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APPARATUS RESOLUTION AND MEASURED
SCATTERING CROSS SECTIONS

by

Larry Omar Christian

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GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Larry Omar Christian entitled Apparatus Resolution and Measured Scattering Cross Sections be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

John C. Leavitt
Dissertation Director

Dec 1, 1965
Date

After inspection of the dissertation, the following members of the Final Examination Committee concur in its approval and recommend its acceptance:*

<u>John Lomont</u>	<u>12-16-65</u>
<u>Philip H. Betts</u>	<u>12/1/65</u>
<u>Ray W. Smith</u>	<u>12/1/65</u>
<u>John C. Leavitt</u>	<u>12/1/65</u>
<u>Ronald Z. Welt</u>	<u>11/19/65</u>
<u>Hosney Mahmoud</u>	<u>12/1/65</u>

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SIGNED: Larry O. Christian

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ABSTRACT

Using the molecular-beam method, an investigation has been conducted in order to determine the effect of apparatus resolution on the measured cross sections of a full thermal cesium beam scattered by the five scattering gases, He, Ne, A, Kr and Xe. The variation of "partial" total cross sections has been measured as a function of the angular resolution of the apparatus (using the Kusch 50% criterion) over the range from 12 to 120 seconds of arc. The accuracy of these relative measurements was within $\pm 5\%$.

The principal problem of interest was to investigate the question concerning the extremely large discrepancies (a range of approximately a factor of three) in the Cs-He total cross section reported by previous investigators. The present experiments have shown that these disagreements cannot be explained by the differences in resolution employed by these workers. It was found that the cross sections for a Cs beam scattered by He, Ne, A, Kr and Xe decreased by 11.5, 10.5, 16, 13 and 15 percent, respectively, as the resolution was varied over the experimental limits employed.

As a by-product of the present work, the "true" total cross sections (with an error of $\pm 25\%$) for the cases

Cs-He, Cs-Ne and Cs-A were obtained by extrapolation of the results to zero resolution. The van der Waals constant, C , was calculated (using the Schiff-Landau-Lifshitz theory and an interatomic potential of the form $V(r) = -C/r^6$) for these three cases.

INTRODUCTION

The general goal of research of the type described in this dissertation has been the investigation of intermolecular forces using molecular-beam techniques. The primary consideration of this particular set of experiments was the investigation of the effect of apparatus resolution on the validity of values of intermolecular force or potential parameters obtained using the molecular-beam method. The primary effort was directed toward the establishment of a reliable method for accurate measurement of these parameters, rather than toward the measurement of large numbers of these parameters.

The qualitative form of the forces between two neutral atoms or molecules is known. The force is repulsive at small intermolecular separations and attractive at large intermolecular separations. Some information concerning these forces has been obtained from quantum mechanical calculations for specific molecular interactions. However, the results of these calculations are not very accurate, since many of the integrals encountered were either approximated or simply neglected due to their complexity. Nevertheless, these calculations have given some indication of the form of the force or potential to be expected.

The usual approach to the determination of the intermolecular potential has been empirical. An intermolecular potential function of reasonable form containing several undetermined parameters was assumed. This potential was then used to calculate quantities which could be measured. These calculated quantities, of course, involved the undetermined parameters of the assumed potential. The parameters were then determined by comparing the calculated quantities with the appropriate measured quantities.

The specific quantities to be measured depended on the experimental method used in the investigation. A large number of experiments involving the measurement of bulk properties of matter have been performed. Examples of these bulk properties are: (i) equilibrium properties of solids (such as density and compressibility at low temperatures), (ii) equilibrium properties of gases (such as the second virial coefficient) and (iii) non-equilibrium properties of gases (such as the viscosity coefficient). The determination of intermolecular potential parameters using these properties suffers from two difficulties. First, these situations involve the close proximity and/or interaction of more than two molecules and, therefore, may not afford the best determinations of the potential between two isolated molecules. Second, in these cases, the dependence of the calculated quantities on the assumed form and parameters of

the assumed potential is not very sensitive. Thus, very high experimental accuracy is required to establish a unique intermolecular potential.

The use of molecular-beam techniques overcomes both of these difficulties. The interaction between two isolated molecules can be studied. Further, the dependence of the calculated quantities on the assumed potential is much more sensitive in the molecular-beam case than in any of the previous cases, thus affording the best chance of a unique determination of the potential.

