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THE PRODUCTION AND MEASUREMENT OF MOLECULAR BEAMS

BY THOMAS H. JOHNSON[1]

ABSTRACT

A new method for studying molecular beams has been developed in which the beam is detected and its intensity measured by the increase in pressure which is produced in an ionization gauge when the gauge is moved to allow the beam to enter it through a narrow slit. This method has the advantage over other methods in use in that it is applicable to beams of molecules of non-condensable and chemically inactive gases. Many details of the construction of the new beam detector have been described and the characteristics of its operation have been studied both experimentally and theoretically. Simple kinetic theory fails to explain the observed pressure changes unless adsorption on the inner walls of the gauge is taken into account. A satisfactory hypothesis for interpreting the observations is that gas is adsorbed by the walls at a rate which is proportional to the molecular density in the volume of the gauge and liberated at a rate proportional to the number of adsorbed molecules. A value of 10^{-4} per collision is found for the probability of adsorption of a mercury molecule on glass. The sensitivity of the gauge method of detecting a beam, although seriously impaired by adsorption, still compares favorably with that of other methods in use. A study of the relation between the beam intensity and the pressure in the source chamber has been made in which the ionization gauge method has been used for the measurements. The results show that beams of far greater intensity can be produced than were thought possible by Knauer and Stern who have made a similar investigation. The results of these investigators, however, are consistent with the results of the present investigation if an interpretation, different from that of Knauer and Stern, is adopted.

THE importance of the technique of producing, detecting, and measuring the intensity of molecular beams has been emphasized by Stern both through his investigations in which beams have been used, and in a paper[2] in which he has stated some of the problems which may be approached by the use of these methods. Molecular beam methods have also been used by Wood, Gerlach and Stern, Taylor, Phipps and Taylor, Knauer and Stern and others[3] for investigating atomic and molecular phenomena.

In all previous work the use of molecular beams has been limited to substances which can be detected by the formation of either a visible deposit or a visible trace due to some chemical activity between the molecules of which the beam is composed and a screen.[4] At the 1926 Montreal Meeting of

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[1] Sterling Fellow at Yale University. (At the time of publication, Fellow of the Bartol Research Foundation of The Franklin Institute.)

[2] O. Stern, Zeits. f. Physik **39**, 751 (1926); **2**, 49; **3**, 417 (1920).

[3] R. W. Wood, Phil. Mag. **30**, 300 (1915); Gerlach and Stern, Ann. d. Physik **74**, 673 (1924); Gerlach, Ann. d. Physik **76**, 163 (1924); Taylor, Phys. Rev. **28**, 576 (1926); Phipps and Taylor, Phys. Rev. **29**, 309 (1926); Knauer and Stern, Zeits. f. Physik **39**, 764; 780 (1926); A. Leu, Zeits. f. Physik **41**, 551 (1927); E. Wrede, Zeits. f. Physik **41**, 569 (1927).

[4] I. H. Solt has reported the use of a platinum wire thermometer for detecting a beam of helium atoms, Phys. Rev. **29**, 904 (1927).

the American Physical Society the writer gave a preliminary report on the use of an ionization gauge for the detection of a beam of gaseous molecules.[5] Since that time this method has been more extensively developed and is now thought to constitute a valuable addition to the methods in use, in that it makes possible the detection of a beam of molecules of any gas and enables one to make direct intensity measurements of such beams.

The present paper describes the ionization gauge method of detecting molecular beams and also an application of this method to an investigation of the intensity and breadth of a beam of mercury molecules studied in relation to the pressure in the chamber in which the beam has its source. A similar investigation by another method has been made by Knauer and Stern[3] who concluded that the most intense beam is produced when the pressure in the source chamber is such that the mean free path of a molecule is equal to the width of the source slit. The results of the present investigation are in disagreement with this conclusion as has been stated elsewhere.[6]

THE IONIZATION GAUGE DETECTOR

The detecting device was a small bulb which contained the usual electrodes of an ionization gauge and was completely closed except for a fine slit. The chamber was mounted in the region traversed by the beam in such a manner that the slit could be moved into or out of the beam at will. When the slit was placed in the beam the gas pressure in the bulb would increase within a few seconds to a value depending upon the intensity of the beam at that position. When the slit was again removed from the beam the pressure in the bulb would return to its former value. These pressure changes were measured by the usual ionization gauge method.[7]

