A DIRECT MEASUREMENT OF MOLECULAR VELOCITIES

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Abstract

A method is described for the direct measurement of the velocities of neutral molecules. The molecules condense on a glass plate fastened to a cylinder which rotates at a high speed, 241 r.p.s. The molecules having velocities from 168 m/sec to 673 m/sec were spread over a band 3 cm wide. A stream of bismuth molecules is studied and the vapor found to be composed of 40 percent Bi and 60 percent Bi_2 at a temperature of 851°C.

Introduction

ONE of the fundamental assumptions of the kinetic theory of gases is the continual heat motion of the molecules in the gas. Even though there was no direct experimental verification of this assumption, the theoretical development progressed rapidly, resulting in the derivation of an expression for the distribution of molecular velocities by Maxwell[1] in 1859 and, later by Boltzmann.[2] This law has found many applications and until 1920 was only indirectly verified.

The first attempt at a direct measurement of molecular velocities was made by Stern[3] who intercepted a stream of silver atoms on a rotating plate. The displacement obtained was not sufficient to allow an analysis of the deposit beyond the location of the maximum. The results for the maximum agreed within the experimental error, about 15 percent, with that calculated from the theory. In 1927 Costa, Smyth, and Compton,[4] using rotating radially slotted disks and a radiometer vane as a detector attempted to secure a "velocity spectrum" of neutral molecules. Their results were in general qualitative agreement with the Maxwell-Boltzmann law but rather unsatisfactory because of the insensitivity of the detector. Eldridge,[5] using rotating disks as a velocity selector and condensing the molecules on a liquid-air cooled target, obtained a density distribution for cadmium which agreed fairly well with the theoretical distribution. Several objections might be raised, for his zero mark is not sharply defined but very broad; the zero of the theoretical curve has to be shifted about 0.05 cm to make the maximum of the theoretical curve coincide with the maximum of the deposit; his temperature measurement is unsatisfactory and his resolution is low. Lammert[6] developed a method for

[1] J. C. Maxwell, "Collected Works," **1,** 378 (1860) Cambridge University Press, Cambridge.

[2] L. Boltzmann, "Vorlesungen über die Gas Theorie," **1,** 15 (1910). Johann Barth, Leipzig.

[3] O. Stern, Zeits. f. Physik **2,** 49 (1920); **3,** 417 (1920).

[4] Costa, Smyth, and Compton, Phys. Rev. **30,** 349 (1927).

[5] J. A. Eldridge, Phys. Rev. **30,** 931 (1927).

[6] Berthold Lammert, Zeits. f. Physik **56,** 244 (1929).

producing molecular beams containing well-defined velocity bands. By taking a series of runs in which the bands had a definite width of 50 m/sec over a range of from 90 to 360 m/sec and determining the intensity of each band, a test of the Maxwell-Boltzmann law for mercury vapor was possible. Except for a systematic difference the results agree quite well with the theoretically expected distribution.

Theory

The aim of this experiment is to develop an apparatus with a resolving power greater than that obtained by Stern and Eldridge and thus allow a more detailed study of the "velocity spectrum" of neutral molecules. This, as shown later, can be attained by increasing the path-length and the speed of rotation.

Consider a gas issuing through a rectangular slit, g_1 (Fig. 1) in a side of the enclosure E which can be maintained at a constant temperature T. Let Knudsen's[7] condition for molecular streaming be satisfied, i.e., let the temperature be so controlled that the mean free path of the molecules within, is greater than the width of the slit g_1. With the aid of the slit g_2 a sharply defined rectangular beam is formed. Let a cylinder D, having a slit g_3 in its periphery and capable of being rotated, be placed in the path of this beam. If the cylinder is at rest, and slit g_3 is in the path of the molecular beam, a deposit forms on the rim at P diametrically opposite the slit. If the cylinder is rotated, the molecules entering g_3 require a finite time to traverse the diameter and consequently strike the rim at a point s to the left of P. The displacement s of a molecule moving with a speed c is given by the equation

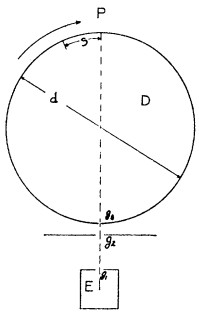

Fig. 1.

$$s = \pi d^2 n/c = A/c \tag{1}$$

where d is the diameter of the cylinder and n is the number of revolutions per second. The equation also shows that, by making d and n large, one may secure large displacements of the molecules, i.e., high resolving power.