There are three distinct approaches to the determination of intermolecular potential parameters by the molecular-beam method. Two approaches will allow the determination of the potential over its full range. One of these approaches involves crossed molecular beams with full thermal velocity distributions (i.e., beams with Maxwellian speed distributions) and the measurement of the differential scattering at all angles (Beck 1962). The other approach involves the passage of a velocity selected molecular beam through a chamber containing a scattering gas and the measurement of the total scattering cross section as a function of the relative velocity of the colliding partners (Rothe, Rol and Bernstein 1963). This method is potentially the best method for light beams and heavy scattering gases and will eventually be used in this laboratory.

The third and simplest approach allows the determination of only the long-range portion of the intermolecular potential. This was the approach used for the work presented in this dissertation. In this case, a collimated full thermal beam of molecules was allowed to pass through a small chamber containing a scattering gas and strike a detector. From measurements of the beam attenuation as a function of scattering gas pressure, the total elastic scattering cross section was determined. This was the measured quantity which was compared with the corresponding quantity calculated from the assumed potential. For this case, the scattering was predominately due to the long-range portion of the potential which was assumed to have a simple inverse sixth power distance dependence and a single undetermined parameter called the van der Waals constant. The relation between the cross section, Q , and the van der Waals constant, C , is discussed in the next chapter.

There have been some criticisms of the use of molecular-beam techniques to determine potential parameters. The two main criticisms have been: (i) the values of the parameters determined experimentally by the molecular-beam method have been consistently higher than either theoretical estimates or values determined by the other experimental methods previously mentioned and (ii) there has been considerable lack of agreement among various investigators using

molecular-beam techniques concerning the measured values of the potential parameters for certain gases. The experiments described in this dissertation were an attempt to answer this second criticism.

A possible answer to the second criticism lies in the study of the effect of apparatus resolution on the measured values of the total scattering cross section. Evidence, which will be cited later, indicates that a possible reason for disagreement among the investigators is due to inadequate apparatus resolution for all the experiments concerned. Note that the measurement of a total scattering cross section requires the detection of all particles which are scattered through any angle whatsoever as being scattered. But, this is impossible, since all detectors and all beams have finite size. This fact leads to the problem of apparatus resolution. It will be necessary to briefly describe the experimental picture in order to discuss this problem.

The molecular beam was formed by the effusion of the beam molecules from a narrow vertical slit in the front of a heated oven and the subsequent passage of these molecules through a narrow vertical collimator slit. The collimated beam then passed through the scattering chamber and on down the machine to the vertical detector wire which was located in the center of the beam. Attenuation measurements were performed by admitting gas into the scattering chamber and

noting the decrease in the number of beam molecules which struck the detector. The oven and collimator slits and the detector wire were all several hundred times as high as they were wide.

The problem of resolution in scattering experiments arises partly because the detector has a finite size. Consider the following. Suppose a beam particle travels in such a direction that it, if not scattered, would strike the detector. Suppose this beam particle is scattered by a gas particle in the scattering region. The fact that the beam particle is scattered does not necessarily mean that it will not still strike the detector. Whether or not the particle is scattered off the detector will depend on the size and shape of the detector and on both the polar and azimuthal angles of scattering.

The usual rough definition of apparatus resolution is the following: if beam molecules which are scattered by an angle θ or greater are detected as scattered, and molecules scattered through angles less than θ are not detected as scattered, then θ is the resolution of the apparatus. This definition may be useful for beams with axial symmetry (i.e., beams of circular cross section and a circular detector). However, it is not a useful definition in connection with molecular-beam experiments, since neither the beam nor the detector have axial symmetry.

Nevertheless, a definition of resolution similar to this was used for many years by molecular-beam workers. This definition will be referred to as the old definition of resolution. The resolution of the apparatus was simply defined as the angle subtended by the detector wire at the center of the scattering region.

The inadequacy of this definition was generally recognized. Kusch (1964) proposed a new definition of apparatus resolution, hereafter referred to as the Kusch 50% criterion. He proposed a reasonable definition of apparatus resolution as the minimum scattering angle, $\varphi_{50\%}$, for which the efficiency of detection of scattering is 50%. In the Kusch 50% criterion, the angular resolution depends primarily on the beam width and only slightly on the detector width. This definition of apparatus resolution has since been generally accepted by workers in the field. A more complete discussion of this definition is presented in the next chapter.

