however, 98% of the particles passing through S1 and S2 also give a Čerenkov count. We conclude that the beam contained roughly 55% K's and 45% π, μ, and e.

It is important to note that when using the Čerenkov counter to monitor the beam, it is seldom necessary to take a complete pressure curve. There is a large range of pressures, 5.6 to 16.8 kg/cm² (80 to 240 psi), over which the counter has at least 97% efficiency for π, μ, and e and at least 5% efficiency for K's. Therefore, the counter can be left at any pressure within this range. A simple count of coincidences (S1 + S2) gives the total number of beam particles and the pressure is raised above the threshold for 5.0 BeV/c K's.

There is some uncertainty in the data of Fig. 6 as to the location of threshold for K's because we did not take time for the gas to come to temperature equilibrium. The pressure corresponding to ßK - ßπ = 0 was calculated assuming the gas temperature was 10°C. A ±10°C uncertainty in the temperature gives an uncertainty in threshold pressure of ±9 psi.

STUDIES of molecular beam scattering at thermal energies have mostly been restricted to beams of alkali metals and their compounds, since these can be readily detected by surface ionization. In order to carry out measurements of collision cross sections for other molecules, we have constructed a Kingdon cage, or "space-charge" detector. This is a simple diode, consisting of a heated cathode filament which passes through a coaxial cylindrical anode, closed except for small holes in the ends to admit the filament and the beam. Molecules entering the diode cage are ionized by a space-charge-limited electron current. The positive ions trapped within the diode are extremely effective in neutralizing part of the space charge and thus produce a large increase in the plate current.1

In a preliminary investigation in 1933, Estermann and Stern2 found the Kingdon cage to be a quantitative and extraordinarily sensitive detector for beams of mercury and benzophenone. But except for some ionization potential measurements,3 it does not appear to have been used as a molecular beam detector. It has found use as a positive ion detector,4,5 and its response for positive ions or for neutral gases at pressures in the micron region has been

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Kingdon Cage as a Molecular Beam Detector*

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A space-charge detector has been constructed to detect beams of neutral molecules. The detector is a diode within which positive ions created by electron bombardment of the beam partially neutralize the space charge and thus produce an increase in the plate current. Beams of rare gases, hydrocarbons, alkyl iodides, nitrogen, and nitric oxide have been studied, and the detector is found to be suitable for measurements of total collision cross sections. The increase in plate current is proportional to the beam intensity raised to a power near unity. The response varies with the beam material and the electrode geometry, but is quantitative and reproducible for a given detector. The minimum detectable intensity is about 10¹¹ molecules/cm²/sec.

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studied. This investigation was undertaken to determine the characteristics of the Kingdon cage detector under typical molecular beam conditions, in which the steady-state pressures built up in the diode are several orders of magnitude below a micron.

CONSTRUCTION OF THE DETECTOR

Although positive ions have a large effect on a space-charge-limited electron current, the fractional increase in the total anode current is quite small (~0.1%). Estermann and Stern measured this current change with a bridge circuit containing two identical diodes. The beam entered only one diode, and minor fluctuations of filament current and background pressure, which affected both diodes in the same way, were thus balanced out. We began by simply duplicating the detector and circuit used by Estermann and Stern. However, the zero-drift was found to be inconveniently large. This was partially alleviated by simply replacing the compensating diode with a battery. In the final version of the detector, the zero-drift was eliminated by use of a modulation technique. A different anode design was also adopted. These changes facilitate considerably the operation of the detector. Most of the performance characteristics described in this paper refer to the modified single-diode detector and the modulation technique, but are also typical of those obtained with the Estermann-Stern setup.

Details of the anode construction are shown in Fig. 1. In previous versions of the Kingdon cage the anode has been constructed entirely of metal, but here the ends of the anode cylinder are ceramic wafers (Al₂O₃). The use of ceramic endplates greatly facilitates assembly of the detector, simplifies the geometry, and eliminates troublesome emission from the region where the cathode filament passed through the metal endplates. There is no loss in sensitivity or signal-to-noise ratio when the ceramic endplates are used.

In constructing the anode, ledges to support the wafers are machined within each end of a stainless steel tube, the wafers are placed inside, and the ends of the tube are then spun down to clamp the wafers tightly in place. Each wafer is provided with a 1.6-mm-diam axial hole to pass the cathode filament. In one of the wafers a 1-mm-diam hole is placed near the periphery, 8.2 mm from the center, to admit the beam. For certain of the scattering experiments this wafer is also provided with a slot 0.75×3.2 mm near the opposite periphery, which is used instead of the 1-mm-diam hole.

