COEFFICIENTS OF SLIP AND MOMENTUM TRANSFER IN HYDROGEN, HELIUM, AIR AND OXYGEN

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Abstract

Coefficients of slip for polished silver oxide surfaces in hydrogen, helium, air and oxygen.-The rotating cylinder method was used, and besides taking precautions to insure spectroscopically pure gases, a continuous circulation of gas was maintained to minimize the effect of the release of occluded gas from the walls of the apparatus. The mean values reduced to 23°C and 76 cm Hg, are: 121(H₂); 190(He); 68.5(Air); 72.1(O₂), all times 10⁻⁷ and accurate to about one per cent. Maxwell's coefficient of diffuse reflection f comes out 1.00, 1.00, .98, and .99 for the four gases. To check these results, measurements of the variation of the deflection with pressure were made at low pressures, .0003 to .0015 mm, where the mean free path is considerably greater than the distance between the cylinders. From a comparison of these results with the slopes computed from kinetic theory assuming complete diffuse reflection, f comes out 0.99, 0.99, 0.97 and 0.96 for the four gases, in good agreement with the values given by the slip measurements. The intercepts for zero pressure indicate the presence of some vapor, but this should not affect the slopes appreciably. It is concluded (1) that for these gases practically all molecules are diffusely reflected from the surfaces used, the percentages specularly reflected being close to zero for H₂ and He, and about 2 or 3 for air and O_2 ; also (2) that values of f deduced from Maxwell's equation of slip are reliable.

INTRODUCTION

FROM the kinetic theory of gases Maxwell deduced that the coefficient of viscosity should be independent of the pressure, and experimental investigations verified this deduction over a wide range of pressures. At very low pressures, however, the viscosity becomes less than at the higher pressures and this deviation is of interest because it may be connected theoretically with the nature of the molecular reflections at the surfaces that are in relative motion. The phenomena may be described conveniently by the introduction of the term "coefficient of slip." Ordinarily the momentum transfer through the gas is given by $\eta(V/d)$ where η is the coefficient of viscosity and V/d the velocity gradient. At low pressures the lessened momentum transfer may be written $\eta V/(d+2\zeta)$ where ζ is called the coefficient of slip in agreement with the hydrodynamical theory for the case of a flowing liquid slipping at a wall.

Maxwell¹ deduced from the kinetic theory the following value for ζ

$$\zeta = \frac{2-f}{f} \cdot \frac{\eta}{p} \cdot \sqrt{\frac{\pi RT}{2M}}$$

The fraction (1-f) represents that portion of the impinging molecules reflected without any momentum transfer, or "specularly" reflected.

Stacy² and later Van Dyke,⁸ using the constant deflection method for the determination of the coefficient of slip, found that f depended upon the nature of the surface. For a machined brass or old shellac surface, using air or carbon dioxide, no specular reflection was found. For oil and fresh shellac surfaces, specular reflection ranged from 8 to 21 per cent, and was greater for carbon dioxide than for air.

Some doubt might be cast on the precision of deductions from Maxwell's equation, since Maxwell himself remarks on the inaccuracy of his assumptions and suggests that the surface conditions arrived at in this way are liable to important corrections. The subject has also been treated by Baule.⁴ His theory leads in a first approximation to an equation for the slip coefficient of the same form as Maxwell's. The fraction fis interpreted in terms of a coefficient which gives the fraction of the molecules that make only one collision with the surface, while the remainder make sufficient collisions to come into equilibrium with it. His formula becomes identical with Maxwell's in case f=1. Thus in both Maxwell's and Baule's theories arbitrary assumptions are made and no idea may be reached as to the degree of approximation attained in the formulas deduced.

The present investigation was undertaken with a view of determining Maxwell's f for the gases hydrogen, helium, air and oxygen from the coefficient of slip, employing the constant deflection method. Further, the attempt was made to check the results obtained from the coefficient of slip by working at pressures so low that the mean free path is considerably greater than the distance between the cylinders. Under these conditions a very simple theory applies, as the momentum is directly transferred, and the number of impacts per cm² per second equals $\frac{1}{4}n\bar{c}$. The tangential force per cm² on the inside cylinder is, therefore, equal to $\frac{1}{4}n\bar{c}mV$, where m equals the mass of the molecule and V is the velocity imparted due to the motion of the outside cylinder. Should the results of both methods be in agreement, the use of Maxwell's formula would be

¹ Maxwell, Scientific Papers, Vol. II, p. 708

² Stacy, Phys. Rev. 21, 239, 1923

⁸ Van Dyke, Phys. Rev. 21, 250, 1923

⁴ Baule, Ann. der Phys. 44, 145, 1914

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justified for the purpose of making deductions as to the nature of the collisions at the walls.