The molecules in the beam possess not one definite velocity, but a distribution of velocities and consequently a "velocity spectrum" is formed on the rim of the cylinder. The density of this deposit should bear some relation to the velocity distribution in the enclosure E. According to the Maxwell-Boltzmann distribution law, the number of molecules dn out of a total number N in equilibrium within the enclosure possessing speeds between c and $c+dc$, is given by the expression

$$dn = \frac{4N}{\alpha^3 \pi^{1/2}} e^{-c^2/\alpha^2} c^2 dc$$

where α is the most probable speed of the molecules within the enclosure. As

[7] M. Knudsen, Ann. Physik **28**, 999 (1909).

shown by Stern,[3] while the molecules within the enclosure are in equilibrium those in the beam are not, for the number passing through the slit per second depends on the size of the opening, the shape of the enclosure, the speed of the molecules and the number of molecules in the enclosure. Let dn_1 be the number of molecules out of N_1 molecules in the beam possessing speeds between c and $c+dc$. Then

$$dn_1 = dn \cdot c \cdot K$$

where K is a constant. From this we get

$$dn_1 = (2N_1/\alpha^4)e^{-c^2/\alpha^2}c^3dc \tag{2}$$

as the expression for the velocity distribution in the beam.

To find the expression for the distribution of the molecules on the receiving plate, P, one can use the method given by Stern.[8] Consider first that the undeflected image is of infinitesimal width and find the distribution of the molecules in the deflected portion of the plate. Consider the velocity range between c and $c+dc$ giving a deflected range between s and $s-ds$. The intensity of the beam in the deflected region may be defined as the number of molecules dn striking and condensing on a length of plate ds assuming the beam to be of uniform and constant intensity across the element of length, or

$$I = dn/ds. \tag{3}$$

From Eqs. (1), (2), and (3) we get

$$I = \frac{2N_1}{\alpha^4 A}e^{-c^2/\alpha^2}c^5. \tag{4}$$

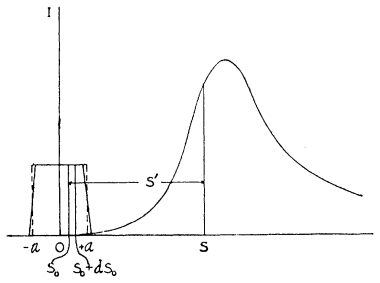

Fig. 2.

The undeflected beam in the actual experiment is of finite width 2a (Fig. 2). Let ds_0 be an element of length in the undeflected region and let dn_0 be the number of molecules striking and condensing on ds_0. Then $I_0 = dn_0/ds_0$. For an undeflected beam of width ds_0, Eq. (4) becomes

$$I = \frac{2I_0 ds_0}{\alpha^4 A}e^{-c^2/\alpha^2}c^5. \tag{6}$$

It will be more convenient to use the intensity distribution in the deflected portion as a function of the distance s from the zero line. Then $c/\alpha = s_a/s$,

[8] O. Stern, Zeits. f. Physik **41**, 563 (1927).

where s_α is the deflection of the molecules having the most probable velocity in the enclosure, and Eq. (6) becomes

$$I = \frac{2I_0 ds_0}{s_\alpha}\left(\frac{s_\alpha}{s}\right)^5 e^{-(s_\alpha/s)^2}. \tag{7}$$

Integrating (7) from $-a$ to $+a$, we get

$$I = I_0\left\{e^{-(s_\alpha/s+a)^2}\left[\left(\frac{s_\alpha}{s+a}\right)^2 + 1\right] - e^{-(s_\alpha/s-a)^2}\left[\left(\frac{s_\alpha}{s-a}\right)^2 + 1\right]\right\} \tag{8}$$

as the theoretical intensity distribution in the deflected region of the plate in terms of s_α and a.

