

## Velocity Distributions in Potassium and Thallium Atomic Beams\*†

R. C. MILLER‡ AND P. KUSCH  
Columbia University, New York, New York

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A high-resolution, high-intensity, spiral velocity selector has been designed for the study of the velocity distributions of the components of atomic and molecular beams. It has been found possible to design oven slits which closely approximate the ideal aperture of kinetic theory. An analysis has been made of the velocity distributions in beams of potassium and thallium over a range of velocity from 0.3 to 2.5 times the most probable velocity in the oven. The agreement between the observed distribution and that deduced, on the basis of the assumptions that the distribution in the oven is Maxwellian and that the aperture is ideal, is very good.

### INTRODUCTION

A NUMBER of investigators have measured the velocity distributions of atoms in an atomic beam.<sup>1-8</sup> In a number of cases, in which the results are of at least a moderate precision, significant differences occur, usually on the low velocity side of the spectrum, between the observed distribution and that calculated from the assumption that the distribution in the beam is the consequence of the effusion of atoms through an ideal aperture from an oven in which the velocity distribution is Maxwellian. In view of the limited agreement between observation and theoretical prediction, it is worthwhile to reinvestigate the velocity distribution of atoms in a beam to establish, on experimental grounds, the reality of the Maxwellian distribution of velocities of particles at thermal equilibrium in an isothermal enclosure. The detector in an atomic or molecular beams experiment measures the number of particles incident upon it in unit time. If the slit in the oven is an ideal aperture, then a Maxwellian  $v^2$  volume distribution in the oven becomes a  $v^3$  distribution at the detector. The design of oven slits to produce an ideal aperture and thus give a reproducible distribution within the beam, derivable from that in the oven, is an important aspect of the present work. The present paper is concerned with the design of a high-resolution velocity selector, with an analysis of the conditions under which the velocity distribution of the beam incident on the detector is derivable from the velocity dis-

tribution in the oven and with a velocity analysis of atoms at equilibrium in an isothermal enclosure.

### VELOCITY SELECTOR

The velocity selector consists of a solid cylinder on whose surface are cut a large number of helical slots and which is capable of rotation about the cylinder axis. This velocity selector has inherent advantages over a selector which employs two or more toothed wheels operating on the same shaft at a fixed relative angular position and at a variable angular velocity, or operating on two separate shafts at the same fixed angular velocity but at a variable relative angular position.<sup>8</sup> With the toothed wheel selectors, the transmission of a beam by the device is possible when the time of transit of the particles over the length of the selector is equal to the time required for the selector to turn through the interval at whose ends the slot in the first disk and that in the second disk transmit the beam. Evidently, if the wheels contain a large number of closely spaced teeth, atoms within a particular velocity interval may be transmitted for several angular velocities of the rotor; and a particular rotor velocity will allow the transmission of atoms in several velocity intervals. In principle, the occurrence of "side bands" may be eliminated since the slots may be so widely spaced on each disk, relative to the angular interval between the slots on the two disks, that the only significant contribution to the intensity lies within a single velocity range. However, since all velocity selectors reduce the transmitted intensity at a particular central velocity with increasing resolution, the intensity problem may become very serious if additional intensity losses must be incurred when the "side bands" are eliminated. When a single cylinder is used, the spacing between adjacent slots may be as small as mechanical considerations permit. The width of the slots, a determining factor in the resolution, may in turn be as small as is mechanically feasible and consistent with the requirement that the intensity of the transmitted beam over the velocity range to be studied is considerably greater than noise. The present selector is similar to a high transmission, slow neutron velocity

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‡ Radio Corporation of America Predoctoral Fellow, 1953-1954. Now at the Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

<sup>1</sup> J. Eldridge, *Phys. Rev.* **30**, 931 (1927).

<sup>2</sup> B. Lammert, *Z. Physik* **56**, 244 (1929).

<sup>3</sup> I. F. Zartman, *Phys. Rev.* **37**, 383 (1931).

<sup>4</sup> C. C. Ko, *J. Franklin Inst.* **217**, 173 (1934).

<sup>5</sup> V. W. Cohen and A. Ellett, *Phys. Rev.* **52**, 502 (1937).

<sup>6</sup> Estermann, Simpson, and Stern, *Phys. Rev.* **71**, 238 (1947).

<sup>7</sup> I. Kofsky and H. Levinstein, *Phys. Rev.* **74**, 500 (1948).

<sup>8</sup> A. Bennett, Jr., and I. Estermann, Ph.D. thesis, Carnegie Institute of Technology, 1953 (unpublished); A. Bennett, Jr., *Phys. Rev.* **95**, 608 (A) (1954).

selector.<sup>9</sup> A similar helical velocity selector has also been used in a study of the characteristics of thin metal films as a function of the incident velocity of the deposited atoms.<sup>10</sup>

The notation used in a discussion of the selector is shown in Fig. 1 as are the dimensions of the rotor used in the present work. The cylinder was made of Dural because this material allowed the cutting of slots to the necessary depth and at close intervals without significant distortion of adjacent slots. The ends of the slots occur at  $0.5^\circ$  intervals on the end faces. To allow adjustment of the line connecting the source slit and the detector parallel to the cylinder axis, it is necessary to have at least one slot parallel to the axis. Actually, two such slots were cut to avoid dynamical imbalance.

