work can be gauged from the sort of agreements found in columns 4 and 6, also from the differences in Table II between the observed and the computed value of $e_1^{2/3}$ and A'. As Table I shows, at these very low pressures the velocities are so high and the fluctuations due to Brownian movements have so largely increased that the errors are perhaps ten times as great as at ordinary pressures. This means that the values of $e_1^{2/3}$ and A' for the individual drops may be as much as 1 or 2 per cent in error.

Tables III and IV give the complete tabulated results obtained on all the drops. Especial attention may be directed to the last column of

TABLE III

Drop No.	$t°C$	*P. D.* (volts)	V_1 (cm/sec.)	(V_1+V_2) (cm/sec.)	n	a (10^{-5}cm)	p (cm Hg)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
*1	23.05	2006	.05786	.004545	15–20	19.19	7.60
2	23.00	1684	.1123	.002652	44–86	26.59	5.29
*3	23.04	2005	.04170	.005836	9–18	15.82	7.72
4	22.83	2556	.03193	.008250	4–7	13.76	8.82
5	22.87	1711	.03403	.005802	4–10	13.83	7.55
*6	23.04	2001	.03348	.008116	5– 7	12.41	7.95
7	23.04	1688	.07345	.004057	20–28	20.05	4.90
8	23.05	1684	.05989	.005010	8–12	14.24	5.70
9	23.07	1681	.04098	.006216	7–12	12.85	5.96
*10	22.98	1336	.02704	.008615	4– 7	10.50	5.33
11	23.06	1684	.02334	.012000	5– 7	9.52	5.44
*12	23.10	1321	.04353	.011601	4– 7	11.14	2.97
13	22.8	861	.02866	.009287	5– 8	8.88	3.65
14	23.15	672.6	.06708	.005040	13–15	13.84	2.18
15	20.3	842	.01981	.01989	1– 4	6.05	3.23
16	23.23	850.5	.01985	.02220	1– 4	5.85	3.11
17	21.0	843.0	.02854	.01899	2– 4	6.89	2.57
*18	22.98	671	.03089	.01834	2– 4	6.79	2.22
19	21.2	167.7	.03523	.005256	8–11	6.60	1.91
*20	23.06	673.6	.01504	.034278	1– 3	4.34	2.86
*21	23.10	674.3	.01421	.040623	1– 3	4.03	2.81
22	21.5	339.0	.03890	.011843	5– 9	6.61	1.73
*23	22.99	669.5	.02039	.034913	1– 2	4.77	2.33
*24	23.00	673.5	.01679	.04104	1– 3	4.24	2.48
25	20.25	343.0	.04093	.01308	4– 7	6.53	1.58
*26	23.80	169.0	.01651	.01225	2– 4	3.99	2.31
27	19.7	336.0	.05844	.01908	5– 7	6.43	1.11
28	21.4	508.5	.02717	.05018	1– 2	4.14	1.51
29	22.47	70.1	.06474	.01922	5– 7	2.640	.962
30	21.2	103.4	.11386	.01133	10–15	6.431	.5332
31	21.5	36.4	.06609	.01766	6–10	2.588	.790
32	21.2	68.9	.10527	.01272	11–13	5.281	.4656
33	21.8	14.1	.10558	.00832	17–22	3.588	.536
34	21.3	75.5	.08046	.02890	4– 5	3.787	.435
35	21.3	80.7	.05617	.04315	2– 4	2.711	.4925
36	21.5	116.7	.05174	.06920	1– 3	2.825	.4933
37	21.3	100.3	.06912	.05412	2– 3	3.213	.4220
38	21.5	143.1	.11421	.06648	2– 4	3.991	.3223
39	21.4	69.5	.14503	.03208	5– 8	4.329	.2755
(1) 40	23.4		.09903		3–10	3.447	.3192

*Starred drops were taken in a condenser of plate distance 1.49174 cm.
Unstarred drops were taken in a condenser of plate distance 1.598 cm.
(1) The voltage here had four values, viz. 24.0, 36.2, 51.2, 81.8.
The corresponding (V_1+V_2) were .014976, .022614, .031922, .04984.

TABLE III (continued)

Drop No.	$t°C$	$P. D.$ (volts)	V_1 (cm/sec.)	(V_1+V_2) (cm/sec.)	n	a (10^{-5}cm)	p (cm Hg)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
41	21.6	63.3	.11282	.04511	3– 4	3.454	.2782
42	22.6	49.8	.14565	.03258	6– 7	3.860	.2389
(2) 43	22.87		.15026		2– 3	3.869	.2320
(3) 44	19.8		.12492		1– 8	3.272	.2410
45	23.0	23.1	.14121	.01981	9–11	3.491	.2258
46	21.9	19.6	.19562	.01550	15–18	3.996	.1823
47	21.8	20.3	.10966	.02346	6– 8	2.905	.2372
(4) 48	22.2		.11013		2– 3	2.748	.2275
49	22.4	30.8	.09669	.05207	1– 3	2.452	.2318
50	23.0	19.4	.18633	.02385	7– 8	3.285	.1626

(2) The voltage here had two values, viz. 111.2 and 143.3.
The corresponding (V_1+V_2) were .07446 and .09581.
(3) The voltage here had four values, viz. 20.15, 38.5, 79.6, 155.2.
The corresponding (V_1+V_2) were .018619, .03567, .07229, and .14397.
(4) The voltage here had two values, viz. 43.3 and 66.3.
The corresponding (V_1+V_2) were .06038 and .09073.