Apparatus

The substance whose velocity distribution is to be determined is vaporized in a steel crucible A (Fig. 3). The vapor then passes through the channel in

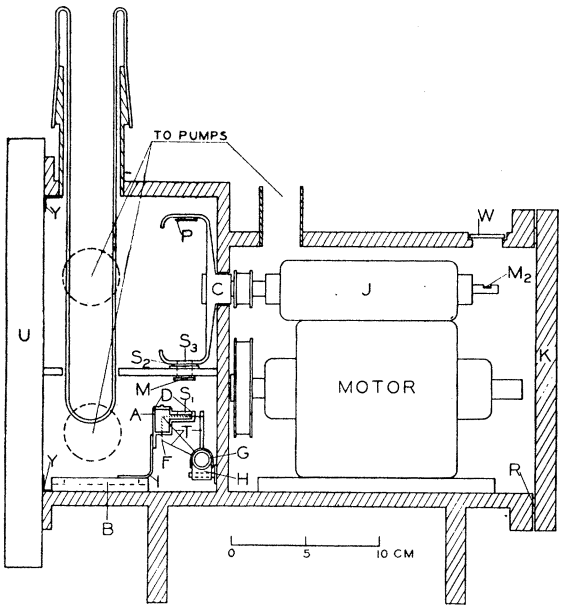

Fig. 3. Diagram of apparatus.

the neck to the slit S_1, there escaping as a molecular beam. The crucible is fastened to the sliding base B by means of a rectangular strip of invar I. This sliding base is fitted into a dove-tailed groove in order that the entire crucible and slit assembly can be easily removed for filling purposes and then replaced without changing the alignment of the slit system. Directly above the neck of the crucible is a second slit S_2 used to define sharply the molecular beam. The crucible slit is 0.05 mm by 10 mm in size while the defining slit is 0.6 mm by 10 mm. The distance between these slits is 3.29 cm. A shutter M magnetically operated from the outside is used to interrupt the beam.

The crucible is heated by radiation from a 300 watt tungsten lamp filament F mounted with the aid of tungsten supports T fused to a glass tube G. The glass tube is fastened in a special holder H allowing the filament to be adjusted in any desired direction. The loss of heat by radiation is reduced by surrounding the crucible and filament assembly with nickel radiation shields. Two chromel-alumel thermocouples fastened at D serve as a means of determining the temperature. The thermocouples are calibrated by comparison with a standardized platinum-platinum rhodium thermocouple. A potentiometer is used to read the electromotive force of the thermocouples.

A cylinder C, 10 cm in diameter, machined out of a solid piece of machine steel, is placed above the slit system. This cylinder is designed to withstand the forces due to high speeds of rotation with the least possible deformation. A knife edge slit S_3, 0.6 mm wide, is cut into the rim of the cylinder. Directly opposite on the inner rim a device is fastened to hold a curved glass plate P. The cylinder is carefully balanced and mounted on the high speed spindle J of an internal grinder. Its speed is determined by the stroboscopic method.

The grinder consists of a 1/6 H.P. universal motor and a high speed spindle mounted on top of the motor housing. A fabric belt is used to drive the spindle. The motor armature has a speed of 10,000 r.p.m. and the spindle 30,000 r.p.m. when connected to a 110-volt circuit. The armature and spindle rotate in ball bearings and the entire assembly is so well-balanced that vibration is negligible at nearly all speeds. The bearings are properly lubricated by vacuum pump oil which has been boiled in a vacuum for several hours to drive off the more volatile products. The residue is sufficiently non-volatile so that a pressure of less than 10^{-4} mm of mercury can easily be maintained in the motor compartment by continual pumping.