The resolution properties of the velocity selector will be derived under the assumption that both source and detector have infinitesimal dimensions. All molecules which are ultimately detected then travel in a plane containing the cylinder axis, oven slit, and detector. The validity of this assumption will be discussed in more detail later. A molecule of velocity  $v_0$  which goes through the slot without changing its position relative to the sides of the slot will satisfy the equation

$$v_0 = \omega L / \phi_0, \quad (1)$$

in which  $\phi_0$  and  $L$  are fixed, and  $\omega$  is the angular velocity.

Since the slots have a finite width, a range of velocities from  $v_{\max} = \omega L / \phi_{\min}$  to  $v_{\min} = \omega L / \phi_{\max}$  will be transmitted by the rotor for a fixed  $\omega$ . The limiting velocities correspond to molecules which enter the slot at one wall and leave the slot at the opposite wall, so that

$$v_{\max} = v_0(1-\gamma)^{-1} \quad \text{and} \quad v_{\min} = v_0(1+\gamma)^{-1}, \quad (2)$$

where  $\gamma = l / (r_0 \phi_0)$  and  $r_0$  is the mean radius. In the present apparatus,  $\gamma = 0.05033$ , a fixed property. A variation of the radius by a few percent will have a negligible effect on the limiting values of  $v$  and thus, the mean value,  $r_0$ , may be used. The admittance  $A$ , the ratio of the effective slot aperture for the velocity  $v$  to that for the velocity  $v_0$  is

$$A = 1 - |(v_0/v) - 1|/\gamma, \quad (3)$$

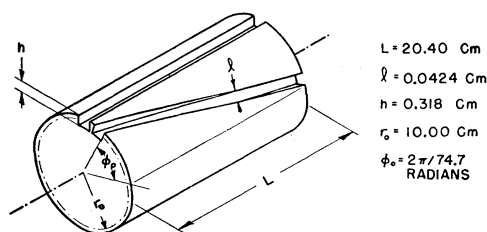


FIG. 1. Schematic diagram of velocity selector.

<sup>9</sup> J. Dash and H. Sommers, Jr., Rev. Sci. Instr. 24, 91 (1953).

<sup>10</sup> H. Levinstein and H. Crane, Phys. Rev. 69, 679 (A) (1946).

§ Note added in proof.—The dimension  $L = 25.40$  cm.

where  $v$  lies between the limits  $v_{\max}$  and  $v_{\min}$ . Over the limited range of  $v$  allowed in the present case, the admittance is very nearly triangular in terms of  $v$ . The resolution calculated in the usual way at  $A = 0.5$  is  $\Delta v / v_0 = \gamma$ .

If it is assumed the velocity distribution incident on the rotor,  $I_0 dv$ , does not change significantly over the range of velocities admitted for a given  $\omega$ , then the transmitted intensity is

$$I_v = -I_0 v_0 \gamma^{-1} \ln(1-\gamma^2) \cong I_0 v_0 \gamma \quad (4)$$

to powers of  $\gamma$  through  $\gamma^2$ .  $I_0 dv$  is the modified Maxwellian distribution,

$$I_0 dv = 2\alpha^4 v^3 \exp(-\alpha^2 v^2) dv,$$

where  $\alpha^2 = m/2kT$ , and the distribution has been normalized to unity. Then Eq. (4) becomes

$$I_v = 2\gamma \alpha^4 v_0^4 \exp(-\alpha^2 v_0^2). \quad (5)$$

Equation (5) becomes exact as the slot width becomes infinitesimal. It will be shown that this expression is sufficiently close to the much more cumbersome exact expression so that it can be used as the theoretical distribution.

To obtain an exact expression for  $I_v$ , the variation of the incident distribution,  $I_0$  over the admittance must be included. Then:

$$\begin{aligned} I_v = & (\gamma^{-1} - 1) \exp[-x_0^2/(1-\gamma)^2] \\ & + (\gamma^{-1} + 1) \exp[-x_0^2/(1+\gamma)^2] \\ & - 2\gamma^{-1} \exp(-x_0^2) + x_0 \gamma^{-1} \\ & \times \left\{ \int_{x_0}^{x_0/(1-\gamma)} \exp(-x^2) dx \right. \\ & \left. + \int_{x_0}^{x_0/(1+\gamma)} \exp(-x^2) dx \right\}, \quad (6) \end{aligned}$$

where  $\alpha v_0 = x_0$ . This expression is unwieldy and gives no insight into the general nature of  $I_v$ . Table I contains

TABLE I. A comparison of the intensity distribution after analysis by the rotor as calculated in several approximations.