The importance of the question of apparatus resolution in connection with the measurement of total scattering cross sections can be seen by considering the measured Cs-He scattering cross sections listed in Table I.

From the table, it appears that the measured Cs-He cross section is a very strong function of resolution $\varphi_{50\%}$.

TABLE I.

Results of Previous Investigators for the Total Cross
Section of a Cesium Beam Scattered by Helium Gas.

Reference	$Q_{\text{Cs-He}} (\text{\AA}^2)$	Resolution ($\varphi_{50\%}$)	Error
Rosin and Rabi (1935)	162	5 min.	4%
Rothe and Bernstein (1959)	266	2 min.	15%
Estermann, Foner and Stern (1947)	446	1 min.	10%

Such a strong dependence on resolution indeed indicates that a carefully designed resolution study was worth the undertaking.

It was thought that possibly none of the workers listed in Table I had obtained high enough resolution to obtain meaningful results. It is of interest to know what resolution is necessary to obtain accurate results for Q by the molecular-beam method. Thus, it was decided to perform the present experiments to see if the variation of $Q_{\text{Cs-He}}$ (and other cases) with $\varphi_{50\%}$ was real.

In the present experiments a full thermal Cs beam was allowed to pass through a scattering chamber which contained one of the rare gases, He, Ne, Ar, Kr or Xe. The

angular resolution, $\varphi_{50\%}$, as defined by the Kusch 50% criterion, was varied from approximately 12 seconds to 120 seconds. The "partial" total cross section (i.e., the cross section corresponding to a particular value of resolution) was measured at specified intervals of resolution. The resulting graph of Q versus $\varphi_{50\%}$ was extrapolated to zero resolution for the cases of Cs-He, Cs-Ne and Cs-A to yield the value for the "true" total cross section (i.e., the cross section corresponding to zero width beam and zero width detector). In these cases the van der Waals constant was determined. In the cases of Cs-Kr and Cs-Xe extrapolation was extremely dangerous and was omitted because the slopes became very steep at small values of $\varphi_{50\%}$.

The main body of the discussion of the present work is broken into three more chapters: (i) a background chapter in which necessary theoretical and experimental information is presented, (ii) a chapter describing the experimental set-up and procedure used and (iii) a chapter containing the results and conclusions of this work. Appendices are also added.

BACKGROUND

The purpose of the present chapter is to supply sufficient information concerning the theoretical and experimental background of the present experiments so that one can understand the difficulties, approximations and formulas encountered in the discussion of these experiments.

The theoretical section includes a discussion of intermolecular forces (with particular emphasis on the dispersion contribution to the van der Waals attraction) and a discussion of the relationship between the total cross section and the van der Waals constant. The experimental section includes a discussion of the formula used to calculate total cross sections from the data of molecular-beam experiments, a discussion of the resolution problem in molecular-beam scattering experiments (with details of the Kusch 50% criterion) and a statement of the specific goals of the present investigation.

I. Theoretical Background

A. Intermolecular Forces

One of the fundamental problems of molecular physics is the determination of the law of force between two

molecules. There are various types of interaction which arise between atoms and molecules. The present discussion is limited to interactions of neutral molecules in their ground states. The force of interaction F between two spherical non-polar molecules (which is the primary case of interest here) is assumed to be a function of the intermolecular separation r only. It is usually more convenient to use the potential energy of interaction $V(r)$ rather than the force of interaction $F(r)$. For cases where the force law depends only on the intermolecular separation, these two functions are simply related:

$$F(r) = -dV/dr; \quad V(r) = \int_r^{\infty} F(r)dr. \quad (1)$$

Thus, in the following discussion, the forces between these molecules are described in terms of such potentials.

For purposes of discussion, it is convenient to divide intermolecular forces into two types: short-range forces and long-range forces. The short-range forces are usually called valence forces or chemical forces and arise when the molecules come close enough together for their electron clouds to overlap. These forces are repulsive in nature and often highly directional. Experimental evidence about the short-range forces comes from studies of crystal structure, properties of surfaces, results of high energy

molecular-beam experiments, etc. A great deal of the information known about short-range forces comes from the specific quantum mechanical calculations for a specific molecular interaction. However, as was mentioned in the introduction, many of these calculations are not very accurate. The long-range forces, however, are better understood, and may be treated in a fairly rigorous manner. But, even here, the calculations can become quite involved. A few comments on the short-range forces, followed by a more lengthy discussion of the long-range forces, are given next. Much of the material presented in the following sections was condensed from chapters 1 and 13 of Hirschfelder, Curtiss and Bird (1954).