An expression for the increase in molecular density which takes place within the bulb when the slit is placed in the beam follows at once from simple kinetic theory considerations. Writing I for the beam intensity (defined as the number of molecules which pass a normal plane per sq cm per sec.), V for the volume of the bulb, A for the area of the slit, and C for the r.m.s. velocity of the molecules at the temperature of the slit, the molecular density (ν) of the gas in the bulb changes when the slit is placed in the beam in accord with the relation,

$$\frac{d\nu}{dt}=\frac{IA}{V}-\frac{\nu AC}{(6\pi)^{1/2}V} \tag{1}$$

When equilibrium is established, the molecular density is

$$\nu_\infty=(6\pi)^{1/2}I/C \tag{2}$$

The time required for the molecular density to reach half of this equilibrium value is

$$T=\left[(6\pi)^{1/2}V/CA\right]\log_e 2, \tag{3}$$

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[5] The writer is indebted to Dr. E. O. Lawrence for first proposing this method of detecting a beam of molecules.

[6] Thomas H. Johnson, Nature, May 21, 1927.

[7] Dushman and Found, Phys. Rev. **17**, 7 (1921).

In case there is residual gas in the gauge when the slit is not in the beam, these expressions concern the increase over the residual molecular density. In this simple theory no account is taken of adsorption of gas by the walls, a phenomenon which is, however, of great importance, as will be shown later.

Experimental Arrangement

Production of the beam. A beam of mercury molecules was formed by two rectangular slits (16) and (14) (Fig. 1), each having the dimensions 0.1 mm by 1 mm. The source slit (16) was supplied with mercury vapor from the boiler (22) which contained liquid mercury. (For the purpose of economy of space the boiler which was joined to the apparatus at (24) is represented at one side of the figure.) To prevent the condensation of liquid mercury in the source slit and the connecting tube, these were maintained at a temperature considerably above that of the boiler by the use of the electrically heated tungsten spiral (17) and the electric oven (19). The trap (20) pre-

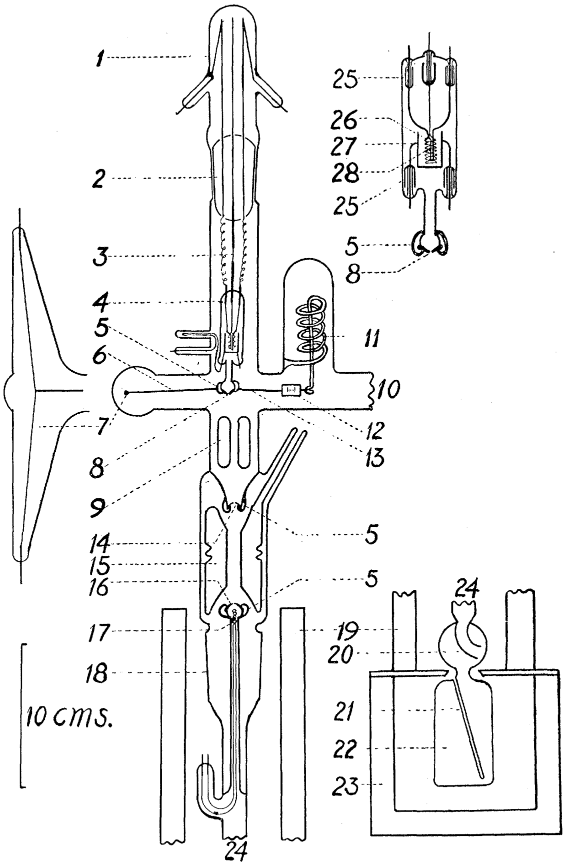

Fig. 1. Experimental arrangement of producing, detecting, and measuring the intensity of a beam of mercury molecules.

vented droplets of liquid mercury from being thrown into the superheated tube leading to the source slit. With these precautions the pressure of mercury vapor at the source slit remained fairly steady and depended only upon the temperature of the boiler. This temperature was controlled by the independent oven (23) and was measured with a copper-constantan thermocouple which was inserted in the long thin-walled tube (21).

The cold surface of the liquid air container (15) completely surrounded the space between the two slits and condensed practically all of the molecules from the source slit at their first impact with the walls. The pressure in this chamber was thus reduced so that molecules moving in the direction of the beam were able to traverse the distance between the two slits without suffering collisions, and only molecules coming directly from the source passed through the image slit (14).