$x_0 = \alpha v_0$	Exact intensity Eq. (6)	Expansion value of intensity Eq. (7)	One-term $v^4$ intensity Eq. (5)
0.000	0.00	0.00	0.00
0.200	0.62	0.57	0.57
0.400	0.80	0.81	0.81
0.600	3.36	3.36	3.34
0.800	8.01	8.00	7.98
1.000	13.62	13.61	13.59
1.200	18.16	18.15	18.15
1.300	19.45	19.47	19.47
1.414	19.98	19.97	20.00
1.500	19.67	19.68	19.71
1.600	18.69	18.68	18.72
1.800	15.15	15.15	15.19
2.000	10.79	10.81	10.83
2.200	6.84	6.84	6.84
2.400	3.87	3.87	3.86

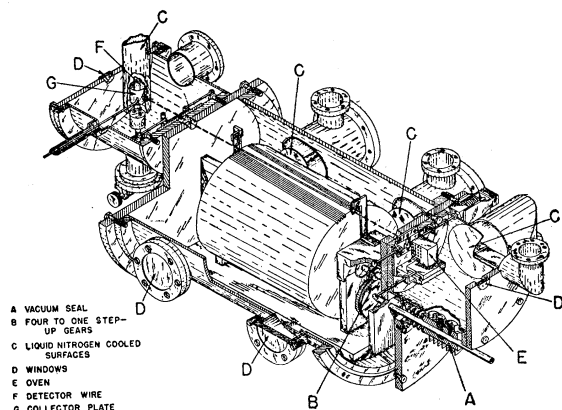


FIG. 2. Schematic diagram of the apparatus designed to measure velocity distributions.

some values of  $I_v$  calculated from Eqs. (5) and (6). Both sets of values have been multiplied by a constant factor to make the maximum intensity,  $I_{v(\max)}$ , of Eq. (5) equal to 20.00. Table I demonstrates that the simple expression, Eq. (5), can be used for calculating theoretical distributions to be compared to the experimental data in the present work, as the average experimental uncertainty is about one percent of  $I_{v(\max)}$ .

The intensity at the detector,  $I_v$ , may be expanded as a series in  $(x_0)^{2n} \exp(-x_0^2)$ , where  $n$  is an integer greater than or equal to two. Then the leading terms are

$$I_v = 2\gamma x_0^4 \exp(-x_0^2) [1 + 2.5\gamma^2 - 13\gamma^2 x_0^2/6 + \gamma^2 x_0^4/3 + \dots] \quad (7)$$

in which the next term in  $x_0^{10}$  has a coefficient no larger than  $\gamma^3$ . Table I contains values of  $I_v$  calculated from Eq. (7) using terms through  $x_0^8$ .

Finite source and detector dimensions produce a beam not all of whose elements are parallel to the axis of the rotor. The effect of the finite vertical dimension of the beam is negligible since for an angle of elevation,  $\theta$ , of a beam element with respect to the axis, the analysis of  $v \cos\theta$  is made and  $\cos\theta$  differs only trivially from 1. The center of the admittance curve for non-parallel beam elements which results from the finite horizontal dimensions, or widths, of the oven slit and detector wire is at either higher or lower velocities than the center of the curve for parallel beam elements. The solution of this problem has been discussed elsewhere.<sup>9</sup> In the present apparatus, the detector and source widths are sufficiently small,  $2.5 \times 10^{-3}$  cm, so that the widths have a negligible effect on the shape of the velocity distribution.

#### GENERAL DESCRIPTION OF APPARATUS

The vacuum envelope consists of the oven, rotor and detector chambers. Other than the pumping connections, through which a free flow of gas between chambers cannot occur, the only openings between the rotor

chamber and the other two chambers are the slits shown in Fig. 2.

A large liquid nitrogen cooled surface is provided in each chamber, to increase the pumping speed of the cold traps for condensable gases. Pressures of  $1.2 \times 10^{-7}$  and  $1.3 \times 10^{-7}$  mm of mercury were obtainable in the detector and rotor chambers respectively, with the rotor at rest.

The velocity selector was provided with a four-to-one stepup gear built into the mount. Power was transmitted to the rotor from the outside of the vacuum envelope by a shaft which rotates in a long, lubricated phosphor bronze bearing. As shown in Fig. 2, two holes were drilled perpendicular to the axis of the bearing, one on the high pressure side so the lubricant could be replenished and one in the middle which was pumped by a mechanical pump. The vacuum seal functioned very well, though there was some tendency for the pressure to increase with increasing rotor speed. The velocity selector was seldom run over 4000 rpm, at which speed the vacuum in the rotor chamber increased to about  $10^{-6}$  mm of mercury.