Table III, which shows the total range of pressures used. It will be seen that these pressures are all below 9 cm, observations at higher pressures having been sufficiently reported in preceding papers,[12] and extend down to .16 cm.

In Table IV it will be interesting to observe that whereas in the tables and graphs previously published the values of $1/pa$ have been reported only as high as 480,[13] the values here begin at 686.7 and extend up to the huge value of 187,240, while the corresponding values of l/a run from 0.495 by fifty fairly uniformly distributed steps up to 134. Columns 3, 4, 5, and 6 show the agreement obtained between the observed values of A' and of $e_1^{2/3}$ and those computed from the final empirical formulas shown at the top of Tables IV. It will be seen from the last column that in general the error is but a fraction of a per cent, and in no case is it as high as 2 per cent.

A glance at the value of A' for the last thirteen drops of Table IV shows that the final value of $(A+B)$ has been reached within the limit of observational error for all these drops. Comparison of the second and fourth columns in the case of these drops shows that though l/a varied from 55 up to 134, A' does not change in that whole range by as much as one third per cent.

Figs. 1, 2, 3, 4, and 5 have been inserted for the sake of showing graphically the relations brought out numerically in Tables III and IV. Fig. 1 is a repetition of the previously published linear relations of $e^{2/3}$ and $1/pa$ up to values of the latter of about 500, which correspond to

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[12] See, for example, Millikan, Phil. Mag. **34**, 11, 1917

[13] See Phil. Mag. **34**, 12, 1917

TABLE IV

$e_1^{2/3}=e^{2/3}\,(1+A'l/a);\ A'=.864+.29\epsilon^{-1.25\,a/l}$

$1/pa$ (1)	l/a (2)	A'(*obs.*) (3)	A' (*calc.*) (4)	e_1 (*obs.*) (10^{-8}) (5)	e_1 (*calc.*) (10^{-8}) (6)	*Difference* (per *cent*) (7)
686.7	.4915	.887	.887	87.75	87.77	+ .02
711.6	.5093	.877	.888	88.42	88.78	+ .4
819.7	.5867	.888	.898	92.97	93.31	+ .4
823.2	.5892	.903	.898	93.80	93.46	− .4
957.8	.6855	.904	.911	99.00	99.29	+ .3
1014.8	.7263	.912	.917	101.6	101.9	+ .3
1018	.7289	.916	.917	101.9	102.0	+ .1
1223.	.8752	.946	.934	111.7	111.1	− .5
1301.	.9310	.940	.940	114.4	114.6	+ .2
1789.3	1.281	.968	.973	139.6	137.3	+ .3
1931	1.381	.975	.986	143.4	143.9	+ .4
3021.6	2.163	1.028	1.027	197.0	196.9	− .05
3083	2.207	1.048	1.029	202.4	199.9	−1.3
3511	2.513	1.027	1.041	218.9	221.0	+1.0
5070	3.620	1.078	1.070	299.7	297.9	− .6
5488	3.933	1.090	1.076	323.1	319.8	−1.0
5713	4.089	1.087	1.087	332.8	329.7	− .9
6644	4.756	1.078	1.088	374.4	377.4	− .8
8033	5.749	1.093	1.098	445.0	447.0	+ .4
8069.2	5.775	1.090	1.098	446.0	448.7	+ .6
8899	6.333	1.107	1.102	489.5	488.6	− .2
8905	6.373	1.111	1.103	494.0	490.8	− .8
9024.8	6.459	1.116	1.103	501.6	496.6	−1.0
9542.9	6.831	1.103	1.106	521.5	522.9	+ .3
9882	7.073	1.084	1.107	529.8	539.7	+1.9
10905	7.805	1.096	1.111	583.8	591.1	+1.2
14397	10.30	1.139	1.121	779.6	766.9	−1.6
16307	11.67	1.144	1.125	877.0	863.2	−1.6
26400	18.89	1.126	1.135	1361	1372	+ .9
29160	20.87	1.137	1.137	1511	1512	+ .007
38640	27.65	1.149	1.141	2002	1990	− .6
40670	29.11	1.142	1.142	2092	2093	+ .005
51940	37.17	1.145	1.144	2663	2660	− .01
60700	43.44	1.150	1.146	3113	3104	− .3
67590	48.37	1.147	1.147	3452	3452	0
71770	51.36	1.126	1.147	3597	3665	+1.9
73710	52.76	1.135	1.147	3721	3763	+1.1
78050	55.86	1.148	1.148	3980	3981	+ .03
83850	60.01	1.153	1.148	4289	4275	− .3
90826	65.00	1.152	1.149	4639	4626	− .3
104100	74.48	1.138	1.149	5243	5294	+1.0
108520	77.76	1.133	1.149	5439	5524	+1.5
111400	79.72	1.133	1.149	5583	5667	+1.5
126733	90.72	1.151	1.150	6443	6435	− .1
126900	90.82	1.152	1.150	6454	6445	− .1
141400	101.20	1.152	1.150	7190	7187	− .05
146830	105.08	1.144	1.151	7383	7449	+ .9
159900	114.45	1.161	1.151	8183	8114	− .9
175800	125.78	1.152	1.151	8926	8910	− .2
187240	134.00	1.167	1.151	9618	9488	−1.2

values of l/a of from 0 to .4. Fig. 2, which is a continuation on the same scale as Fig. 1 shows nicely how at about a value of $1/pa = 700$, or $l/a = .5$, this linear relation begins to break down, the last drop on Fig. 2 showing a departure from the straight line much greater than the observational error. Fig. 3, which is on the same scale as the other two figures but con-