Detection and measurement of the beam. The detecting device was a 6 cc Pyrex glass bulb (4) (shown in detail at the upper right of Fig. 1), containing the three electrodes of an ionization gauge. Because of the small size of this bulb and its position in the vacuum, certain special features in its construction were found necessary. With a short fine tungsten filament (28) for the electron emission no vacuum difficulties were experienced due to the heating of the glass. The grid (26) was a double spiral of 7 mil. tungsten wire mounted so that it could be heated for purposes of outgasing. The filament and the grid projected well into the closed nickel cylinder (27) which was used as the positive ion collector, so that the space where the ionization took place was well shielded from variable static charges on the glass. The insulating surface of the glass was protected against the condensation of evaporated metals by cup-shaped glass shields (25) which preserved a band of clean glass around each lead wire.

The only opening in the gauge was a rectangular slit[8] (8). Two different sizes of slits were tried but most of the results reported were obtained with the larger slit which had the dimensions 0.1 mm by 1 mm.

The ionization gauge was suspended from a ground glass conical plug (2) by means of two thin nickel ribbons (3) which served both as grid leads and as a hinge about which the gauge was free to swing. The control for moving the gauge was a taut nickel wire (7) (top view shown at the left of Fig. 1) which was connected to the gauge and thence to the glass spring (11) by the metal rods (6) and (13). The slit on the gauge could be precisely set at

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[8] The three slits used in the apparatus were cut in the following manner. A blunt cone 5 mm in diameter was first punched from a piece of 0.003 inch nickel sheeting. This cone was placed, vertex down, on a piece of soft iron while a hardened steel punch, with its tip ground to the exact size of the desired slit, was pressed into the nickel a distance slightly in excess of its thickness. The boss thus formed was filled with wax and ground off on the outside until the wax could be seen through the slit. The wax was then dissolved out, leaving a slit with well defined edges. Slits as narrow as 0.02 mm could be cut by this method. Other materials and other thicknesses were tried but none gave as satisfactory results as the 0.003 inch nickel. The nickel cone with the slit cut in it was fused into the end of a glass tube. Since the nickel used was too thick to make a metal-to-glass seal which would not crack, the glass supports (5) were fused on to prevent the cones from becoming dislodged.

any position within a range of 5 mm by adjusting an electric current which heated and expanded the wire (7), allowing the spring to move the gauge. Relative positions of the slit were determined with a high degree of accuracy from the scale (12) which moved with the gauge. The scale, of which the smallest division was 1/20 mm, was read through a 100-power microscope. All connections to the lower extremities of the gauge were easily detached so that the gauge and its mounting could be removed through the top of the tube when cracked off at (1).

Alignment of the slits. The two lower slits were made parallel during the process of construction by the use of a traveling microscope, with an ocular cross-hair, the adjustment depending upon the parallelism of the ways of the microscope mounting. The slit in the ionization gauge was made parallel to the axis of the hinge about which the gauge swung, and this in turn was placed parallel to the lower slits. The position of the gauge was such that, when it was near the middle of its range, the three slits were in line. This adjustment was accomplished during the construction by placing each slit upon the axis of the ground glass cone (18). The position of the slit with reference to this axis could be tested by observing the slit through a stationary microscope as the tube was rotated about the cone. For this operation the cone was seated in a stationary matrix. All the adjustments referred to above were made by heating and bending the glass.

Vacuum. The apparatus was exhausted by a mercury vapor diffusion pump connected at (10) through a liquid air trap. It was outgassed for an average period of twelve hours at a temperature below 350°C, higher temperatures having been avoided to preserve the alignment of the slits. In addition to this general baking, the metal cylinder within the gauge was heated to a bright red for as long as was necessary to reduce the pressure within the gauge to less than 10^{-7} mm. This heating was accomplished by radiation from the grid.

While the beam was in operation the pressure in the upper chamber was reduced by placing liquid air in the container (9), the construction of which was similar to that indicated in the figure in the case of (15). Under these conditions the pressure in the gauge when the slit was out of the beam was practically constant for measurable beams varying in intensity by a factor of over one hundred. (See curve II, Fig. 2.)