The entire assembly is enclosed in a phosphor-bronze housing which is divided into three compartments, a motor, a cylinder, and a crucible compartment. A hole in the wall between the motor and cylinder compartments, slightly larger than the hub of the cylinder, allows the high speed spindle to pass through and at the same time prevents the passage of large quantities of vapor from the motor to the cylinder compartment. A water jacket surrounds the outside of that portion of the housing subjected to heating. The end of the motor compartment is flanged and can be closed by bolting a metal plate K to this flange. A rubber gasket R is placed between the flange and plate to render the joint vacuum tight. The flange surrounding the cylinder and crucible compartments is scraped to fit a plate glass cover U. The joint between the glass cover and the flange is made vacuum tight by giving it a thin uniform coating of a special stopcock grease to which more pure rubber and paraffin has been added than is customary.

The entire system is evacuated through an opening in each compartment. All openings and tubing are large in diameter and the tubing is kept as short as possible in order that all vapors can be quickly removed. Three mercury vapor pumps each backed by a Hyvac pump are used to evacuate the compartments. Liquid air traps are used to prevent the mercury vapor from diffusing into the system. A glass tube which can be filled with liquid air passes

vertically through the cylinder chamber into the crucible chamber. A vacuum tight joint is made by the ground-glass, metal joint at the top. Copper shields Y are fitted into the corners formed by the glass cover and the sides, top and bottom of the housing. Copper strips attached to these shields are fastened to the glass tube. The liquid air in the tube cooled these shields to a sufficiently low temperature to condense most of the vapors from the stopcock grease. The tube itself also acts as a large cooled surface which condenses all condensible vapors coming in contact with it. No difficulty is experienced in maintaining a pressure of less than 10^{-5} mm of mercury in the crucible and cylinder compartments.

In order that the density of the deposit can be measured by a microphotometer it is desirable to use glass plates as receivers. These plates (6 by 1.5 by 0.03 cm) are cut from microscope cover glasses. They are bent so as to fit the inner circumference of the cylinder by balancing them on a carbon block having the proper curvature, and then placing the block in an electric oven. The temperature is raised slowly until the plate bends under its own weight to the shape of the carbon form.

For the bismuth molecules to condense on the glass plate at room temperature it is necessary to place an initial, thin and uniform layer of bismuth upon it. This is accomplished by a piece of apparatus which allows the glass plate to be cooled to near the temperature of liquid air and then uniformly exposed to a stream of bismuth molecules. This apparatus consists of an electrically heated crucible and a glass liquid air container mounted in a brass housing which can be made vacuum tight and evacuated. The glass plate upon which the initial deposit is placed is held against the curved flat bottom of the liquid air container by two flat springs. The crucible containing the substance to be deposited is mounted on a shaft so that it may be rotated from one side of the plate to the other. This rotation is accomplished from the outside of the housing by fastening a bent arm to the shaft and enclosing the arm within a sylphon. A fork, attached to a motor-driven slow-speed gear, engages the sylphon thus transmitting the motion to the crucible.

Experimental Procedure

The bismuth used in this experiment is the analyzed product of Powers-Weightman-Rosengarten Company, Philadelphia. In order to get rid of any adsorbed gases it is heated in a vacuum to a temperature of 450°C for about five hours and then allowed to cool before air is admitted.

A bent glass plate is thoroughly cleaned and dried, then placed in the "initial depositing" apparatus and given a thin uniform coating of bismuth. The plate is fastened to the cylinder. The cylinder is adjusted with the aid of a traveling microscope until the slit S_3 is observed to be directly above the defining slit S_2. It is then fixed in this position. The system is evacuated, the crucible heated to about 800°C and the plate exposed to the molecular beam for about 20 seconds. This operation gives a visible deposit on the plate and forms the zero mark from which the displacements are measured. After ad-

mitting air to the system, the plate is removed and a microphotometer record obtained of the density of the initial deposit and location of the zero mark.

