

EXPERIMENTAL TEST OF MAXWELL'S DISTRIBUTION LAW*

BY JOHN A. ELDRIDGE

ABSTRACT

A method is described for obtaining a velocity spectrum of a metallic vapor. The apparatus consists of a number of coaxial discs with radial slots which rotate at high speed and serve as a velocity filter for the molecules. The velocity can be measured directly somewhat as in the Fizeau experiment. The apparatus has been used to measure the distribution law of molecular velocities in cadmium vapor and it is found to agree with that of Maxwell within experimental error.

ONE of the most famous achievements of the mathematical physicist is the law of distribution of molecular velocities in a gas. Originally derived by Maxwell, the proof has been varied and presumably rendered more precise by Boltzmann, Lorentz, and Jeans; yet no proof has been above criticism. More recently the newer quantum mechanics has led to a different law but, characteristically, this degenerates with close approximation into the classical law of Maxwell except at low temperatures and high pressures.

Strangely enough, no rigorous experimental test of the law has ever been made. In general such tests as have been made have agreed with the predictions of the law within the precision of the experiment. The older methods were indirect. Richardson has shown that the Maxwellian distribution held for electrons emitted from a hot wire and the measurement of the Doppler broadening in the spectrum from a discharge tube has been found to be in accord with that expected from the law. The first direct measurement of molecular velocities of silver vapor was made by Stern and quite recently Costa, Smyth and Compton¹ have used a method rather similar to that which is to be described to determine the velocity in several permanent gases. The precision of these experiments was quite low and can hardly be said to constitute a verification of the law.

The present experiment aimed to find the distribution of velocities in cadmium vapor. The apparatus used is shown diagrammatically in Fig. 1. In a large glass tube was mounted the system of discs shown. The lowest heavier disc acts as the rotor of an induction motor—the other thinner discs have in each a hundred radial slots cut in their periphery and serve as a velocity filter. Leading off from the main tube the bent side tube contains the cadmium metal and projecting from it into the main tube a closely fitting aluminum tube. The protruding end of this tube is closed except for a fine slit (one or two tenths of a millimeter wide) cut in aluminum foil and placed as close as practicable below the lowest of the filter discs. This side tube is

* A report on the earlier results of this work was given before the Iowa Academy of Science in May, 1927.

¹ Stern, *Zeits. f. Physik* **2**, 49 (1920); Tykocinski-Tykosiner, *Journ. Opt. Soc. Am.* **14**, 423 (1927); Costa, Smyth and Compton, *Phys. Rev.* **30**, 347 (1927).

heated by suitable furnaces. Above the filter a glass tube with a flattened end is shown—this contains a little liquid air and acts as collector for the filtered molecules. The success of the experiment depends upon the prompt condensation of all scattered molecules. To accomplish this the walls of the large tube and the disc system were coated with cadmium and surrounded so far as practicable with liquid air. To eliminate more perfectly the collection of these scattered molecules a stationary plate (not shown) was used as a baffle to keep the scattered molecules from reaching the upper part of the tube.

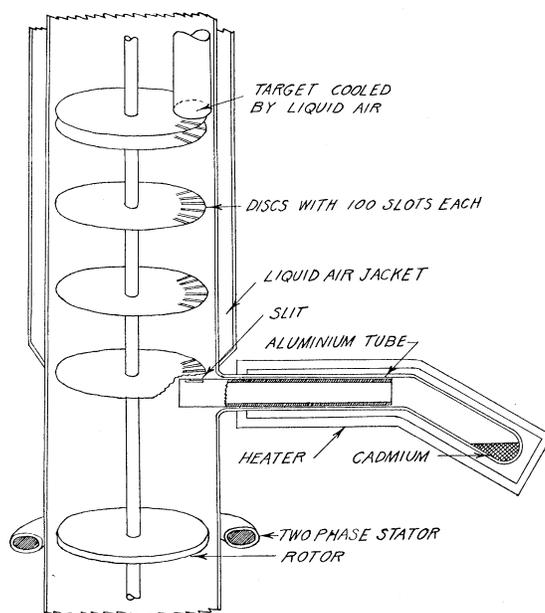


Fig. 1. Diagram of apparatus.