Calibration of the gauge. The calibration constant (k) of the gauge will be defined by

$$P = ki/e$$

where P is the pressure expressed in mm of mercury in those parts of the apparatus which were at room temperature (25°C) and i is the ionization current formed by the electron current e under the conditions which simultaneously existed in the ionizing region. For this proportionality between P and i/e to remain valid it is necessary that the temperature of the ionizing region have a constant value, a condition which was approximately satisfied throughout the investigation.

In calibrating the gauge, the ionization was measured when the apparatus was filled with mercury vapor in equilibrium with liquid mercury at 0°C. According to the International Critical Tables[9] the pressure of mercury vapor at 25°C in equilibrium with liquid mercury at 0°C, taking account of thermal effusion,[9] is 1.94×10^{-4} mm. Under these conditions i/e was found to be 25.4×10^{-4}. The pressure of mercury vapor in those parts of the apparatus which were at 25°C was therefore given by

$$P(mm)=0.076\ i/e$$

RESULTS

Empirical relation between the beam intensity and the boiler pressure. Curve I of Fig. 2 shows the relation between the boiler pressure and the ionization in the gauge with the slit in the center of the beam. The measurements extended over a range of boiler pressures from 0.2 mm, at which the beam was just detectable, to 143 mm. Between each pair of successive readings the slit was removed from the beam to eliminate, in so far as possible, the accumulation of adsorbed vapor. The accuracy with which readings could be repeated indicated that no appreciable error was incurred from

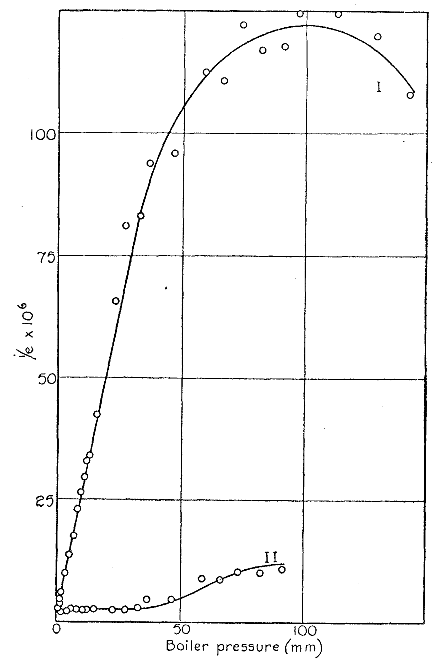

Fig. 2. Experimental curves showing the relation between the ionization in the gauge and the boiler pressure (I) with the slit in the center of the beam and (II) with the slit out of the beam.

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[9] The writer is indebted to Prof. J. Johnston and Dr. F. Fenwick for placing this datum at his disposal prior to its publication.

this source. The ionization increased with the boiler pressure, at first linearly, but above a boiler pressure of 35 mm less rapidly, passing through a maximum at 100 mm. Over the linear portion of Curve I the pressure in the gauge was 1.91×10^{-7} of the pressure in the boiler, a value which will later be compared with a theoretical calculation.

Curve II represents the ionization in the gauge when its slit was removed from the beam as far as the control would carry it (about 3 mm). In this position the ionization remained about constant up to a boiler pressure of 35 mm showing that the residual pressure in the gauge was independent of the beam intensity. It may therefore be stated that the ionization recorded in curve I was due entirely to molecules which came directly from the beam and to no others. Above a boiler pressure of 35 mm scattered molecules from the beam were in sufficient numbers appreciably to raise the pressure in the gauge when the slit was out of the beam.

According to the interpretation which Knauer and Stern have placed upon their results, a maximum would be expected in curve I at the very low boiler pressure of 1.0 mm whereas the curve continues to rise with boiler pressures up to 100 mm. These authors have supposed that for boiler pressures in excess of an optimum pressure, at which the mean free path is equal to the width of the source slit, frequent collisions in front of the slit give rise to the formation of a diffuse cloud. Instead of originating in the slit, the beam then starts from the surface of this cloud which, according to their view, must be supposed to have a surface density always lower than the density at the slit with the optimum boiler pressure. A more plausible view of the matter, especially in the light of the results of the present investigation, seems to be that of considering the intensity of the beam at its source to be proportional to the boiler pressure, a condition which is known to hold at low pressures and, because of the linearity of the curve I, is thought to hold at least approximately at higher pressures. The beam, however, passes through the region between the two slits which, because of reflected molecules from the uncooled areas and scattered molecules from the beam, contains an absorbing atmosphere whose density may likewise be supposed to be proportional to the boiler pressure. The resulting intensity of the beam after it has passed the second slit can be expressed, on the basis of these assumptions, in the form

$$I = APe^{-BP} \tag{5}$$

where P is the boiler pressure and A and B are constants. Indeed it is possible, both in the case of the present results and those of Knauer and Stern, to select values of A and B which make this equation fit very closely the experimental data. In the present investigation the more effective condensation between the two collimating slits, with the consequent smaller value of the constant B, explains the occurrence of the maximum at the higher boiler pressure.