#### OVENS

The ovens used in these experiments were much like conventional molecular beam ovens, the main differences being in the slit construction and the oven material. Since the interpretation of velocity distribution data requires that the beam be produced at a known equilibrium temperature, the ovens must be made of high conductivity material to avoid significant temperature gradients. Thus the present ovens were constructed of oxygen-free, high-conductivity copper, instead of the customary iron or nickel. Preliminary experiments in the present work have shown that in the neighborhood of 900°K, temperature differences of 30°C occur between the front and back of a conventional iron oven. This temperature difference is roughly six times the estimated accuracy of the measured temperatures. When the same measurements were repeated with a copper oven, the temperature difference was reduced to 3.5°C.

Kinetic theory considerations indicate that the width of the slit in a direction parallel to the direction of the propagation of the beam must be much smaller than the mean free paths of the atoms in order to eliminate scattering in the neighborhood of the slit. The defining slits were made of 0.0038 or 0.0025 cm thick steel strips held on the face of the oven with copper strips, whose edge extended to within about 0.25 mm of the slit itself, so that the orifice was determined by the thin steel strips. At a nominal temperature of 900°K, a thermocouple inserted in one of the copper strips indicated a temperature 0.7°C lower than the temperature measured with a thermocouple mounted in the front part of the oven as shown in Fig. 3. This temperature difference is small compared to the estimated

$\pm 0.5$  percent accuracy of the temperature measurement and has no observable effect on the results.

The oven temperatures were measured with Chromel *P*-Alumel thermocouples peened directly into the oven as shown in Fig. 3. All available information and auxiliary checks against a Pt, Pt-Rh thermocouple indicate the temperature measurement to be accurate to  $\pm 0.5$  percent of the measured temperature in degrees absolute. The beam intensity is very sensitive to the temperature of the oven, so a temperature control unit, essentially an on-off switch to control a portion of the oven heater current, was employed to maintain the oven within  $0.25^\circ\text{C}$  of the nominal desired temperature.

The beam was detected on a tungsten surface ionization detector. In the case of thallium, oxygen was sprayed on the detector wire to increase the detection efficiency. The filament was conditioned so that the detected beam was relatively insensitive to the filament temperature in the neighborhood of the operating temperature. The detection efficiency for potassium can be made greater than 99 percent,<sup>11</sup> while for thallium this may not be true. Preliminary experiments have shown that a variation of the over-all detection efficiency has no observable effect on the shape of the velocity distribution as long as the over-all detection efficiency remains constant during the run. This shows that if there is a velocity-dependent detection efficiency, it is not very sensitive to the over-all detection efficiency.

### RESULTS

Differentiation of Eq. (5) shows that  $\alpha^2 v_0^2$ , or  $x_0^2$  equals two at the intensity maximum, so that Eq. (5) can be written

$$I_v = 8\gamma V^4 \exp(-2V^2), \quad (8)$$

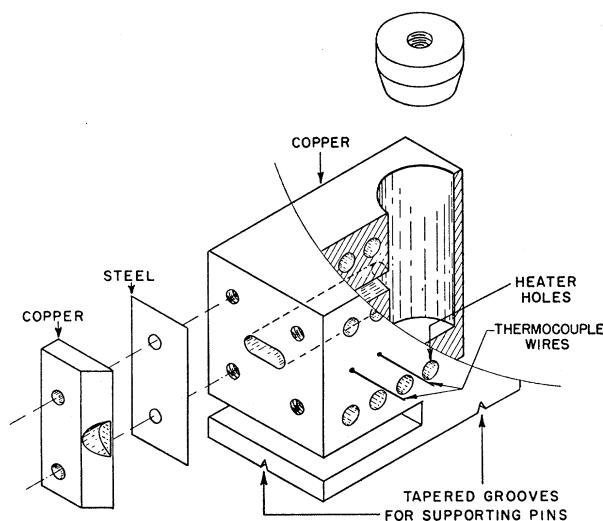


FIG. 3. Copper oven used for potassium showing details of slit construction.

<sup>11</sup> G. E. Cogan and G. E. Kimball, *J. Chem. Phys.* **16**, 1035 (1948).

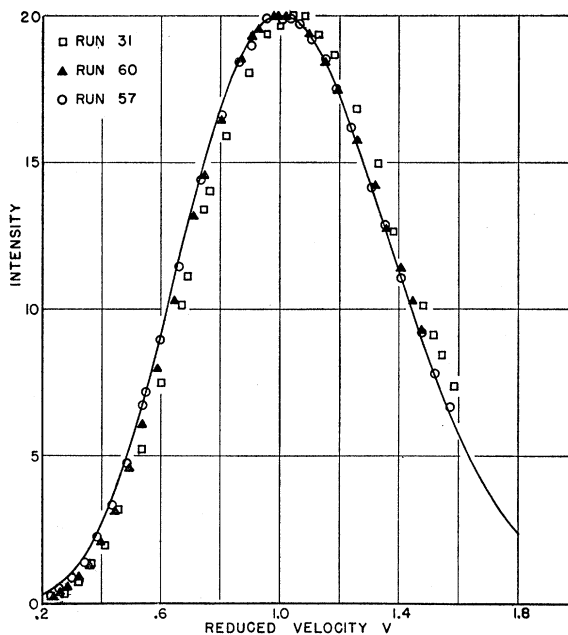


FIG. 4. Typical potassium velocity distributions. The vapor pressures in the ovens are given in Table II. Run 31 was made with thick oven slits and runs 57 and 60 with thin slits.