The plate is again fastened to the cylinder, the crucible filled with bismuth and the system evacuated. A slow increase in the temperature is necessary to avoid the violent expansion of gas bubbles in the molten metal which results in a "spitting" of the metal through the slit. When the temperature of the furnace reaches equilibrium and the motor speed is adjusted by varying the resistance in the line to the absence of beats, the shutter is opened and the beam allowed to pass to the plate. The maximum of the deposit first becomes visible in from three to six hours depending upon the temperature and speed of the run. The run is continued for periods ranging from eight to twenty-two hours. The plate is removed from the cylinder and again photometered. Finally, the two photometer curves are superimposed and the density due to the velocity distribution is measured.

RESULTS

The results of four runs are given. Runs 1 and 2 are represented with their theoretical curves in Fig. 4. Fig. 5 is a contact print of the photometer record from which the data for curve 1, Fig. 4, are taken. The horizontal distances are twice the actual distances on the glass plate.

TABLE I.

Run	t	n	Length of run	Bi	Bi_2
1	851°C	120.7 r.p.s.	12 hours	0.40	0.60
2	851	241.4	22	.40	.60
3	851	60.35	7	.40	.60
4	795	120.7	8	.30	.70

In all cases the experimental results would not agree with the theoretical distribution for Bi or Bi_2 as given by Eq. (8). The work of Leu[9] on the magnetic deflection of bismuth suggests that the beam is composed of Bi and Bi_2. On the basis of this suggestion various percentages of Bi and Bi_2 were assumed and using Eq. (8) the resultant intensity distributions plotted. These distributions were then compared with the experimental results. The theoretical distribution which best fitted the experimental results is taken as the composition of the vapor stream.

In Fig. 4 the solid lines represent the theoretical distributions for the conditions of operation given in Table I. The circles represent the experimental results obtained from Run 1, and the crosses those from Run 2. The experimental points are in close agreement (within the experimental error) with the theoretically derived curve except for a few points on the high velocity side. These points disagree by an amount greater than the experimental error. The disagreement is probably due to the lack of a sharply defined molecular beam during the entire course of the experiment. It may also be due to a "slipping"

[9] Alfred Leu, Zeits. f. Physik **49**, 498 (1928).

Fig. 4 also gives the velocities corresponding to various displacements for a speed of rotation of 241.4 r.p.s.

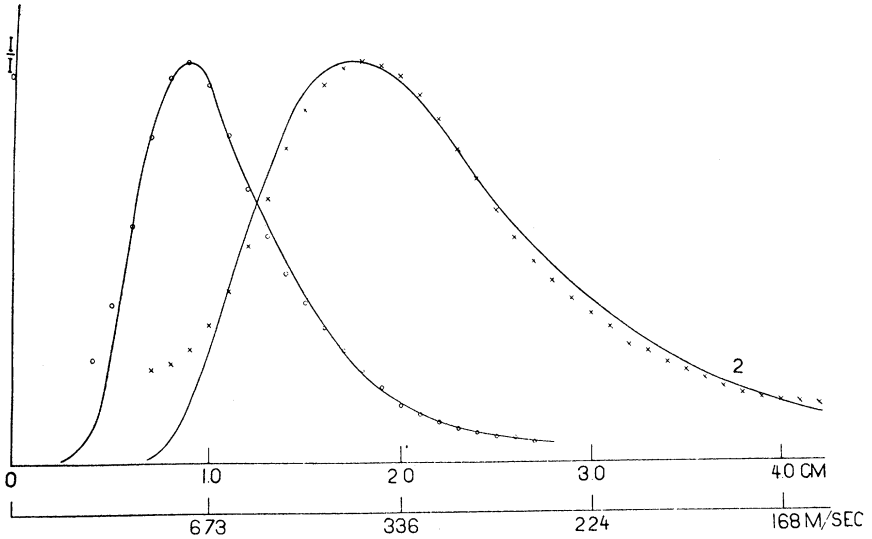

Fig. 4. Theoretical and experimental intensity distributions assuming a vapor composition of 40 percent Bi and 60 percent Bi_2. T equals 851°C. Curve 1, $n=120.7$ r.p.s., curve 2, $n=241.4$ r.p.s. Bottom line gives the molecular velocity corresponding to several displacements at a cylinder speed of 241.4 r.p.s.