Breadth of the beam. Fig. 3 shows the ionization in the gauge as a function of the position of the slit. The data represented in curve II, for which the ordinate scale is given at the right, was taken with a constant boiler pressure of 2 mm. Curve I, which is plotted to the smaller scale shown at the left, is for a boiler pressure of 42 mm. The dotted line represents the relative intensities as calculated from the geometrical arrangement of the slits. It is, perhaps, a noteworthy fact that many of the points shown represent the ionization at positions separated by only 1/100 mm. A series of observations similar to those shown in Fig. 3 indicates that, when the boiler pressure was below about 35 mm, the beam had the width calculated from the geometry of the slit system, but, because of scattering, the beam became broader and more diffuse as the boiler pressure was increased above this value.

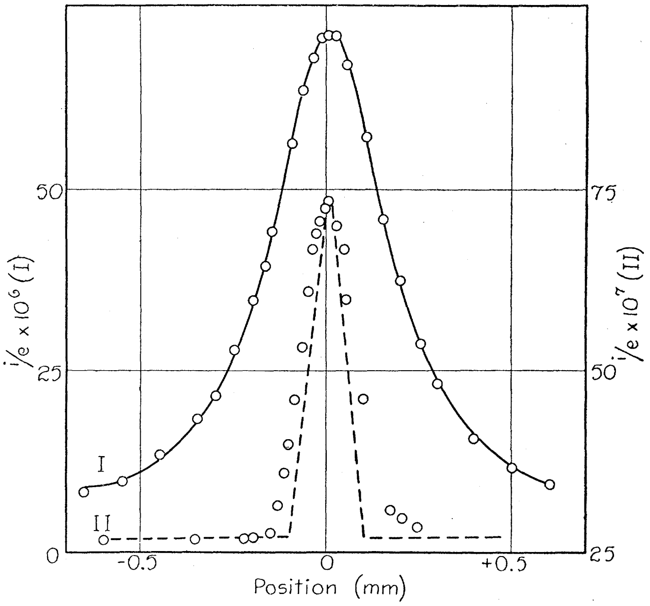

Fig. 3. Relation between the ionization in the gauge and the position of the slit (I) with a 42 mm boiler pressure and (II) with a 2 mm boiler pressure.

Both the sharpness of the beam and the linearity of curve I, Fig. 2, indicate that at boiler pressures below 35 mm the scattering in the beam due to the overtaking of one molecule by another is inappreciable.

The period of the gauge. The time required for the pressure in the gauge to reach half its equilibrium value, according to the simple kinetic theory, is given by Eq. (3). On this basis the ionization should fall off after the gauge is removed from the beam according to the dotted line of Fig. 4. The observed change in ionization is plotted with the full line. The discrepancy between the calculated and observed values is doubtless due to the effective increase in the capacity of the gauge because of adsorption, and to the slow liberation of the adsorbed gas.

Adsorption of gas in the gauge. It has been mentioned above that the adsorption of gas in the gauge has probably caused no error in the measurement of the *relative* beam intensities. There are three lines of evidence, however, which indicate that adsorption was an important factor in the action of the gauge as a beam detector, its effect being to impair the sensitivity.

The most direct evidence lies in a comparison between the observed value of the pressure which was built up in the gauge when apparently in equilibrium with the beam, and that which may be approximately calculated.