The complete detector assembly is shown in Fig. 2. The anode and the filament are mounted on a stainless steel shell. The mounting clamp which encircles the anode and the rear filament support are insulated from the shell by 3-mm-diam Pyrex rods. The front filament support is a nickel wire fastened to the grounded endplate of the shell. The cathode filament is a 0.050-mm-diam tungsten wire. It is spot-welded to the nickel wire and to a spring wound from 0.025-mm-diam tantalum wire and fastened to the rear filament support. The mounting shell is grounded and wrapped in copper screen to reduce stray pickup.

The detector circuit is shown in Fig. 3. The molecular beam is modulated at 10 cps by a two-blade rotor driven by a small synchronous motor. Thus the total voltage drop across the plate resistor (usually 500 Ω) consists of a dc voltage (~5 V) on which is superposed a small ac voltage (~5 mV) due to the effect of the positive ions formed from the modulated beam. The ac component is amplified by a capacitively coupled amplifier, filtered, and fed to a lock-in amplifier which is tuned to the modulation frequency by a reference signal from a photodiode mounted near the outer edge of the rotor. A phase shifter allows the phase of the reference signal to be adjusted with respect to the signal in order to give a maximum output on the recorder.

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13 D. M. Millst, Phil. Mag. 37, 323 (1946).
17 D. Fuchs, Vakuum-Tech. 9, 104 and 201 (1960).
EXPERIMENTAL PROCEDURE

It is important to outgas the detector thoroughly and age the filament before use. The anode is initially cleaned by boiling it for one day each in toluene and in acetone. After assembly of the detector, it is operated overnight with the filament heated to \( \sim 1000 \text{K} \) to promote outgassing. The filament is then gradually heated to \( 2600 \text{K} \) and allowed to age for 2 or 3 h. Just before use, and periodically during use, it is flashed at \( \sim 2750 \text{K} \) for 5-10 min; this often reduces the noise considerably. Measurements are usually made with the filament at \( 2600 \text{K} \) (which required a heating current of 0.59 A) and with the anode biased 70-80 V positive with respect to the filament.

Under the operating conditions, the lifetime of the cathode filament is typically 40-50 h. During this period, enough of the evaporated tungsten is usually deposited on the ceramic endplates to make them conducting. Also, it was found that after several hours of continuous use, the sensitivity of the detector is impaired if it is turned off and reused a day or more later. However, since the anodes are cheap and readily mass-produced, it proved convenient simply to replace both the anode and the filament at the end of each day's runs and to allow the new detector to outgas overnight.

The detector is mounted in a differentially pumped and liquid nitrogen trapped chamber in which the background pressure could be maintained at \( 5 \times 10^{-8} \text{ mm Hg} \) in the presence of a condensable beam. The beam can be interrupted by a "flag" so that the background signal may be measured separately. Adjustable slit jaws fastened to the front plate of the detector shell define the effective aperture of the detector (usually 0.025 mm wide, 3.2 mm high).

Total scattering cross sections are determined in the usual way by inserting a scattering chamber in the beam path and measuring the attenuation of the beam as a function of the scattering gas pressure. A preliminary calibration of the variation of the detector response with beam intensity is necessary, since the response is found to be nonlinear and to vary somewhat with the detector geometry. For these calibrations, the "beam decay" method is used. The gas line feeding the beam source is switched, by turning a stopcock, from barostat supply to an isolated 5-liter bulb, so that as gas effuses from the source the pressure in the source and the beam intensity decay exponentially with time. The decay constant is measured with a McLeod gauge, with suitable corrections for the volume of the gauge.