The disc system had hardened steel pivots which were seated in fiber and lubricated. The system could be rotated more or less synchronously up to 7200 R.P.M. Its rate of rotation was measured with a stroboscope.

The theory of the filter is almost self-evident. Consider at first only the two extreme filter discs and suppose each to have but a single slit, the one above the other. The discs are first rotated very slowly and a deposit is obtained marking the "unshifted line." When the discs rotate rapidly the upper disc travels a small distance while the molecule travels the filter length, giving a band of deposit with the fastest molecules registering most closely to the unshifted line. When more slits are used as is desirable to shorten the experiment we get into trouble from "cross fire"; this can be eliminated by using intermediate discs, lined up so as to block all but the desired ray path. As a matter of fact the slots through which a molecular beam travels are not exactly parallel (because of the rotation of the disc during the transit) and

the intermediate discs tend to diminish the effective aperture for the molecules with the larger deflections; this difficulty is easily remedied by making the slots of the intermediate discs somewhat wider than those of the two end discs and by introducing a partially compensating twist in lining up the discs.



Fig. 2. Photograph of film obtained in a typical run.

Fig. 2 shows the film obtained in a typical run² and the points in Fig. 3 give the measured densities as read with a microphotometer by measuring films of known density ratios. The abscissas of the curve and the distances from the base line to a point in the velocity spectrum are proportional to $1/v$ instead of to v .

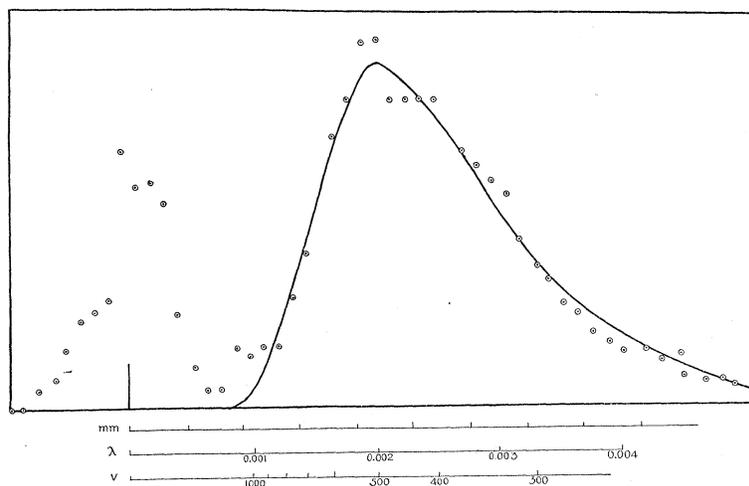


Fig. 3. Densities of the film as measured with a microphotometer.

There are two reasons why the blackening of the film or the ordinate of the curve do not correspond to the ordinate of the Maxwell curve. (1) The densities for low velocities are reduced because these slowly moving molecules are spread out between the center of density and infinity, and the faster molecules, concentrated between the center of density and the origin, have

² The photograph (Fig. 2) of the cadmium deposit was taken several months after deposition. It shows the peculiar evaporation or absorption which takes place locally in such films. The dark spots are air bubbles in the glass but the prominent white spot and the smaller white spots in the deposit as well as the disappearance of the central portion of the undisplaced line are phenomena which took place gradually during the course of several months. The "evaporation" seems to be entirely local; a remeasurement of the density of deposit agreed within experimental error with those taken at the time of deposit except in those places where the metal had very obviously and almost completely disappeared.

much greater densities than corresponds to the usual Maxwell probability. (2) What is measured is not the number of molecules of a particular velocity *present* at any instant (as given by the distribution law) but the number *passing through* the slit and landing upon the collecting plate in a certain time which further emphasizes the faster molecules. We may consider the case in more detail.