1. Short-range Forces

The short-range contribution to the intermolecular potential is usually approximated in one of the two following manners: (i) a simplified expression representing an exponential decrease with distance of separation, i.e., $V(r) = a \exp(-cr^n)$, in which a , c and n are constants or (ii) an expression which varies with an inverse power of the distance of separation, i.e., $V(r) = A/r^b$, in which A is a constant and the index b is an adjustable parameter in some calculations. Since these approximations involve no directional dependence of the short-range force, the usefulness of these assumed potentials is rather limited. No work

was done in connection with the present experiments concerning these short-range forces and, therefore, no further discussion about them is given here.

2. Long-Range Forces

The various contributions to the long-range portion of the potential are assumed to vary inversely as powers of the intermolecular separation. It is convenient to divide the long-range contributions to the interaction potential of neutral molecules into three parts: (i) the electrostatic contribution, (ii) the induction contribution and (iii) the dispersion contribution. A qualitative summary of the general nature of these contributions is presented next. The first two types of interaction may be explained by straightforward electrostatic considerations, but the third type (dispersion forces) needs a quantum mechanical treatment for adequate explanation.

1. Electrostatic Contributions

Attention is given here to neutral molecules which may possess permanent electric dipole moments (μ). The interaction energy between two polar molecules, treated as ideal dipoles, is a function of the orientation of both dipoles, being positive (repulsive) for some angles and negative (attractive) for others. When both these interactions are averaged over all possible orientations (using

the Maxwell-Boltzmann distribution function $\exp(-V/kT)$, where V is the angle-dependent potential function) the resulting expressions give a temperature-dependent attractive interaction. The net attraction follows from the distribution law, which statistically favors the orientations of low potential energy, corresponding to attractions, over the orientations of high potential energy, corresponding to repulsions. For large separations or high temperatures, the averaged dipole-dipole interaction is found to be

$$V_{d-d}(r) = \left(-\frac{2}{3kT}\right)\left(\frac{\mu_1^2 \mu_2^2}{r^6}\right), \quad (2)$$

where μ_1 and μ_2 are the permanent dipole moments of the two molecules. This expression is known as the Keesom alignment energy (Keesom 1921).

ii. Induction Contributions

A different type of electrostatic effect arises from the induction of a moment in one molecule by the field due to a permanent moment in the other molecule. This is an important contribution to the potential of interaction between a polar and a non-polar molecule. The result, averaged over angles (as in the dipole-dipole interaction), is known as the Debye-Falkenhagen induction energy (Debye 1921), and is given by

$$V_{\text{ind}}(r) = - \frac{\alpha_2 \mu_1^2 + \alpha_1 \mu_2^2}{r^6}, \quad (3)$$

where μ_1 and μ_2 are the permanent dipole moments and α_1 and α_2 are the polarizabilities of the two interacting molecules. Note that this contribution is independent of temperature.

iii. Dispersion Contributions

When two non-polar molecules interact there are long-range forces of attraction between them. These forces are referred to as dispersion forces, since they may be expressed in terms of quantities called oscillator strengths which appear in the theory of the dispersion of light. Although quantum mechanical theory is needed to adequately describe these forces, the following classical discussion shows qualitatively the origin of them.

It is assumed that neither of the two interacting molecules possesses a permanent dipole moment, and the effects of higher moments are neglected. All atoms and molecules have instantaneous dipole moments, but these fluctuate very rapidly. The absence of a permanent moment means that the instantaneous moments average to zero. Molecules are polarizable, i.e., they acquire induced dipole moments in the presence of an electric field. The instantaneous moment of each molecule gives rise to an electric field at the site

of the other molecule and, since the molecules are polarizable, a dipole moment is induced in the other molecule. The interaction between the instantaneous dipole in one molecule and the dipole it induces in the other leads to an attraction between the two molecules which varies as the inverse sixth power of separation. This is seen as follows. The electric field at molecule 2 due to an instantaneous moment μ_1 in molecule 1 is proportional to μ_1/r^3 . The induced moment μ_2 is proportional to the inducing field, and the constant of proportionality is called the polarizability α_2 of molecule 2. Hence, μ_2 goes as $\alpha_2\mu_1/r^3$. The interaction energy between either dipole and the field due to the other is proportional to $\mu_1\mu_2/r^3$ and, hence, to $\alpha_2\mu_1^2/r^6$. Similarly, if the instantaneous dipole is located in molecule 2, one obtains an energy of interaction proportional to $\alpha_1\mu_2^2/r^6$. In this explanation, no angular dependence was considered, but it suffices to show the $1/r^6$ dependence. Note, although the average μ is zero, the energy of interaction depends on μ^2 and this does not average to zero (Leighton 1959, p. 324).