PERFORMANCE OF THE DETECTOR

Beams of rare gases (Ar and Xe), hydrocarbons (C\(_2\)H\(_6\) and C\(_3\)H\(_6\)), alkyl iodides (CH\(_3\)I and C\(_3\)H\(_7\)I), nitrogen, and nitric oxide have been detected, with roughly comparable sensitivity. From the source pressure and apparatus geometry it is calculated that, at full intensity, the beam entering the diode cage is about \( 10^{11} \) molecules per sec; this sets up a steady-state partial pressure of about \( 10^{-9} \text{ mm Hg} \) within the diode. The corresponding increase in current to the detector anode observed is about \( 10^{-4} \) A. Thus about \( 10^4 \) electrons are released to the anode for each beam molecule which enters the diode. It appears likely that a large fraction of the beam is ionized within the diode, since this magnification factor of \( 10^4 \) is about the same as the ratio between the increase in plate current and the positive ion current estimated by Kingdon and others. As the signal-to-noise ratio approaches unity when the beam intensity is decreased by about a factor of 100, the minimum detectable intensity is about \( 10^9 \) molecules per sec, or \( 10^{11} \) molecules per cm\(^2\)/sec. This is about \( 10^4\) times higher than that detectable with universal detectors.
ploying electron bombardment ionization and mass analysis.\textsuperscript{21,22}

Both N\textsubscript{2} and NO were found to produce an effect opposite to that expected from the destruction of space charge: under the usual operating conditions, they reduce the plate current. A possible explanation is suggested by other data\textsuperscript{23} which indicates that bombardment of a tungsten filament with positive nitrogen or oxygen ions increases the work function of the filament. This effect has not been investigated further.

**Variation of Response with Beam Intensity**

The measurement of scattering cross sections requires that the detector response provide a metrical and reproducible measure of changes in the beam intensity. It is necessary to establish first that the detector is not merely responding to a general pressure increase in the experimental chamber, but is actually detecting the beam. This is confirmed by the beam profile measurements shown in Fig. 4. For all of the gases studied, the “beam decay” method was used to examine the relation between the relative detector signal S/S\textsubscript{0} and the relative beam intensity I/I\textsubscript{0}. Typical results are shown in Fig. 5. At low source pressures (0.1 mm Hg or less) the detector signal and the source pressure both decay exponentially with time, but with somewhat different decay constants. This implies the relation S/S\textsubscript{0} = (I/I\textsubscript{0})\textsuperscript{a}. The detector response is nonlinear, unfortunately, but only rather weakly nonlinear, since the total range found for the index a is 0.72 to 1.42. Also for a given gas and detector, the standard deviation of the value of a obtained in replicate calibrations is about 5% or less. The Kingdon cage, therefore, is suitable for measurements of scattering cross sections.

There appears to be no way to determine the index a other than by a preliminary calibration. For a given detector, a differs noticeably for various gases, and for a given gas a is evidently sensitive to the exact geometry of the diode. For example, over a period of a year a large number of beam decays made with the same type of experimental set-up (in particular, a 1-mm-diam hole as the anode beam entrance) gave a=1.06–1.42 for CH\textsubscript{3}I and a=0.72–0.95 for Ar. These variations appear to arise from very slight differences in the assembly of the various detectors used. A marked shift to lower values of a occurred when the rectangular slot shown in Fig. 1 was cut in the ceramic wafer and used as the anode beam entrance; for example a=0.87–1.02 was thereafter observed for CH\textsubscript{3}I beams.

Other studies\textsuperscript{13–17} employing the Kingdon cage as a detector for positive ions or for neutral gases at higher pressures have also found the response to be nonlinear. However, only the measurements of Fuchs\textsuperscript{17} extend to the pressure range relevant to beam work, and he found a≈\frac{1}{2} for Hg, Ar, and N\textsubscript{2}.

Although cross section measurements involve only the relative intensity I/I\textsubscript{0}, it should be mentioned that the absolute signal obtained from the Kingdon cage also appears to vary with the detector geometry by roughly an order of magnitude for a given gas. In addition it decreases slowly with time; this is not a handicap since the drift is usually steady and gradual (roughly 2%/h). The absolute sensitivity of the detector is expected to decrease with decreasing molecular weight of the beam, as the increase in molecular speed reduces the time the beam molecules or ions formed from them remain within the diode. In practice, this appears to be a minor effect, less significant than a general decrease in net signal and signal-to-noise due to the increase in background pressure when the beam is a noncondensable gas. Thus, the experimental sensitivity was found to be of the same order-of-magnitude for the various gases studied, although markedly better for heavy, condensable species such as CH\textsubscript{3}I than for noncondensable species such as Ar, Xe, and C\textsubscript{2}H\textsubscript{2}.