in which the dimensionless variable  $V$ , the reduced velocity, is the atom velocity  $v_0$ , divided by the velocity of the intensity maximum of the distribution. This is a very convenient expression for examining the agreement between theoretical and experimental curves since Eq. (8) is a theoretical "universal curve," that is, it will be the same for all velocity distributions which result from a single molecular species. To take into account the effect of finite rotor slot width, the actual theoretical distribution used in this work was a "universal curve" obtained from Eq. (6) with  $x_0$  replaced by  $V\sqrt{2}$ .

Figure 4 shows universal plots of typical velocity distributions for potassium; each distribution corresponds to different experimental conditions. To compute the reduced velocity  $V$ , the experimental velocities were divided by the theoretical velocity of the intensity maximum calculated from the measured oven temperature. Since the uncertainty in temperature measurement does not exceed  $\pm 0.5$  percent, the velocity corresponding to the maximum intensity in the theoretical distribution will be accurate to  $\pm 0.25$  percent. The observed intensity measurements have been multiplied, in all cases, by an appropriate factor to give coincidence of theoretical and experimental intensities at the maximum.

Some of the important results are tabulated in Table II. The velocity at which the maximum intensity occurs can be determined directly from the experimental velocity distribution and may also be calculated from the oven temperature. The agreement of the two velocities is one criterion which must be satisfied if the

TABLE II. Experimental conditions and results for measured velocity distributions.

Beam	Run	Temperature deg K	Oven pressure in mm of mercury	Velocity of $I_{\max}$ in m/sec	
				From oven temp	From exp distr
K	57	466 $\pm$ 2	4.5 $\times 10^{-3}$	628 $\pm$ 2	630 $\pm$ 3
K	60	544 $\pm$ 3	1.2 $\times 10^{-1}$	678 $\pm$ 3	679 $\pm$ 3
K	31	489 $\pm$ 2	1.4 $\times 10^{-2}$	644 $\pm$ 2	682 $\pm$ 3
Tl	99	870 $\pm$ 4	3.2 $\times 10^{-3}$	376 $\pm$ 1	376 $\pm$ 2
Tl	97	944 $\pm$ 5	2.1 $\times 10^{-2}$	392 $\pm$ 1	395 $\pm$ 2

present work is to be a critical test of the Maxwellian distribution. The vapor pressures given in Table II were obtained from the literature<sup>12</sup> and represent the equilibrium pressures of the vapor over the sample in question.

Of the three potassium distributions, Run 57 shown in Fig. 4 provides the best agreement with the theoretical curve. In this case, the vapor pressure in the oven was as low as was experimentally feasible. It was not possible to obtain velocity distributions for markedly lower oven pressures since the beam intensity which depends directly on the oven pressure, would then be so low that the several sources of noise would give data of limited value long before statistical fluctuations play a significant role. The experimental points are seen to be in excellent agreement with the theoretical curve over the major part of the distribution. However, there is an observable deficiency of atoms on the low velocity side of the maximum. The value of  $v_{\max}$  calculated from the oven temperature agrees with experimental value.

It has been observed that the deficiency of atoms on the low velocity side increases with increasing oven pressures and with increasing slit depth. The deficiency also increases with decreasing velocity. Run 60 was made with the same oven as Run 57 but the potassium vapor pressure was markedly increased. The experimental points of Run 60 are in good agreement with the theoretical curve in the neighborhood of the intensity maximum, but there is a pronounced deficiency of atoms on the low-velocity side and an observable excess of atoms on the high-velocity side. It appears as if the velocity distribution had undergone a velocity-dependent scattering which was not serious enough to shift the maximum of the distribution.

Run 31 illustrates the effect of a deep slit on the velocity distribution. These slits were made of copper strips which were 0.317 cm thick. In this case, the entire distribution has been shifted in the high velocity direction. It was also found that when the 0.003-cm or 0.004-cm steel shims which formed the orifice from which the beams effused from ovens like those shown in Fig. 3 were omitted, so that the orifice was determined by the knife edges of the copper strips, the velocity

distributions were shifted slightly to the high velocity side of the theoretical curves. The shift corresponds to a beam temperature of the order of three percent higher than the measured oven temperature. The depth of the knife-edge copper slits was estimated to be 0.008 cm to 0.012 cm.