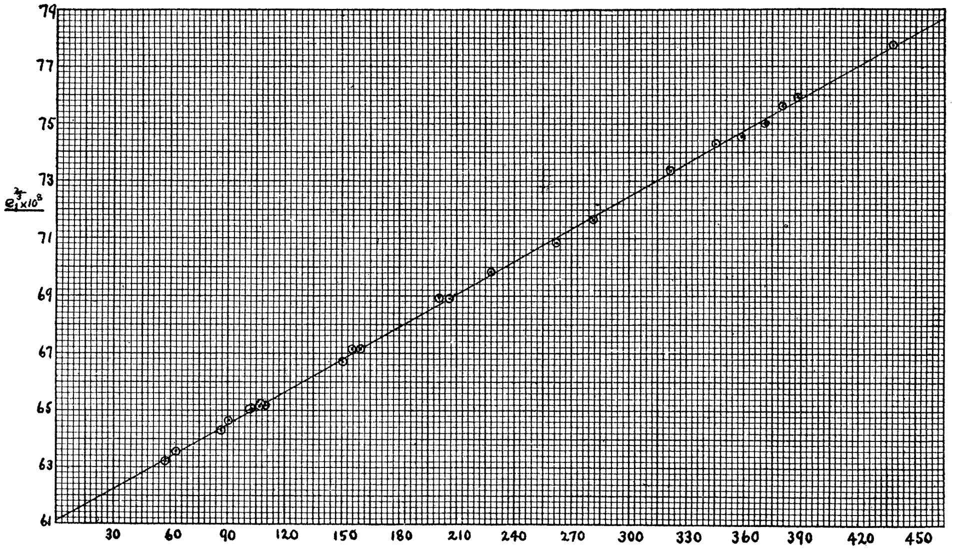

Fig. 1. $e_1^{2/3}$ as function of $1/pa$, for l/a up to 0.4.

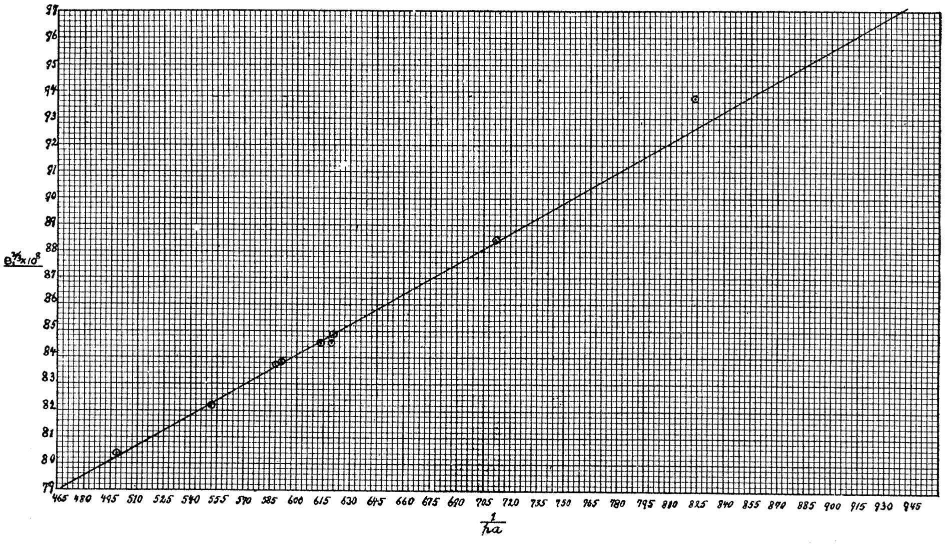

Fig. 2. $e_1^{2/3}$ as function of $1/pa$, for l/a 0.4 to 0.7.

tinuing to the higher values of $1/pa$ shows this departure very strikingly. In Fig. 4 the $1/pa$ scale has been reduced to 1/20 its former value, and the progression of $e_1^{2/3}$ with $1/pa$ up to values of the latter of 7000 is shown. In Fig. 5 is shown on a scale about 1/400 of that used in Fig. 1, 2, and 3,

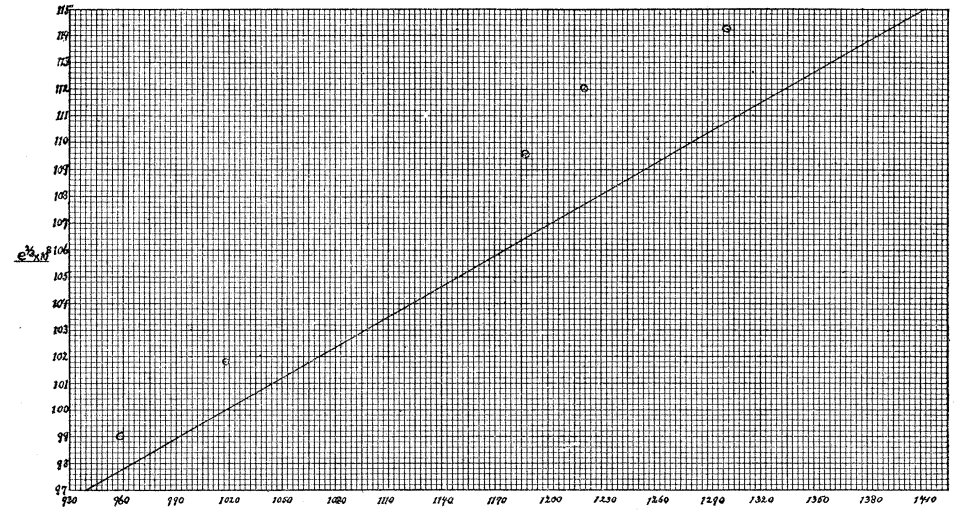

Fig. 3. $e_1^{2/3}$ as function of $1/pa$, for l/a 0.7 to 1.0.