**Bias Dependence**

The bias voltage applied to the anode must be sufficiently high to produce electrons energetic enough to
ionize the beam, but not so high that the current to the anode ceases to be space charge limited. Figure 6 shows the variation of the detector signal with bias voltage for a filament temperature of 2300 °K. The “appearance” potential is lower than the ionization potential\textsuperscript{24} of 9.67 eV for CH$_3$I because of the thermal velocity distribution of the electrons and because the filament is not an equipotential surface. The decrease in signal above 12 V is attributed to the onset of saturation in the diode.

Figure 7 shows the signal versus bias for a filament temperature of 2600 °K, the usual operating temperature. Here a bias voltage of up to 100 V is insufficient to saturate the diode; consequently Fig. 7 corresponds to the increasing portion of the curve in Fig. 6. In this region, the signal may be characterized by a relationship of the form $S = \beta V^2$, with $\beta$ a constant. This function gives a better representation of the data than the relation $S = \beta \exp(\gamma V)$ which was observed by Fuchs\textsuperscript{17} at higher pressures. The $V^2$ dependence is also attractive since the total current in a space-charge-limited diode is proportional to $V^3$, according to the Child-Langmuir formula.\textsuperscript{25}

**Variation with Modulation Frequency**

An unmodulated beam will set up a steady-state partial pressure in the diode of about 10$^{-9}$ mm, as estimated by equating the flux of beam molecules into the diode to the pressure dependent effusive flow out of the diode. When the beam is modulated, the pressure in the diode will decrease, as the beam is not long enough for it to attain the peak value. It is readily shown that the ratio of the pressure generated at modulation frequency $f$ to that at zero frequency is given by

$$\frac{P_f}{P_0} = \left[1 - \exp\left(-B/2f\right)\right]/\left[1 - \exp\left(-B/f\right)\right],$$

where $B = \frac{1}{2}(\bar{v}\Sigma A_i/V)$, with $\bar{v}$ the average velocity of molecules within the diode, $V$ the volume of the diode, and $\Sigma A_i$ the sum of the effective areas (geometrical areas divided by Knudsen’s “kappa factor”) of the openings in the diode.

Figure 8 shows the variation with modulation frequency of the signal obtained from a CH$_3$I beam. The solid curve is calculated from Eq. (1) with $V = 6.3$ cm$^3$ and $\Sigma A_i = (0.024/2 + 0.01/1.1 + 0.02/1) = 0.041$ cm$^2$ as the sum of the effective areas of the beam slit, beam entrance hole, and filament entrance holes. The temperature of the gas within the diode is taken as 800 °K, the equilibrium temperature of the anode as calculated from the power radiated from the filament. The experimental points and the theoretical curve are normalized to unity at $f = 10$ cps. The close agreement obtained suggests that the gas is effectively in thermal equilibrium with the anode. Similar results were obtained by Fuchs.\textsuperscript{17}

At least in principle, the frequency dependence of the signal offers a means by which different species could be differentially detected in scattering experiments. For example, the dashed curve in Fig. 8 shows the behavior expected for H$_2$, again at 800 °K.

**DISCUSSION**

At present there is no entirely satisfactory explanation of either the magnitude of the Kingdom cage effect or of its deviation from linearity. In most discussions\textsuperscript{1,11,15,16} the amplification factor associated with destruction of the electronic space charge ($\sim 10^4$ electrons released per incident neutral molecule) is regarded as, essentially, just the ratio of the lifetime of a positive ion to that of an electron.\textsuperscript{9,10,11,15,16}

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\textsuperscript{10} I. Langmuir, Phys. Rev. 21, 419 (1923).
within the diode. The mass disparity alone provides an amplification factor of the order of 100, since the velocity of the ions is lower than that of the electrons in the ratio \( (m_{\text{ion}}/m_e)^1 \sim 100 \). Kingdon\(^1\) postulated that the positive ions would spiral around the cathode many times before discharging and thus enjoy a prolonged lifetime. Although there is some evidence for such an effect,\(^1,15,16\) Karr and Varney\(^11\) demonstrated that there is no loss in amplification if spiraling is excluded by the use of a large diameter cathode. Another possible mechanism, also originally considered by Kingdon, was emphasized by Varney\(^11\) and by Bott.\(^10\) This notes that within a space-charge-limited diode the potential has an extremum. For electrons this is a maximum and only the most energetic electrons are able to surmount the barrier and coast to the anode. For positive ions, the extremum is a potential minimum, and it was proposed that the ions might be trapped for a relatively long period in this minimum.