According to Maxwell the proportionate number of molecules with velocities between v and $v+dv$ which are present at any time in a definite volume is

$$\frac{dN}{N} = \frac{4}{\pi^{1/2}} \frac{v^2}{\alpha^3} e^{-v^2/\alpha^2} dv$$

or combining the constants, $dN = C_1 v^2 e^{-v^2/\alpha^2} dv$, where α is the "most probable velocity." If we confine our attention to the molecules within the aluminum tube which are moving in such a direction as to pass through the slit, we select from the totality a certain small group of molecules whose velocities have certain definite orientations but the distribution law has the above form. However the number of these which pass through a given boundary (the slit) in a given time is proportional to the speed as well as the number present.

$$dN = C_2 v^3 e^{-v^2/\alpha^2} dv \quad (2)$$

where the meaning of dN has been changed to represent the number of molecules *passing through the slit* in a given time with velocities between v and $v+dv$. But the number of molecules which strike the collector at a distance between x and $x+dx$ and produce the blackening is equal to the number having reciprocal velocities ($\lambda = 1/v$) between λ and $\lambda+d\lambda$. Changing the independent variable then we get

$$dN = (\partial N / \partial v) (dv / d\lambda) d\lambda = C_2 v^5 e^{-v^2/\alpha^2} d\lambda$$

The number of molecules then passing through a slit with "slowness" between λ and $\lambda+d\lambda$ is according to the Maxwell law given by an expression of this form and the blackening of the film should correspond. It is well known that α , the velocity corresponding to the maximum of the Maxwell curve, is the root mean square velocity (\bar{v}) times the factor $(2/3)^{1/2}$. The "most probable slowness" the value of λ for which our curve has a maximum can readily be found to be

$$\lambda_m = \frac{1}{\alpha} \left(\frac{2}{5} \right)^{1/2} = \frac{1}{\bar{v}} \left(\frac{3}{5} \right)^{1/2}$$

In the present experiment the temperature was approximately 400°C. The corresponding root mean square velocity (\bar{v}) is 388 m/sec, "the most probable velocity" α is 317 m/sec and λ_m , the maximum of our slowness curve, is $\lambda_m = 1/500$ sec/m.

With a disc of 3.15 cm radius rotating 85 revolutions per second and length of filter 12.7 cm, 1 mm shift in spectrum corresponds to a reciprocal speed $\lambda = 1/2140$ sec/m.

The curve is seen to be in good agreement with the theory. Perhaps the agreement is somewhat fortuitous and indeed we have taken some liberty in assigning our zero point which has been taken several tenths of a millimeter away from the most probable center of the undisplaced line to make the points superimpose upon the theoretical curve. The resolution is not as high as desired—the undisplaced line is broader than necessary and if this lack of resolution is considered the agreement between the curve and theory is too good. The measurement of temperature was unsatisfactory—the cadmium was heated and the aluminum tube superheated; the temperature of this tube was determined by an earlier heating when a thermometer was inclosed in the aluminum tube—a direct measurement by thermocouple would be better. The results however are such as to encourage the belief that a really critical test of Maxwell's law is possible.

One consideration of which nothing has been said is the necessity of keeping the vapor pressure of cadmium within the source tube so low that the mean free path is long compared with the slit width. If this were not the case the velocity distribution in the neighborhood of the slit would be far from Maxwellian, and the emerging molecules would collide after leaving the slit and further complicates matters. In the experiment the slit width was less than 0.2 mm and the free path (cadmium at 320°C) was probably of the order of 1 mm. It goes without saying that the gas pressure of the tube must be maintained low enough to make collision during the molecular transit unlikely. In an earlier experiment where these conditions were not suitably attained a curve agreeing rather well with the theory for the faster molecules but departing badly for the slower ones was obtained.

UNIVERSITY OF IOWA,
September 28, 1927.

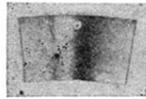


Fig. 2. Photograph of film obtained in a typical run.