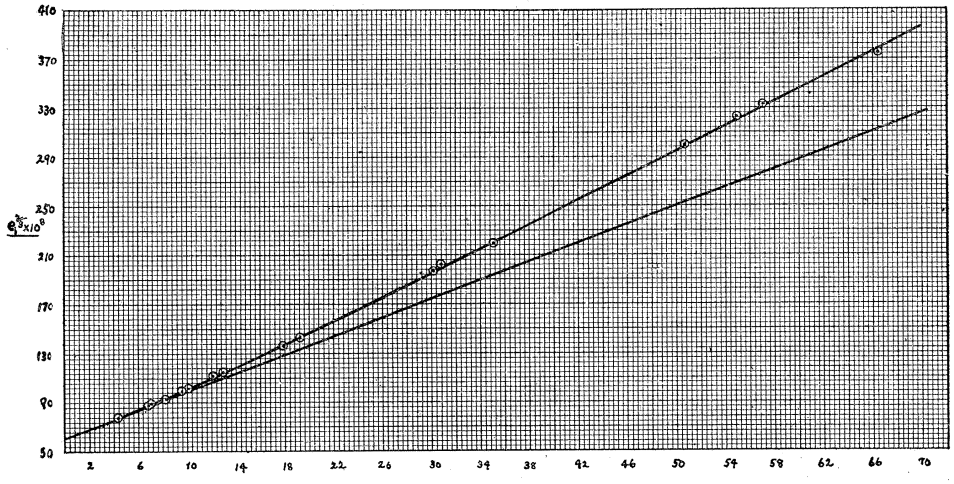

Fig. 4. $e_1^{2/3}$ as function of $1/pa\times10^{-2}$, for l/a from 0 to 5.

the last twenty-eight drops at the end of Table IV. The first eleven drops on the left side of this scale may well be ignored, since, in view of the smallness of the scale, the error in plotting in this region is so large as to nearly mask the fact that the drops are all slightly above the line as they should be. The last seventeen drops at the upper end of the scale brings out strikingly, however, how completely the final value of the slope has been attained. This makes it altogether unnecessary to push observations to any higher values of 1/pa since, from theoretical considerations previously advanced, it is necessary that this slope remain constant for all higher values. *It is clear, then, that we have obtained the general formula for the complete law of fall of a spherical liquid drop through air.*

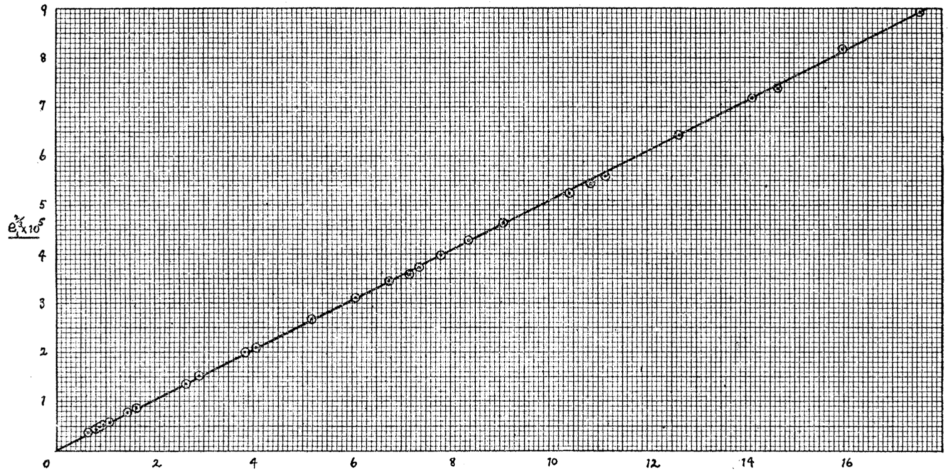

Fig. 5. $e_1^{2/3}$ as function of $1/pa\times10^{-4}$, for l/a from 0 to 125.