The potassium distributions were not extended further into the high-velocity region because this extension requires what appeared, at the time, to be a dangerously high speed of revolution. In the case of thallium, more complete distributions were obtained.

The thallium distributions are quite similar to the potassium distributions already discussed. Runs 99 and 97 shown in Fig. 5 indicate an excellent agreement between experimental points and the theoretical curves, better than previously noted. It is seen that the largest discrepancies occur on the high-velocity side of the maximum, where there is a small excess of atoms in the experimental distribution. It should be noted that the experimental points could be plotted with the high-velocity side matched to the theoretical curve. The intensities at the maximum velocity would no longer coincide and the experimental distribution would then appear to be deficient of atoms on the low-velocity side. The observed discrepancies are again more pronounced at higher oven pressures.

When thallium beams were observed, the tungsten detector wire was constantly sprayed with oxygen to maintain a good oxidized surface on the wire. The quantity of oxygen sprayed into the apparatus was kept so small that the increase in pressure due to the oxygen was about  $5 \times 10^{-8}$  mm of mercury in the detector chamber and less in the other chambers.

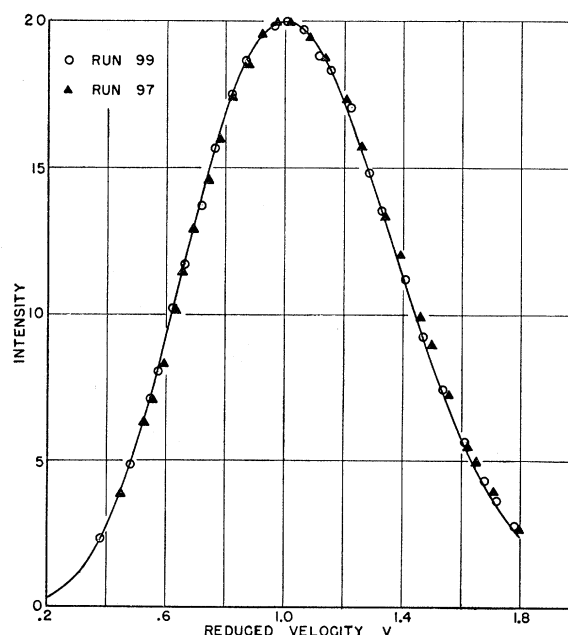


FIG. 5. Typical thallium velocity distributions. The data were taken with thin oven slits at vapor pressures given in Table II.

<sup>12</sup> S. Dushman, *Vacuum Technique* (John Wiley and Sons, Inc., New York, 1949), pp. 746, 748.

## BEAM PURITY

The vendor of the potassium reported that it contained 2 percent sodium and 0.5 percent lithium. Because of the low vapor pressure of these two constituents compared to that of potassium, no measureable amount of sodium or lithium is expected to be present in the beam. A search was made for sodium transitions in the potassium beam with a magnetic resonance atomic beam apparatus, but no sodium transitions were observed. The sensitivity of the test was such as to make it unlikely that an amount of sodium sufficient to give an observable distortion of the velocity distribution was in the beam.

The thallium metal was reported to be 99.95 percent thallium, exclusive of the oxide on the surface. The remaining 0.05 percent was largely lead, copper, and cadmium, all of which are undetectable. Since no beam was detected with an unoxxygenated detector wire, it is certain that there were no measurable amounts of cesium, rubidium, or potassium in the thallium beam.

There is the possibility that the beam may also contain dimers of the atomic species. In the case of thallium and potassium the beam in question is investigated with an atomic beam apparatus that will reject atoms with magnetic moments of the order of a Bohr magneton, which characterize the atomic states of potassium and thallium. Molecules of  $K_2$  are in a  $^1\Sigma$  states as are, presumably, those of the  $Tl_2$  if they exist. They have magnetic moments of the order of a nuclear magneton and are not significantly deflected by inhomogeneous magnetic fields which deflect atoms through great excursions.

The molecule of potassium,  $K_2$ , is known to be present in a potassium beam, but the data on the fraction of molecules is inconsistent. In a molecular beam experiment<sup>13</sup> in which the nuclear magnetic moment of potassium was measured, it was found that the ion current produced at the detector by the molecular component may be as great as one percent of that produced by the total beam. Since each potassium molecule may produce two ions, the abundance of  $K_2$  is probably a little less than 0.5 percent. Under more favorable experimental conditions, Rosenberg<sup>14</sup> obtained 0.25 percent  $K_2$  in a potassium beam at 500°K. The fraction of  $K_2$  may be shown from thermodynamic considerations to increase with increasing oven temperatures. Thus the distortion of the velocity distribution which accompanies an increase in oven temperature cannot be the result of a larger fraction of  $K_2$  as the dimer would shift the velocity distribution to the low velocity side. If 0.25 percent  $K_2$  is assumed to be present in the beam, the maximum increase in the experimental velocity distribution at any velocity at which observations have been made would be only 0.5 percent of the maximum intensity. The effect of

$K_2$  is negligible in the present work. A search for  $Tl_2$  was made with a molecular beam apparatus. It was concluded that there was less than 0.05 percent  $Tl_2$ , an amount wholly negligible in the present analysis, in the beam.