To eliminate troubles formerly experienced due to the release of occluded gases from the walls and consequent contamination of the gas under investigation, the "constant flow" method was used. It was thought that by continuous circulation, the gas could be kept sufficiently pure at these low pressures to admit of reliable measurements.

Apparatus

The apparatus consisted of two concentric cylinders, the outer one rotated at a constant rate by a driving mechanism operated by a falling weight, the inner one suspended by a steel wire, the deflection being observed by a telescope and scale. Because of slight variations in the de-



Fig. 1. Diagrammatic sketch of apparatus.

flection, scale readings were taken every half minute, the size of the drum upon which the chronograph record was made allowing about thirty such readings to be taken. The average of these was regarded as the deflection for the pressure recorded. The pressure in every case was a mean of four or five pressure readings taken during the run.

The brass surfaces were coated with a thin coat of silver oxide by rotating the cylinders in a silver nitrate solution. The silver deposited was immediately oxidized. This surface was later polished and made as smooth as mechanical means would permit. Before mounting, the surfaces were carefully cleaned with benzene, ether and alcohol. The details concerning the construction of the driving mechanism and cylinders are fully described by Gilchrist⁵ in his paper on the viscosity of air.

The modifications and additions that were made so that continuous circulation of the gas would be possible are clearly shown in the dia-

⁵ Gilchrist, Phys. Rev. 1, 124, 1913

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grammatic sketch. The gas was pumped out of the apparatus by a mercury diffusion pump through a liquid air trap E. It was allowed to flow into the apparatus through a capillary and finally through liquid air trap D. It was found that the pressure in C could be kept very constant during the time that the run was being taken. To change the pressure to any desired value, it was only necessary to allow gas to flow into the reservoir B from the storage tank A.

The dimensions of the cylinders are as follows: Radius of outer cylinder 6.063 cm; radius of nner cylinder 5.341 cm; length of inner cylinder 24.88 cm; distance between cylinders .722 cm.



The scale was about 236 cm distant from the mirror on the suspension and deflections of 30 to 70 cm were obtained in the slip observations.

While the slip observations were being made, the gas was allowed to circulate continuously through the apparatus.

The hydrogen gas was taken from a tank and allowed to pass through a long tube of heated copper filings for the purpose of removing any oxygen present, then through tubes of NaOH and P_2O_5 .

The helium was also taken from a tank, and purified by passing through charcoal tubes kept at liquid air temperature. For slip determinations in helium, the apparatus was changed slightly in order to purify the gas more rapidly and also to save the gas. The outlet of the mercury diffusion pump was connected to the inlet of the helium reservoir and the same gas circulated continuously through the apparatus. In this way purification was effected very quickly, only a few minutes being required for all the air lines at first visible in the spectrum, to disappear.

Oxygen was prepared by heating potassium permanganate and was then allowed to flow through liquid air into the reservoir.

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The air used was carefully dried by passing through phosphorous pentoxide and calcium chloride tubes.

All the gases were examined spectroscopically and found pure.

Theory

(A) Low pressure. Kinetic theory gives that the number of impacts per cm² per sec. $=\frac{1}{4}n\bar{c}$. If the velocity of the outside cylinder is V, and a fraction f of the impinging molecules is diffusely reflected, the tangential force per cm² of the inside cylinder equals $\frac{1}{4}nm\bar{c}Vf = \frac{1}{4}\rho\bar{c}Vf$, where ρ is the gas density.

From kinetic theory it can also be shown that $\rho \bar{c} = 2p \sqrt{(2M/\pi RT)}$.

We have, therefore, that the tangential force on the inside cylinder per cm² is $\frac{1}{2} \sqrt{(2M/\pi RT)} \cdot V f p$ where M=molecular weight, R=gas constant, T=absolute temperature, and p=pressure.



At high pressures the tangential force per $\text{cm}^2 = \eta V/d$ where η is the coefficient of viscosity and d is the distance between the cylinders.

Since the deflection of the inner cylinder, d_p , is proportional to the force per cm², the constants of the apparatus can be eliminated if the force at low pressures is divided by the force at high pressure, and the ratio placed equal to the ratio of the deflections respectively.

We then obtain

$$\frac{d_p}{d_p} = \frac{f_p}{f_p} = \frac{d}{\eta} \sqrt{\frac{M}{2\pi RT}} \cdot fp = Kf$$

where $K = (d/\eta) p \sqrt{(M/2\pi RT)}$, a constant for a given gas at a fixed temperature. Since all observations are reduced to a common velocity, V does not enter in this formula. f, the quantity sought, is then equal to the ratio of the slope of the line found experimentally by plotting de-

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flection against pressure, to K, which can be computed from well-known constants.