4. The Significance of the Value of $(A+B)$

a. Possible modes of reflection of molecules. So long as the viscosity of the medium is the sole cause of the resistance, it will be seen from the method used[5] in deducing the lower limit to the theoretical value of A (.7004), that the tangential force on unit surface, which is what determines the value of A, is precisely the same whether the molecules are diffusely reflected from the surface, are condensed and reëvaporated without preference as to direction, or whether they are returned with a preference for the direction of the normal to the surface. For if the molecules coming out all emerge *symmetrically* with respect to the normal to the surface, they give up to it their total mean *tangential* momentum, and so exert the same drag quite independently of how they emerge, *provided, only, they have upon emergence no average component parallel to the surface.*

Not so at the other extreme where the gas is so rare that the resistance is to no extent a result of viscosity but is due wholly to the inertia of *those particular molecules which make direct encounters with the sphere,* no streaming motion of the gas outside the cylindrical volume of section πa^2 having to be taken into account. If the character of these encounters be known, the resistance may be computed. But in this computation it is necessary to differentiate the four following cases:

Case A. Specular reflection. This case has been worked out by Langevin,[14] Cunningham,[15] Lenard,[16] and Epstein,[17] all of whom agree in finding the resisting force F acting on a sphere of radius a moving with velocity v through a gas of density ρ and average molecular velocity, $\bar{c}$ to be given by

$$F=(4/3)\pi\rho a^2\bar{c}v \tag{6}$$

This case has, of course, no actual existence, but it is of importance to have it worked out because of the evidence recently brought forward[5] for the existence, quite in accord with the theory advanced by Maxwell[18] fifty years ago, of a definite fraction f of the molecules which are specularly reflected.

Case B. Condensation and reëvaporation. In this case all of the molecules are assumed to impinge inelastically and the emerging ones are assumed to come out in equal numbers from all unit areas of the sphere, and hence to exert no resultant force whatever upon it. This case has been worked out by Lenard[16] and Epstein,[17] who agree in finding the resistance precisely the same as in case A. Cunningham also gave a solution for this case, but appears to have made two numerical errors, one of which was pointed out in 1911,[19] and the other of which Epstein discusses in a following paper. When these errors are corrected Cunningham is brought into agreement with Lenard and Epstein.

Case C. Diffuse reflection. This case will be divided into two subcases. *In Case C_a, diffuse reflection, Lenard,* all of the molecules striking each particular element of the surface are assumed to emerge from that same element, each with its incident speed but in directions which are uniformly distributed over the hemisphere which faces the element. Both Lenard and Epstein have solved this case, and they agree in finding

$$F=(16/9)\pi\rho a^2\bar{c}v.$$

Epstein's analysis shows, however, that this case cannot actually exist since it involves the same sort of a violation of the second law of thermo-

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[14] Langevin, Ann. de Chem. et Phys. **5**, 266, 1905

[15] Cunningham, Proc. Roy. Soc. **83**, 359, 1910

[16] Lenard, Ann. der Phys. **61**, 672, 1920

[17] Epstein, Phys. Rev., August, 1923

[18] Maxwell, Scientific Papers, **2**, 705

[19] Millikan, Phys. Rev. **32**, 380, 1911

dynamics as will presently be discussed in connection with case D. It is here mentioned solely because of its historical interest.

In Case C_b, diffuse reflection, Epstein, which will be understood henceforth when the term "diffuse reflection" is used without qualification, the assumption is the same as in C_a in that all of the molecules incident upon a given element of surface must emerge from that same element, but it differs in that the distribution of the emerging molecules is Maxwellian both in the matter of speeds and in that of the "random distribution" of directions. This is the only case of diffuse reflection which has any physical probability and which is not in contradiction with the second law. For it Epstein obtains

$$F=[(4/3)+(\pi/6)]\pi\rho a^2\bar{c}v=1.857\pi\rho a^2\bar{c}v \qquad (7)$$

Case D. Radial reflection. This purely hypothetical case assumes the return of all impinging molecules normally to the surface and without change of energy. Although such an ideal case is of course impossible, McKeehan,[7] Gaeda,[20] and Lenard[21] have all contended for the possibility of a *preference*, at least, of the emerging molecules for normal emission. Lenard and Epstein agree in finding for this case

$$F=(20/9)\pi\rho a^2\bar{c}v. \qquad (8)$$

Now the foregoing formulas may be used for computing the value of $(A+B)$ corresponding to each particular case. Thus, it was shown above that in the limiting case of a very rare gas the resistance must be proportional to a^2. Although viscosity has nothing to do with the resistance, it is legitimate to retain, if we like, the viscosity coefficient in the resistance-constant, and hence to write for this limiting case in conformity with Eq. (2), in Case A for example, since $(A+B)$ is as yet quite undetermined,

$$F=\frac{6\pi\eta av}{1+(A+B)l/a}=(4\pi/3)\rho a^2\bar{c}v$$

Writing, then, in accordance with the convention consistently used in this work, $\eta=.3502\rho\bar{c}l$, and solving for $(A+B)$, there results, when l/a is so large that unity is negligible in comparison with $(A+B)l/a$,

For Case A : $(A+B)=1.575$
For Case B : $(A+B)=1.575$
For Case C_a: $(A+B)=1.181$
For Case C_b: $(A+B)=1.131$
For Case D : $(A+B)=\ .945$

While, then, the determination of slip-coefficient (i.e. of A) does not enable us to differentiate at all between condensation and re-evaporation,

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[20] Gaede, Ann. der Phys. **41,** 323, 1913

[21] Lenard, Ann. der Phys. **60,** 372, 1919

diffuse, and radial reflection (cases B, C, and D, respectively), the foregoing measurements at very low pressures, combined with certain theoretical considerations, supply a precise criterion for so doing.