London (1930) developed the first quantum mechanical explanation for these dispersion forces and, consequently, they are often referred to as London dispersion forces. He used second order perturbation theory to derive the expression

$$V_{\text{disp}}(r) = \left(-\frac{3\alpha_1\alpha_2}{r^6}\right)\left[\frac{U_1U_2}{U_1+U_2}\right], \quad (4)$$

where α_1 is the static atomic polarizability and U_1 is some average excitation energy of atom 1. The ionization potentials of the atoms are often put equal to U . Other theoretical attempts to describe these dispersion forces have been made by Slater and Kirkwood (1931) who used the variational method to obtain the expression

$$V_{\text{disp}}(r) = \frac{3eh}{2(m)^{\frac{1}{2}}r^6} \frac{\alpha_1\alpha_2}{\left(\frac{\alpha_1}{N_1}\right)^{\frac{1}{2}} + \left(\frac{\alpha_2}{N_2}\right)^{\frac{1}{2}}} \quad (5)$$

where N_1 refers to the number of outer electrons in atom 1, e and m represent the electronic charge and mass and h has its usual meaning. The variational approach was also used (Kirkwood 1932, Müller 1936) to obtain the Kirkwood-Müller formula,

$$V_{\text{disp}}(r) = \frac{6mc^2}{N_0r^6} \frac{\alpha_1\alpha_2}{\frac{\alpha_1}{\chi_1} + \frac{\alpha_2}{\chi_2}} \quad (6)$$

where c is the velocity of light, N_0 is Avagadro's number, and χ_1 is the diamagnetic susceptibility per mole for atom 1. It may also be shown that there are further terms (much smaller in magnitude) in the dispersion energy which vary as $1/r^8$ (induced-dipole-induced-quadrupole), and $1/r^{10}$ (induced-quadrupole-induced-quadrupole), etc.

To a first approximation, the long-range intermolecular potential for two molecules is the sum of the three types of forces described which all vary as $1/r^6$. The sum of these three contributions are commonly referred to as the van der Waals attraction. This attraction is assumed to represent the entire intermolecular potential very accurately in cases of thermal energy alkali beams and the inert scattering gases. Hence, for these cases,

$$V(r) = -C/r^6. \quad (7)$$

Here C is called the van der Waals constant and can be expressed

$$C = C_{d-d} + C_{ind} + C_{disp}, \quad (8)$$

where C_{d-d} is the coefficient of $1/r^6$ in Eq. (2), C_{ind} is the coefficient of $1/r^6$ in Eq. (3) and C_{disp} is the coefficient of $1/r^6$ in Eq. (4), (5) or (6). For the cases under consideration in the present experiments none of the atoms possesses a permanent dipole moment. Thus, $C_{d-d} = C_{ind} = 0$, and the entire contribution to the van der Waals constant arises from the London dispersion forces, i.e., $C = C_{disp}$.

The use of Eq. (5) to evaluate C_{disp} has the obvious advantage that it requires only a knowledge of the

polarizabilities. Following the procedure of Rothe and Bernstein (1959), the constants in the expression can be calculated and the result is

$$C_{\text{disp}} = \frac{A\alpha_1}{B + \left(\frac{\alpha_1}{N_1}\right)^{\frac{1}{2}}}, \quad (9)$$

where C_{disp} is given in units of 10^{-80} erg cm⁶, α_1 is the polarizability of the inert gas under consideration in Å³, $N_1 = 8$ for the inert gases (except for He, where $N_1 = 2$), and $A = 1057.1$ and $B = 6.480$ for Cs beam atoms. The polarizability of cesium used to calculate A and B was taken as 42.0 Å^3 (Scheffers and Stark 1934).

The next section discusses the relationship between the van der Waals constant C and the total elastic scattering cross section Q .