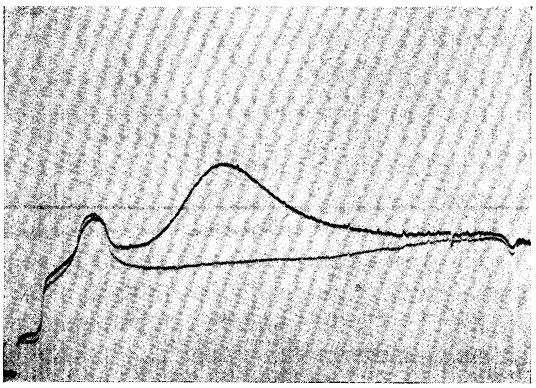

Fig. 5. Contact print of photometer record of Run 1, $n=120.7$ r.p.s. Abscissas twice actual deflections.

TABLE II.

Displacement interval	Velocity band
1.0–1.1 cm	61 m/sec
2.0–2.1	15
3.0–3.1	7
4.0–4.1	4

of the molecules forming the zero mark. This possibility is being investigated.

Table II gives several displacement intervals of 1 mm width and the velocity band covering that interval. The high resolution is quite evident.

As Leu[9] observed, the dissociation of Bi_2 increased with the temperature and at about the same rate. His results disagree among themselves at the same temperature by 10 percent in some cases. If there is no "slipping" of molecules on the plate a variation in the composition of the vapor of less than 5 percent is detectable in this experiment and this method thus forms a more accurate means for the study of the dissociation of certain vapors, the results of which can be applied to calculating the heat of dissociation.

Errors

The temperature and speed could be kept constant to within one percent although it is doubtful if the temperature itself could be read accurately to within several percent. A possible source of error is that not all the molecules striking the plate remain there. It is possible that some escape, however this number is assumed to be negligible. It is not so certain that all molecules striking the plate remain at the point where they first make contact. There is the possibility for surface motion or "slipping." Evidence for a small amount of surface motion on fixed plates is presented by Cockcroft.[10] Any motion of the molecules on the glass plate due to the high speed of rotation must be negligible since the results obtained from Runs 1, 2, and 3, taken at the same temperature but at different speeds, indicate the same percentage vapor composition.

A test showed that no error is introduced in assuming that the electrometer deflections on the photometer records are directly proportional to the densities of the deposits.

Conclusion

A method is described for the direct measurement of molecular velocities. Results are presented in which the molecules are spread over a distance of more than 4 cm at a cylinder speed of 241.4 r.p.s. with an error of less than 5 percent. This resolution is many times that obtained by Stern, an analysis of the distribution of the deposit being impossible from his results, and several times that obtained by Eldridge who spread a velocity band of 900 to 200 meters per second over a plate length of 1 cm while in this experiment a velocity band of 673 to 168 meters per second is spread over 3 cm.

It is a pleasure to acknowledge my gratitude to Professor Elmer E. Hall under whose direction the problem was undertaken, for his advice and inspiration; to Professor Leonard B. Loeb for the many helpful discussions and encouraging remarks, and to Mr. G. P. Kraus, mechanician, for his willing cooperation in the mechanical details.

[10] J. D. Cockcroft, Proc. Roy. Soc. **A119,** 293 (1928).

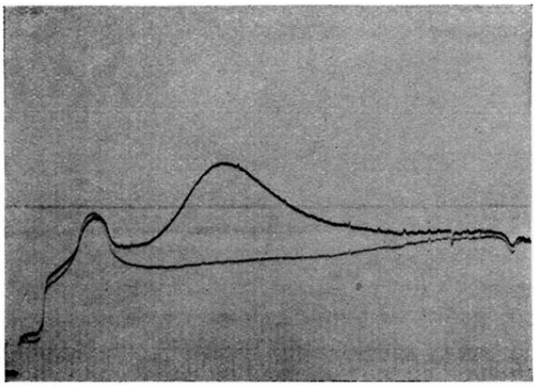

Fig. 5. Contact print of photometer record of Run 1, $n = 120.7$ r.p.s. Abscissas twice actual deflections.