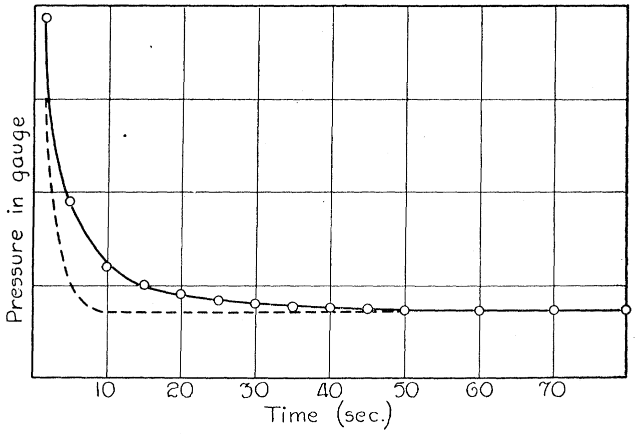

Fig. 4. Experimental and theoretical (dotted) curves showing the decrease in pressure in the gauge after the slit is removed from the beam.

As a basis for an approximate calculation of the beam intensity, assume that the vapor diffuses through the source slit as it would at very low pressures, and that no collisions are suffered by molecules after they pass this slit. If ν_1 is the molecular density of the vapor in the region below the source slit, C_1 the r.m.s. velocity of the molecules at the temperature of the source slit, A_1 the area of this slit, and L the distance between the source slit and the slit on the ionization gauge, then the intensity of the central portion of the beam at the position of the ionization gauge is[11]

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[10] M. Knudsen, Ann. d. Physik **31,** 205; **33,** 1435 (1910).

[11] Consider the contribution to the beam intensity of a volume element$(L+r)^2 d\omega dr$, where r is the distance from the volume element to the source slit and $d\omega$ is an element of the solid angle which is subtended by the source slit from the point at which the intensity is measured. The number of molecules starting out anew after having made a collision within the volume element is

$$(\nu_1 C_1/\lambda_1)(L+r)^2 d\omega dr$$

of these a fraction $1/4\pi(L+r)^2$ are directed towards a normal unit area at a distance $L+r$ and only a fraction e^{-r/λ_1} succeed in reaching the rarefied region beyond the source slit without making a collision. The net contribution to the measured intensity by this volume element is therefore

$$dI = (\nu_1 C_1/4\pi\lambda_1)e^{-r/\lambda_1}\, d\omega dr.$$

Integrating over all of the volume below the source slit which is exposed to the view of a point at the distance L (the limits of the integration are from $r=0$ to $r=\infty$ and from $\omega=0$ to $\omega=A/L^2$), the total intensity is

$$I = \nu_1 C_1 A_1/4\pi L^2$$

If the Maxwellian velocity distribution is taken into account the numerical factor 1/4 must be replaced by . $1/(6\pi)^{1/2}$

$$I=\nu_1 C_1 A_1/(6\pi)^{1/2}\pi L^2 \tag{6}$$

According to Eq. (2), when the slit is placed in the beam the molecular density should build up to

$$\nu_\infty=(\nu_1 A_1/\pi L^2)(T_1/T)^{1/2} \tag{7}$$

where T and T_1 are the temperatures of the boiler and the gauge respectively. The ratio of the pressure in the gauge to that in the boiler is then

$$P_\infty/P_1=(A_1/\pi L^2)(T_1/T)^{1/2}=3.5\times 10^{-6} \tag{8}$$

The observed value of the same ratio is 1.9×10^{-7}, or about 1/19 of the calculated value. The discrepancy may be accounted for by the adsorption of gas on the walls of the gauge, as will be apparent from the discussion which follows.

Further evidence for adsorption lies in the peculiar behavior exhibited by the gauge when the apparatus was suddenly filled with mercury vapor. The liquid air on the trap was replaced by an ice bath, and within a few seconds the pressure, as measured by the gauge, went up to about 10^{-5} mm, apparently coming to a quasi-equilibrium at this value. After an half hour had elapsed the pressure was still but slightly over 10^{-5} mm, but after this interval it began to increase again and at the end of an hour it had reached a real equilibrium at the pressure of the surrounding region, i.e., 1.94×10^{-4} mm. From a calculation based upon the rate of diffusion through the slit, it is estimated that a single molecular layer must have formed over the surface of the glass before the pressure started to rise the second time.

The effect of adsorption on the action of the gauge as a beam detector is especially noticeable when the results with different slit areas are compared. According to the simple theory, the equilibrium pressure in the gauge with the slit in the beam is independent of the area of the slit as long as this is small compared with the cross sectional area of the beam. Table I shows the results found with two different slits when the pressure in the gauge was in apparent equilibrium with the beam. Contrary to the prediction of the simple theory the ionizations in the two cases are not the same but are roughly in the same ratio as the slit areas, a result which is theoretically understandable on the basis of simple assumptions, as will be shown presently.