b. Thermodynamic considerations and Case D. It has already been pointed out by Gaede[22] that it is impossible, without a violation of the second law of thermodynamics, that the reactions on any *stationary* surface due to the molecules emerging from it, should be different from the reactions due to the molecules incident upon it. But the distribution of the *impinging* molecules is the Maxwellian and therefore follows the cosine law (diffuse incidence). Hence the reactions on a surface *at rest*, due to the emerging molecules, must also correspond to those of diffuse emergence. If this were not so, it would be possible to make surface B (Fig. 6), a rough one, which necessarily gives rise to diffuse emergence, and to coat A with a liquid or with any other substance which by hypothesis gives rise to a preferential radial emission. The incidence reactions on A and B would then be balanced, but the emergence reactions on A would exceed those on B and rotation about M in the direction of the arrow would result, thus violating the second law of thermodynamics. It is to be noted that this condition is not at all at variance with the existence of *specular* reflection, since such reflection gives the same distribution to the emerging and the incident molecules. *It is, however, completely at variance with the assumption that such fraction of the molecules as are absorbed and re-emitted have any tendency whatever toward normal emergence.* Gaede assumes such preferential normal emission from all *liquid* surfaces, and calls into existence his hypothetical gaseous film condensed upon his glass-surfaces, in order to make these surfaces act like a liquid in producing a preferential normal emission, a condition which he needs for one phase of his argument. He then attempts to avoid the thermodynamic difficulty which he himself has presented as

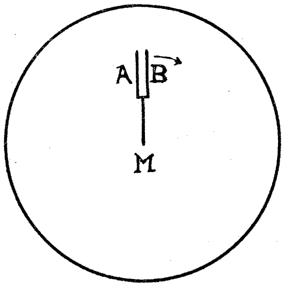

Fig. 6.

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[22] Gaede Ann. der Phys. **41**, 331, 1913

in the foregoing, by assuming that the surface upon which this gas film is condensed has such a degree of *mechanical* irregularity as to re-distribute the emerging molecules in all directions. *Since, however, some of the surfaces dealt with in the present experiments are already those of liquids (oil drops), it is clearly impossible to invoke complete mechanical roughness to produce the diffuse emission demanded by the thermodynamics.* Furthermore, Gaede's assumption obviously requires that there be no differences of mechanical roughness whatever among different surfaces, but rather that all surfaces, whether liquid or solid, act like surfaces which are mechanically rough. Such an assumption is not only of improbable correctness from *a priori* considerations, but it is completely at variance with the facts of specular reflection which I have previously reported, and which are fortified by the results to be presented below.

It is also permissible to add that the argument given by both Gaede and Lenard in the endeavor to render intelligible from a mechanical viewpoint the assumed radial emission from a liquid surface is, as it seems to me, invalid. That argument is that in view of the forces existing near the surface, the molecules which attempt to escape obliquely are more likely to be pulled back into the surface than are those which escape near the vertical and that therefore the emission is primarily in the direction of the vertical. But I think it more correct to say that although it is true that the molecules which *start* to emerge near the normal are the only ones which can escape, yet the action of the normal surface-force must result in the distribution of the angles of emission of these molecules in all directions by the time they succeed in getting through.[23] Indeed, this is demanded by the Maxwell Distribution-Law which as is well known, holds as well for the molecules emerging from a liquid surface as for those on either side of the surface; for the Maxwellian distribution means *random distribution of directions*, as well as a particular distribution of speeds. *In other words, from neither mechanical nor thermodynamic considerations it is possible to admit a preferential emission of molecules from any surface, liquid or solid, in the direction of the normal.* This disposes entirely of the need of further consideration of Case D, and makes it necessary to reconcile the experimental value of the constant $(A+B)$ with the types of emission or reflection represented in Cases A, B and C.

c. The elimination of Case B. The experimental value of $(A+B)$, namely, 1.154, is altogether irreconcilable with the theory of condensation and subsequent re-evaporation which is uniform over all parts of

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[23] This dynamical argument against the possibility of a preference for normal emission, was first called to my attention by Mr. C. G. Darwin.

the surface (Case B). It is also irreconcilable with any combination of specular reflection with a condensation and re-evaporation of this sort, since for both of these cases the value of $(A+B)$ should be 1.57. From the results obtained by Knudsen,[24] Langmuir,[25] and Wood[26] on the reflection of the molecules of metallic vapors, it might at first be thought that Case B would be nearly realized with mercury droplets falling through the vapor of mercury, for example; for the foregoing authors find that in such cases practically all impinging vapor-molecules do suffer condensation. And both the rotation of the droplets, because of their Brownian movements, and their high thermal-conductivity, might be expected to distribute the emitted molecules more or less uniformly. However, Epstein shows in his paper that when the impacts are as infrequent as is the case for very large values of l/a, even a substance like oil behaves as a perfect conductor of heat, so that the high conductivity of metallic droplets would not cause them to behave any differently in this respect from the oil droplets. Also, since the observed value of $(A+B)$ for oil shows that the Brownian movements of the oil drops have in fact no appreciable effect in distributing the emerging molecules uniformly, they could not do so in the case of metals either. It appears then, in view of Epstein's analysis combined with the foregoing experimental results, that Case B may be definitely eliminated for all kinds of drops. This leaves only A and C to consider.

d. The combination of Cases A and C. As indicated in the foregoing, the observed value of $(A+B)$, namely, 1.154, corresponds nearly to Case C_b which should theoretically give a value 1.131. But it was shown in the preceding paper, in connection with the determination of A alone, that in the case of air and oil $10\frac{1}{2}$ per cent of the molecules of the air suffer specular reflection from the surface of the oil. Computing then, from Case A the value of $(A+B)$ due to $10\frac{1}{2}$ per cent of specularly reflected molecules and $89\frac{1}{2}$ per cent of diffusely reflected ones, we find as the theoretical value of $(A+B)$, 1.164 in place of the observed value 1.154. *The agreement is probably within the limits of experimental error and furnishes excellent confirmation of the existence of specular reflection.*