B. Calculation of Total Cross Section in Terms of the Intermolecular Potential Parameter C

1. Landau-Lifshitz Calculation of Q for van der Waals Potential

It is shown in many sources (Schiff 1955, Landau and Lifshitz 1959, Powell and Craseman 1961) that, in the case of elastic scattering in which the interaction between the

scattered particle and the scatterer can be represented by a potential energy function $V(r)$, the total elastic cross section is given by the standard formula

$$Q(k) = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2 \delta_{\ell}(k). \quad (10)$$

This formula is derived using the familiar method of partial waves. The quantity $\delta_{\ell}(k)$ is the phase shift of the ℓ^{th} partial wave. k has its usual significance of being the magnitude of the plane wave propagation vector.

In the Landau-Lifshitz formula which is briefly derived next, the phase shifts δ_{ℓ} are evaluated using the WKB approximation. The validity of this approximation for the phase shifts in the case of molecular-beam scattering has been found to be reliable by Marchi and Mueller (1963) by actual comparison with the exact numerical solution of the Schrödinger equation for particular choices of potential parameters. By definition,

$$\delta_{\ell} = \left[\int_{r_{01}}^{\infty} \left\{ k^2 - \frac{(\ell + \frac{1}{2})^2}{r^2} - \frac{2\mu V}{\hbar^2} \right\}^{\frac{1}{2}} dr + \frac{1}{4}\pi \right] \\ - \left[\int_{r_{02}}^{\infty} \left\{ k^2 - \frac{(\ell + \frac{1}{2})^2}{r^2} \right\}^{\frac{1}{2}} dr + \frac{1}{4}\pi \right], \quad (11)$$

where the first bracketed term represents the phase of the ℓ^{th} scattered partial wave and the second bracketed term represents the phase of the ℓ^{th} partial wave when no scattering potential V is present. r_{o_1} and r_{o_2} represent the zeroes of the respective integrands, i.e., the integration is over only the classically accessible region. Here μ is the reduced mass of the colliding particles ($\mu = m_1 m_2 / (m_1 + m_2)$). It is to be noted that the "Langer approximation" (Mott and Massey 1952, p. 127) whereby $\ell(\ell + 1)$ is replaced by $(\ell + \frac{1}{2})^2$ has been employed. The next step is to replace the r_o 's by the approximate value of ℓ/k and, by realizing that V is small in the region of integration, one readily obtains

$$\delta_\ell = - \frac{\mu}{\hbar^2} \int_{\ell/k}^{\infty} \frac{V}{k^2 - \frac{(\ell + \frac{1}{2})^2}{r^2}} dr. \quad (12)$$

In the Landau-Lifshitz approximation, $\ell + \frac{1}{2}$ is replaced by ℓ throughout all calculations. Making this substitution, inserting the attractive potential $V = -C/r^S$ and letting $\xi = \ell^2/k^2 r^2$ to aid in integrating, we obtain

$$\delta_\ell = \frac{\mu C k^{S-2} \pi^{\frac{1}{2}} \Gamma(s/2 - \frac{1}{2})}{2 \hbar^2 \ell^{S-1} \Gamma(s/2)}. \quad (13)$$

Next the summation in Eq. (10) is replaced by an integral and again $l + \frac{1}{2}$ is replaced by l to yield

$$Q = \left(\frac{4\pi}{k^2}\right) \int_0^\infty 2l \sin^2 \delta_l \, dl . \quad (14)$$

Substituting the expression for δ_l from Eq. (13) into Eq. (14), one obtains finally (Landau and Lifshitz 1959, p. 416) the result

$$Q(v_r) = 2\pi^{\frac{s}{s-1}} \Gamma\left(\frac{s-3}{s-1}\right) \sin\left(\frac{\pi}{2} \frac{s-3}{s-1}\right) \left[\frac{\Gamma(s/2 - \frac{1}{2})}{\Gamma(s/2)}\right]^{\frac{s}{s-1}} \frac{1}{h^{\frac{s}{s-1}}} \left(\frac{C}{v_r}\right)^{\frac{s}{s-1}}, \quad (15)$$

where $v_r = \frac{hk}{\mu}$ is the relative velocity of the colliding particles.

For the case of interest here, $s = 6$, and the resulting simplification yields

$$Q(v_r) = b_{LL} \left(\frac{C}{v_r}\right)^{2/s}, \quad (16)$$

where $b_{LL} = 4.992 \times 10^{11}$ cgs units.