## COMPARISON WITH OTHER RESULTS

The experimental techniques used in two early attempts to measure velocity distributions<sup>1,2</sup> were not sufficiently refined to permit an accurate test of the Maxwell velocity distribution law to be made. The work of both Eldridge and Lammert shows deviations from theoretical predictions, deviations which are greater than the experimental uncertainties. Zartman<sup>3</sup> investigated the velocity distributions in bismuth beams. Unfortunately, no critical test of the Maxwell distribution could be made since bismuth vapor contains significant amounts of molecular species other than atomic Bi. Thus Zartman actually measured the superpositions of distributions of Bi,  $Bi_2$ , and  $Bi_8$ . When he adjusted the amount of  $Bi_2$  so that the agreement was good on the low-velocity side, there was a pronounced excess of molecules on the high-velocity side. The amount of  $Bi_8$  was small so that it had little effect on the major part of the distribution.

Ko<sup>4</sup> used essentially the same apparatus as Zartman to measure the fraction of  $Bi_2$  in bismuth beams as a function of the oven temperature and pressure. From his data, he was able to calculate the dissociation energy of the  $Bi_2$  molecule. When the amount of dimerization was adjusted to give good agreement on the low-velocity side of the distribution, there were too many molecules on the high-velocity side. He also found evidence that  $Bi_8$  was present in the beam.

Cohen and Ellett<sup>5</sup> measured velocity distributions in sodium and potassium beams. As a velocity selector they used an inhomogeneous magnetic field which was perpendicular to the direction of propagation of the beam. Since the deflection of beam atoms is proportional to the gradient of the magnetic field, it is important that the field inhomogeneity be constant over the height and width of the beam. They assumed the gradient to be constant if the observed distribution could be fitted to the theoretical distribution after the adjustment of constants not determinable from *a priori* considerations. The nature of the constants is such that an independent check of the observed maximum and that deduced from the temperature cannot be made. Subject to these limitations, they observed no systematic deviation from Maxwell's theory at low oven pressures. At high oven pressures, they observed serious deviations from theory, notably a deficiency of atoms on the low-velocity side. They predicted that knife-edge slits would give better results than their 2-mm thick rectangular slits. However, on the basis of the present work, there is some doubt that the theoretical distributions could be observed with deep slits even at low pressures.

<sup>13</sup> Kusch, Millman, and Rabi, Phys. Rev. **55**, 1176 (1939).

<sup>14</sup> R. Rosenberg, Phys. Rev. **55**, 1267 (1939).

In 1947, Estermann, Simpson, and Stern<sup>6</sup> measured the velocity distributions in cesium beams by use of the free fall due to gravity as a velocity selector. They observed a pronounced deficiency of atoms on the low-velocity side and noted that the discrepancy increased with increasing oven pressure. They attributed the deficiency to collisions near the oven slit. An order of magnitude calculation is given which indicates that the deficiency might be explained on the basis of Cs-Cs collisions in the neighborhood of the slit.

The most recently reported results on velocity distributions are those of Bennett and Estermann<sup>8</sup> who measured potassium velocity distributions. Their experimental velocity distributions were in good agreement with theoretical distributions on the high-velocity side of the intensity maxima, but there was always a deficiency of atoms on the low-velocity side, a deficiency which increased with increasing oven pressure and with a decreasing velocity. Even at the lowest oven pressure at which experimental results were obtained,  $1.8 \times 10^{-3}$  mm of mercury, the intensity was about 90 percent of the theoretical intensity for atoms at a velocity one-half the velocity of the intensity maximum. The deficiency of atoms on the low-velocity side was greater if the oven slits were rectangular than if they were knife edges. The velocities at which the experimental intensity maxima occurred were usually found to agree within three percent with the predicted values.

In the present work, experimental velocity distributions of both potassium and thallium were found to be in good agreement with theoretical velocity distributions. It has been shown that the experimental and theoretical distributions, for small beams, do not differ by more than one percent of the maximum intensity over the entire range of the measured distributions, extending from as low as 0.2 to as high as 1.8 times the velocity of the intensity maximum. Furthermore, the velocities at which the intensity maxima occur agree within 0.5 percent with velocities calculated from the measured oven temperature. These results provided the best agreement to date between observed distributions and theoretical distributions calculated from the assumption that the beam is a consequence of a Maxwellian distribution within the oven which effuses through an ideal slit.