It is interesting that the observed value is, if anything, a trifle lower rather than higher than the computed value. There is but one cause which could push it down, and this should have but a very minute effect with liquid spheres, but it is of importance to consider it because of a later application. The whole resistance F to the motion of the sphere

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[24] Knudsen, Ann. der Phys. **47**, 697, 1915

[25] Langmuir, Phys. Rev. **8**, 149, 1916

[26] Wood, Phil. Mag. **30**, 300, 1915

arises from the difference in the number of impacts which the surrounding molecules make upon the *front* half of the sphere and those which they make upon the back half. If, then, there are any *mechanical* irregularities of any kind on the surface of the sphere, it is clear that the faces of the protuberances which are turned toward the direction of motion, are going to be hit by molecules more frequently than are those which are turned away from it, so that even if each element of the surface reflects diffusely, the total momentum transferred to the sphere by the excess of molecules which impinge on the front face, is somewhat larger, by virtue of these mechanical irregularities, than it would be if the surface were perfectly spherical and each point reflected diffusely, as was assumed in the working out of Case C_b. In other words, even with each element of the surface reflecting diffusely, any sort of mechanical irregularities, however slight, would tend to increase the resistance and therefore to produce a value of A smaller than 1.164. It is possible that this effect may be responsible for the slight difference between 1.154 and 1.164.

e. Significance of the term diffuse reflection. Although the results herewith obtained are apparently quite unambiguous in demonstrating that a law of reflection corresponding closely to Case C_b is the correct one, it is to be particularly emphasized that the method here used is incapable of distinguishing between diffuse reflection without interchange of energy with the surface, and condensation and re-evaporation *of such sort that each element of the surface re-evaporates all of the molecules which fall upon it.* The distinction between these two cases can only be made by measurements upon the flow of heat through these surfaces. In other words, no definite conclusions with regard to the value of "accommodation coefficients"[27] can be drawn from measurements upon $(A+B)$. It is, of course, true that specular reflection, such as has been here found, necessarily means an accommodation coefficient less than 1, since specular reflection undoubtedly means the return of molecules after a single impact. The fraction of the molecules which are not specularly reflected, however, may be thought of, so far as these experiments are concerned, either as "condensed and re-evaporated from the same spot," or as "diffusely reflected." The fact that they must be re-evaporated from the same spot (for the number of incident molecules varies from a maximum in front to a minimum behind) seems to make the term "diffuse reflection" more appropriate, while the fact that the distribution of the emergent molecules is the Maxwellian and therefore is determined by conditions existing on the sphere itself and not by the conditions of

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[27] See Smoluchowski, Wied. Ann. **64**, 101, 1898; Phil. Mag. **46**, 199, 1898; and Knudsen, Ann. der Phys. **34**, 593, 1911

incidence (for, on account of the motion of the sphere, the distribution of the incident velocities is not Maxwellian) seems to make the designation condensation and re-evaporation more appropriate.

5. GENERAL VALIDITY OF THE FOREGOING LAW OF FALL

It was pointed out in the preceding paper that with an oil surface, the value of A varies from .815 for hydrogen to .90 for helium, these figures corresponding to a variation in the percentage of specular reflection from 7.5 in the case of hydrogen to 12.6 in the case of helium. It might at first be thought that such changes in the percentage of specular reflection would exhibit themselves as considerable differences in $(A+B)$, but the working out of the actual numerical values by the method just employed shows that a combination of $7\frac{1}{2}$ per cent of specular reflection with $92\frac{1}{2}$ per cent of diffuse reflection, gives rise to a value of $(A+B)$ of 1.154, and the combination of 12.6 per cent of specular reflection with 87.4 per cent of diffuse reflection, corresponds to a value of $(A+B)$ only slightly greater, viz. 1.170. In other words, unless my values of $(A+B)$ are reliable to better than 1 per cent, it would be impossible to observe any differences between the theoretical values of $(A+B)$ for oil and air (1.164), for oil and helium (1.170) and for oil and hydrogen (1.154). Even in the case of shellac and air, which, according to slip-measurements shows 21 per cent specular reflection or nearly three times that found in the case of hydrogen and oil, the value of $(A+B)$ comes out but 1.197, or only a little more than 3 per cent higher than the value for air and oil. It is to be expected, too, that solid spheres of shellac will show more mechanical irregularities than would liquid spheres of oil, and this would mean that the 1 per cent of diminution of $(A+B)$ which we have attributed to mechanical irregularities in the case of oil, would presumably be larger for the shellac. *It is not then to be expected that the final resistance factor* $(A+B)$ *will be found to depend to any appreciable extent upon either the nature of the ambient gas or the nature of the droplet.* The recent measurements of Mr. Eglin who has repeated, at my suggestion, my measurements on oil-drops in air and has extended them to other gases, particularly the monatomic gas helium, are in excellent agreement with these predictions.

It is also interesting to observe, as will be more fully pointed out in the next section, that Knudsen's observations on glass and air lead to a value of $(A+B)$ which is within 1 per cent of the value here found for oil and air. *All of these results are important in that they show that the complete law of motion herein developed is of very general validity and can be used without fear of large error in considering the motions of any kind of* *particles in the rarefied atmosphere of the earth.* It is even probable that metallic spheres would show very close to the same value of $(A+B)$ as is here found for oil.