We shall consider a simple model which attributes the amplification to the decrease in the potential barrier for the electrons caused by the presence of the positive ions. Since the electrons have a thermal velocity distribution, the anode current \( I \) may be written as

\[
I = I_o \exp(-\phi_m/kT),
\]

(2)

where \( I_o \) is the saturation current and \( \phi_m \) is the potential maximum (with the cathode at zero potential). If \( \phi_m \) is lowered an amount \( \phi_m \), by the presence of positive ions, a larger anode current \( I' \) will result, with

\[
I' = I_o \exp(-e[\phi_m - \phi_m]/kT).
\]

(3)

For \( e\phi_m \ll kT \) the increase in current, \( \Delta I = I' - I \), is given by

\[
\Delta I/I \approx e\phi_m/kT.
\]

(4)

It is now necessary to estimate \( \phi_m \), the positive ion potential at the position of maximum electronic potential. Since the distribution of positive charges is unknown, an exact solution is not possible. However, according to Wheatcroft,\(^26\) for diodes of the kind used here the calculation of the potential distribution and plate current may be well-approximated by the parallel-plane case treated by Langmuir.\(^25\) In order to estimate the positive ion charge density, we assume that the ions are produced mostly near the anode. The electric field will accelerate the ions towards the cathode. Although they encounter a potential minimum, according to Langmuir's tables\(^26\) (with \( I = 12 \) mA, \( I_e = 80 \) mA, \( T = 2600^\circ \text{K} \)), this should be located only 0.0072 cm from the cathode, with \( \phi_m = 0.42 \) V, and thus the 70-eV positive ions are not likely to be "trapped" and we assume they immediately discharge at the cathode. We further assume that the contribution of an ion to the charge distribution in a given region is proportional to the time it spends there, and we roughly approximate the potential between the electrodes as linear.

In this case, the electric field, \( E = -\nabla \Phi = -K \), and the force, \( m\vec{x} = -eK \), are constant and the positive ion charge density is given by

\[
\rho_e = C'(dl/dx) = C(x_a - x)^{-3},
\]

(5)

with \( C = C'(m_{\text{ion}}/2eK)^{1/3} \). This result is obtained by integrating the acceleration, with \( x = x_a \) and \( x = 0 \) at \( t = 0 \); the origin \( x = 0 \) is at the cathode and \( x = x_a \) at the anode. An expression for \( \Phi_m \) may now be found by integrating Poisson's equation, \( d^2\Phi/dx^2 = -\rho_e/e_n \), with the conditions \( \Phi = 0 \) and \( d\Phi/dx = 0 \) at \( x = 0 \). This yields

\[
\Phi_m = \frac{1}{2} (C/e_n)x_a^{2}x_{m}^{-3},
\]

(6)

for \( x_m \ll x_a \). Since the number of positive ions per unit anode area, \( n_i/A \), is given by

\[
en_i/A = \int \rho_e dx = 2Cx_a^4,
\]

(7)

we may rewrite Eq. (4) as

\[
\Delta I/I = e^2x_a^2n_i/4kTAe_nx_a,
\]

(8)

or

\[
\approx 8 \times 10^{-12}\mu_i,
\]

(9)

where the units are mks, \( A \) is the area of the anode (12.6 cm\(^2\)), \( x_a \) the distance from the cathode to the cylinder of maximum electronic potential (0.0072 cm), \( x_n \) the electrode spacing (0.91 cm), and \( T = 2600^\circ \text{K} \).

For a typical beam intensity of about \( 10^{10} \) molecules per sec entering the diode, the steady-state density within the diode is about \( 3 \times 10^{10} \) beam molecules per cm\(^2\). If all of the molecules were ionized, Eq. (9) would predict \( \Delta I/I \approx 1.5 \times 10^{-3} \), as compared with the observed ratio of about \( 10^{-4} \). Although there is no direct evidence, it seems likely that a large fraction (<10\%) of the molecules entering the diode are ionized, since the observed amplification ratio (10\(^4\) electrons released per incident particle) is of the same order as that observed for detection of positive ions.\(^1,1,15,11,17\) Thus it appears that this primitive treatment can account for the order of magnitude of the Kingdon cage effect, without invoking assumptions about spiraling or trapping of the positive ions.

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