(B) Slip determinations. From the definitions in the first paragraph, it is seen that the deflection at low pressure is less in the ratio $(1+2\zeta/d)$. ζ is found to be inversely proportional to the pressure so that the coefficient of slip reduced to 76 cm pressure or $\zeta p/76$ may be calculated from the ratio of deflections at high and low pressures.

Further theoretical discussions on the determination of the slip coefficient are given in a recent paper by Professor Millikan.⁶

OBSERVATIONS

The coefficients of slip, reduced to 76 cm of mercury, are tabulated in Table I, with the corresponding pressures in the adjacent column. The average for each gas is compared with the value computed from Maxwell's formula, putting f equal to unity. For hydrogen and helium the experimental and theoretical values differ by less than one per cent, which is well within experimental error. For air and oxygen, the experimental value is about three per cent higher than the theoretical value, indicating a slight amount of specular reflection.

Hydro	Hydrogen		Helium		Air		Oxygen	
<i>p</i> (mm)	ζ ₇₆₀ (10 ⁻⁷)	∲ (mm)	ζ ₇₆₀ (10 ⁻⁷)	∲ (mm)	ζ ⁷⁶⁰ (10- ⁷)	<i>p</i> (mm)	ζ ₇₆₀ (10 ⁻⁷)	
0.397	121	0.339	189	0.102	67.7	0.102	71.9	
0.315	122	0.316	191	0.103	68.8	0.102	71.9	
0.304	120	0.312	193	0.0918	68.2	0.103	72.6	
0.270	118	0.314	192	0.125	68.9	0.0982	72.5	
0.360	121	0.316	188	0.128	68.8	0.0921	72.3	
0.305	122	0.397	188			0.0893	71.8	
0.249	120	0.394	188					
		0.390	193					
Aver.	121		190		68.5		72.1	
Theor.*	121		191		66.2		70.2	

TABLE I

Coefficients of slip

All readings are reduced to 23°C and 760 mm pressure.

*Computed assuming f = 1.

The results obtained at very low pressures are best shown graphically. Two graphs are given for each gas.

Figs. 2–5 in which the deflections are plotted against the pressure, clearly show the existence of a linear relation at these low pressures, and of a deflection intercept. At the low pressures, trouble was expected due to the presence of mercury vapor, since the rotating cylinder was operated

⁶ Millikan, Phys. Rev. 21, 217, 1923

from the outside through a mercury seal, although it was thought that the constant circulation of gas through liquid air would minimize the effects of mercury vapor.

In all cases the deflection at low pressures was a linear function of the pressure, but always indicated a deflection at zero pressure. Observations at higher pressure showed a gradual decrease in slope. This deflection intercept became smaller the longer the liquid air remained in contact with the apparatus, although the change after the liquid air had been on for about seventy-five hours was slight. Accompanying this decrease in intercept was an increase in slope. This intercept was no doubt due to vapors arising from stop-cock grease as well as to mercury vapor, and the longer the liquid air remained on the traps, the more vapor was condensed out. This slight increase in slope as the vapor disap-



peared is what wou'd be expected if the vapor is relatively more important at the lowest pressures read, due to a freer evaporation when the pressure is very low. Two or more curves are given for each gas to show the decrease of intercept and corresponding increase of slope as the liquid air remained longer in contact with the apparatus.

In each case the slope that was used for the computation of f was the slope of the curve having the smallest intercept and computed from data taken three days or more after the liquid air was put on.

For the gases hydrogen and helium specular reflection is entirely absent. Both investigations clearly indicate this. In oxygen and air, the two heavier gases, there seems to be a slight amount of specular reflection, possibly two or three per cent.

The values of f obtained from the slope at low pressures are slightly less than those obtained from the coefficient of slip, but this difference is

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to be expected as the intercept of the line from which the slope was taken was not zero, and a further slight increase in slope, and therefore a slight increase in f would take place if the intercept were zero. Nevertheless,

TABLE II	
Maxwell's f	
From slip	From slope
1.00	0.99
1.00	0,99
0.98	0.97
0.99	0.96
	TABLE II Maxwell's f From slip 1.00 0.98 0.99

since the values obtained, as shown in Table II, agree to one per cent, it can be concluded that the results of both methods are in accord.



This agreement between the two methods indicates that the deduction of diffuse reflection of the molecules at a wall from Maxwell's equation for slip is quite justifiable.

In conclusion I wish to express my indebtedness to Professor A. J. Dempster who suggested this investigation at low pressures, for the interest shown throughout this research, and for the ready help and advice he has accorded me. I wish also to thank Professor H. G. Gale and other members of the staff at Ryerson for helpful suggestions and interest shown.

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