#### REFLECTION FROM THE ROTOR SLOTS

It has been assumed that all molecules which strike the wall of the slots in the velocity selector are removed from the beam. If the beam were very narrowly collimated so that the detector would intercept only atoms which arrive along a line parallel to the rotor axis and which leave the oven along the same line, the assumption would be justified. However, no collimation other than that provided by a source and detector of small width was provided in the original design of the apparatus. An attempt was made to improve the collimation

of the beam by placing a 0.005-cm slit at each end of the velocity selector; but it was impossible to observe a velocity distribution with this arrangement, since vibration caused by the rotating velocity selector produced serious unsteadiness in the beam. Sufficient enlargement of the collimation slits to reduce variations in the beam intensity consequent to vibration reduces the collimation of the beam to the point where the slits no longer serve to prevent the detection of atoms which may have undergone reflections from the wall of the slots and the slits were eventually removed. However, before the slits were removed, an attempt was made to reflect potassium atoms from the wall of one of the two straight slots when the rotor was at rest. There was no evidence at all of specular reflection. The diffused reflection and scattering of atoms was so small that the intensity intercepted on the detector when not in the direct line of the beam was less than 0.1 percent of the beam and hence not important in the present work.

#### SCATTERING FROM RESIDUAL GAS

The theoretical velocity distribution to be observed at the detector has been derived under the assumption that a Maxwellian distribution occurs in the oven and that the slit of the oven is an ideal aperture. It is interesting to investigate the occurrence of a possible distortion of the velocity distribution due to velocity dependent scattering of the beam atoms by the residual gas in the apparatus. The mean free path of a molecule with velocity  $v$  in a single Maxwellian gas is<sup>15</sup>

$$L_v = \alpha_1 v \pi^{1/2} / n_1 S$$

$$\times \left[ \exp(-x^2) + (2x + x^{-1}) \int_0^x \exp(-y^2) dy \right]^{-1}, \quad (9)$$

where  $\alpha_1^2 = (1/2)m_1/(kT_1)$  in which the subscript 1 refers to the scattering gas,  $n_1$  is the density of the gas,  $x$  is equal to  $\alpha_1 v$  and  $S$  is the collision cross-sectional area. To make any calculations from Eq. (9), one has to assign a value to  $\alpha_1$  and the cross-sectional scattering area. In the case at hand, the scattering gas probably consists of air plus all sorts of condensable vapors, including pump oil dissociation products. The temperature of the residual gases is not defined but an "effective" temperature may range from slightly above room temperature to liquid nitrogen temperatures. Since the vacuum in the apparatus tends to deteriorate with increasing rotor speed, there may be a change in composition of the gas at different values of  $x_0$ . Thus it is virtually impossible to calculate  $L_v$  for this situation. To estimate the magnitude of the effects due to scattering, it will be assumed that the residual gas approximates air at room temperature and that the cross-sectional scattering area is  $4.0 \times 10^{-14}$  cm<sup>2</sup>. This area is

<sup>15</sup> E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), p. 109.

close to the value found by Mais<sup>16</sup> and Rosenberg<sup>14</sup> for the scattering of potassium beams by nitrogen.

The probability that an atom will travel from the oven slit to the detector wire without a collision is

$$P_v = \exp(-s/L_v), \quad (10)$$

where  $s$  is equal to the distance between the oven slit and the detector wire, 60 cm. Then  $P_v$  can be calculated from Eqs. (9) and (10). If Eq. (5) is multiplied by the appropriate value of  $P_v$  when account is taken of the variation of the pressure with rotor velocity, a distribution is obtained whose shape is only trivially distorted on the scale of Figs. 4 and 5. In view of the uncertainty in the composition of the gas, the gas temperature, and the related cross sections, the result is subject to a corresponding uncertainty. However, the excellent results for low and moderate beams of potassium and thallium make it clear that any distortion due to scattering by the residual gas in the apparatus must be small.

#### DISCUSSION AND CONCLUSIONS

The results presented in this work demonstrate that the experimental velocity distribution can be predicted with good accuracy from the assumptions that the velocity spectrum in the oven is Maxwellian and that effusion occurs through an ideal aperture. It may be thought that the excellent agreement is somewhat fortuitous, i.e., that an oven slit design was discovered

with the property that a non-Maxwellian distribution effusing through a nonideal aperture gives a distribution experimentally indistinguishable from that arising under our assumptions. An ideal aperture is one in which the dimensions of the aperture are much smaller than the mean free path of the molecules in the gas. The slit used in the present experiments has been designed precisely to meet this condition within the range of experimental feasibility. The agreement between theoretical prediction and observed distributions is therefore, not fortuitous and the result of the present work demonstrates within relatively narrow limits of error that a gas in thermal equilibrium with its surroundings possesses a Maxwellian velocity distribution.

In view of the success of this work, a study of the velocity distributions of alkali halide molecular beams has been made, in which it has been assumed that the experimental velocity spectrum is the superposition of the Maxwellian velocity distribution of the molecular components which are in thermal and chemical equilibrium within the oven chamber. The results of this work will be published elsewhere.

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<sup>16</sup> W. H. Mais, Phys. Rev. **45**, 773 (1934).