TABLE I

Variation with slit area of the ionization current at a constant boiler pressure of 70 mm.

	A	B	Ratio A/B
Slit area:	0.1	0.007	14.3
Increase in i/e one minute after slit is placed in beam:	115×10^{-6}	6×10^{-6}	19.2

A complete theory of the pressure changes which take place in the ionization gauge when the slit is placed in the beam must take account of the phenomenon of adsorption. If it is assumed that the number of molecules adsorbed per sec. is proportional to the molecular density (ν), and that the number liberated per sec. from the walls is proportional to the number (n) of molecules in the adsorbed state, then the molecular density in the gauge changes according to the relation

$$\frac{d\nu}{dt}=\frac{IA}{V}-\frac{CA\nu}{(6\pi)^{1/2}V}-\frac{1}{V}\frac{dn}{dt} \tag{9}$$

where

$$dn/dt=\alpha\nu-\beta n \tag{10}$$

Eq. (9) then becomes

$$\frac{d\nu}{dt}=\frac{IA}{V}-\frac{CA\nu}{(6\pi)^{1/2}V}-\frac{\alpha\nu}{V}-\frac{\beta n}{V} \tag{11}$$

At the final equilibrium ν_∞ has the same value as was given by the simpler theory. As noted above, however, shortly after the slit is placed in the beam the pressure within the gauge reaches a quasi-equilibrium state which persists for a considerable time before the pressure rises to the final equilibrium. We shall see that this condition can be accounted for if we assume that the rate of adsorption of gas by the walls is very large and continues for a long time before saturation is reached. For in this case it will obviously result that in the initial stages the value of $\beta n/V$ will be small compared with $\alpha\nu/V$. Neglecting it, we obtain

$$\frac{d\nu}{dt}=\frac{IA}{V}-\frac{CA\nu}{(6\pi)^{1/2}V}-\frac{\alpha\nu}{V}$$

If, further, the rate of adsorption of gas by the walls is large compared with the rate at which it diffuses back through the slit the term $CA\nu/(6\pi)^{1/2}V$ is negligible compared with $\alpha\nu/V$ and there results the approximate expression,

$$\frac{d\nu}{dt}=\frac{IA}{V}-\frac{\alpha\nu}{V}$$

The equilibrium value of ν to which this equation leads is to be associated with the observed quasi-equilibrium and is

$$\nu_\infty'=IA/\alpha$$

which is proportional to the area of the slit, in agreement with the observations.

To account for the difference between the quasi-equilibrium pressure observed and the calculated value of the true equilibrium pressure, it is necessary to take the value of α to be 95. This value of α also gives agreement between the quasi and real equilibria observed in the experiment where the apparatus was filled with mercury vapor in equilibrium with liquid mercury in the ice bath.

The value of the constant α divided by the area of the walls gives the probability of adsorption per sq cm. The area of the interior of the gauge was about 24 sq cm so that the rate of adsorption by one square centimeter is about 4ν per sec. Since $C\nu/(6\pi)^{1/2}$ molecules strike one sq cm of the walls per sec. it follows that the probability of adsorption per collision with the walls is $4(6\pi)^{1/2}/C$ which has the approximate value of 10^{-4}, which, of course, depends upon the temperature and surface conditions of the glass.

CONCLUSION

The ionization gauge method of detecting and measuring the intensity of molecular beams will receive its strongest recommendation because of its application to beams of non-condensable and chemically inactive gases. It may also find application to beams of molecules which might be detected by other simpler methods because, by its use, relative intensity measurements may be directly made. In regard to its sensitivity the ionization gauge method compares favorably with the condensation method. A change of pressure in the gauge of 3×10^{-8} mm (a 3 mm deflection on the galvanometer scale) corresponds to a beam intensity of about 5×10^{13} molecules per sq cm per sec. A beam of this intensity would produce a barely visible trace by condensation in about one minute. Because of the experimental difficulties in its manipulation as compared with obtaining traces by condensation or other methods, the ionization gauge method for detecting a beam will probably not supersede these methods in cases where either may be used.

In conclusion the writer wishes to express his very sincere appreciation of the many helpful suggestions given during the course of this work by Professor W. F. G. Swann, under whose direction it was carried out.

THE SLOAN PHYSICAL LABORATORY,
YALE UNIVERSITY,
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