6. Comparison with Results of Other Observers

There are two results by Knudsen with which the foregoing observations and conclusions may be compared. The first is that in which he obtained, by measuring the damping factor of oscillating glass spheres, the law of resistance represented by Eq. (4). It is interesting to observe that a part of the difference between the numerical values of his constants $(A, B, \text{and } c)$ and mine is due to the fact that he uses a different convention in the formula for viscosity, namely: $\eta = .310\rho cl$, whereas I, merely for the sake of uniformity with my other work, have used the value .3502 in place of his .310. *When this difference is allowed for, it is found that Knudsen's value of* $(A+B)$ *for his glass spheres, in terms of my convention, is 1.164 which is within a trifle less than 1 percent of my value.* It is true that his value of A is more than 10 per cent lower than mine, namely, .768 while mine is .864; but it is my judgment that while Knudsen's method is reliable for obtaining the value of $(A+B)$ that is, the resistance when the gas is exceedingly rare, it is open to serious objection when the gas is dense, because of the well established retarding influence of the walls of a vessel[28] upon the motion of a sphere moving through a *viscous* medium within the vessel. I do not therefore think Knudsen's formula for the law of fall is as trustworthy as my own, but I see no reason why his value of $(A+B)$ for glass may not be about as good as mine for oil. *There is nothing but specular reflection on glass to push this value from its theoretical limit 1.13 up to its observed value 1.164.*

The second result of Knudsen's which appears at first sight to be at variance with the conclusions drawn in this and the preceding paper on the coefficient of slip, is found in the fact that both he and Gaede in their measurements upon the outflow of greatly rarified gases through capillary tubes, apparently establish the validity of the law of diffuse reflection from glass surfaces, whereas I find what seems to me to be unimpeachable evidence that there is $10\frac{1}{2}$ per cent of specular reflection under the same circumstances. Knudsen's argument rests upon the fact that when he computes the rate of flow of a gas at very low pressures through his capillary tube upon the assumption of the diffuse reflection of the molecules, he obtains a result which is within the limit of observational error of his observed rate of flow. *It should be pointed out, however, that if there*

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[28] See Arnold, Phil. Mag. **22,** 757, 1911

are any mechanical irregularities in the inner surface of the glass tube, such as were assumed in a preceding section, the rate of flow at very low pressure through a capillary tube should be less than that corresponding to the law of diffuse reflection. It is quite clear that at pressures so low that the molecules, if properly directed, can shoot the whole length of the tube without making an impact, mechanical irregularities *such as must exist on the inside of the tube*, are bound to receive more impacts on the faces which are turned toward the point of high pressure than on the opposite faces, and even if the law of reflection from each element of surface is "diffuse," there is still a tendency for these protruding irregularities to throw back the molecules in the direction from which they came and therefore to give rise to a rate of flow which is *less* than that corresponding to diffuse reflection. Gaede[22] points this out with great clearness when he is picturing these mechanical irregularities as covered with a film of gas, but he seems to forget that the same reasoning holds equally well when there is no film of adhering gas.

In a word, then, if Knudsen and Gaede obtain at sufficiently low pressures a rate of flow through tubes which is in agreement with the law of diffuse reflection, *the result can only be interpreted as meaning that there was in their experiments a tendency toward specular reflection from the glass which increased the rate of flow by just such an amount as to neutralize the retarding effect of the mechanical protuberances here under consideration. In other words, even Knudsen's results seem to call for specular reflection for their proper interpretation.*

It is to be noted that this phenomenon of a general return of the molecules after impact in the direction from which they came, in the case of flows through capillary tubes, will theoretically begin to diminish when the mean free path becomes smaller than the length of the tube, and that it will become less and less appreciable as the mean free path becomes smaller and smaller in comparison with the dimensions of the tube, disappearing entirely when the conditions of viscous flow have set in, for then the mean free path has become very minute and the velocity in the layer next the outside wall has become completely negligible in comparison with the molecular velocity. The lower theoretical value of A should then be that corresponding to diffuse reflection, viz: $A = .7004$, as computed in a preceding paper.

The very marked minimum which Gaede found in "G" when he was measuring the outflow of gas *in a thin sheet* instead of through a circular cross section, and which was reached at the high value of the pressure of 23 mm, probably has its explanation in the changing of the stream lines within the vessel as the flow changed from one governed by the laws of viscous flow to one governed by the laws of molecular flow. *It is particularly significiant that Gaede reports no such marked minimum when he worked with a cylindrical vessel, that is, one which is symmetrical with respect to the axis of flow.* In that case he found only a slight tendency toward a minimum, as Knudsen had done before him. This may have its cause in the effect just mentioned, which should persist to some extent even in tubes of circular section, or it may be due, as Knudsen suggested, to water vapor or other residual gases.

The present results remove entirely such discrepancy as seemed to exist between my original results on the correction of Stokes' law and those of McKeehan, whose value of A came out some 15 per cent higher than mine. Since some of McKeehan's results were taken at relatively high values of l/a, his large A is in reality a mixture of the present constants A and $(A+B)$, the precision of his measurements not being sufficient to bring to light the two slopes which actually exist.

I wish to thank Dr. Yoshio Ishida for his assistance in the experimental portion of this investigation.

NORMAN BRIDGE LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
December 30, 1922.