One might wonder what effect the neglect of a repulsive part of the intermolecular potential has upon this result for Q . Bernstein (1961) has shown that, for a thermal velocity molecular beam, the attractive van der Waals term dominates the scattering, except for the case of light atoms

at low velocities. The influence of the repulsion only produces undulations in $Q(v_p)$. At very high velocities, the repulsive forces would become important (Amdur and Pearlman 1941).

For purpose of completeness, two other approximations for Q using the van der Waals potential are briefly discussed next.

2. Massey-Mohr and Schiff Approximations

for Q

Historically, the first to derive the $v_p^{-2/5}$ dependence of Q for the van der Waals potential were Massey and Mohr (1934). They employed the random-phase approximation for the large, low-order phases ($l < L$, where $\delta_L = \frac{1}{2}$). The summation, Eq. (10), is broken into two parts: (i) $l < L$, in which $\sin^2 \delta_l$ is replaced by its average value of $\frac{1}{2}$, and (ii) $l \geq L$, where δ_l is approximated by the WKB method and the summation is replaced by integration. Their result is the same as Eq. (16) except for the value of the constant b . In their approximation, $b_{MM} = 4.662 \times 10^{11}$ cgs units.

Still another approximation formula for Q is due to Schiff (1956). For a central potential the Schiff formula gives the same result as the Landau-Lifshitz approximation. Thus, $b_S = b_{LL} = b_{SLL} = 4.992 \times 10^{11}$ cgs units.

The Schiff-Landau-Lifshitz approximation appears to be superior (Bernstein and Kramer 1963) to that of Massey and Mohr because a numerical calculation showed that it agreed better with the "true" cross section calculated by a complete partial wave analysis (actually in Bernstein and Kramer's appraisal of the approximation formulas, their calculations were done using $s = 12$, i.e., a pure repulsive potential).

Thus far, it has been assumed that v_r in Eq. (16) is a constant. However, for measurements using a Maxwellian beam and a Maxwellian scattering gas, an average relative velocity must be used in all calculations. An expression in the literature (Rothe and Bernstein 1959) for the average relative velocity can be written in a more compact form, namely,

$$\bar{v}_r = \frac{3}{2} \left(\frac{2kT_g}{\pi m_g} \right)^{\frac{1}{2}} \left[1 + \frac{q^2 + 3}{3q} \tan^{-1} \left(\frac{1}{q} \right) \right], \quad (17)$$

which is valid when

$$q = \left(\frac{m_b T_g}{m_g T_b} \right)^{\frac{1}{2}} > 1, \quad (18)$$

where the subscripts b and g refer to beam atoms and gas atoms respectively of mass m at absolute temperature T.

Hence, in this type of molecular-beam work concerned with a determination of C , one measures the total cross section Q by a procedure to be described in the next section, uses Eq. (17) to yield \bar{v}_r , and then calculates C directly from Eq. (16).

II. Experimental Background

A. Total Cross Section in Terms of Experimentally Obtained Data

As already emphasized, it is the total elastic scattering cross section which was obtained from measurements in the present type of molecular-beam research. The formula for this cross section in terms of measurable quantities, which will be referred to as the Rosin-Rabi formula (since they were among the first molecular-beam investigators to employ it), is derived in many books on the kinetic theory of gases (e.g., Jeans 1925). An outline of the derivation is given here.

Let P_{v_b} equal the probability per unit time that a single beam particle of mass m_b and specific speed v_b collides with the scattering gas atoms in the scattering chamber. Using the familiar Maxwellian speed distribution for gas particles in a box, one obtains

$$\begin{aligned}
 P_{v_b} = & \frac{2m_g}{v_b} \left(\frac{m_g}{2\pi kT_g} \right)^{3/2} \int_0^\infty v_g \exp\left(-\frac{m_g v_g^2}{2kT_g}\right) dv_g \\
 & \times \int_{|v_b - v_g|}^{v_b + v_g} Q(v_r) v_r^2 dv_r . \quad (19)
 \end{aligned}$$

Here n_g is the number density of the scattering gas; m_g , T_g and v_g are the mass, absolute temperature and speed, respectively, of the scattering gas atom; and $Q(v_r)$ is the collision cross section for colliding atoms of relative speed v_r .

Next assume that $Q(v_r)$ is actually independent of v_r (recall from the Schiff-Landau-Lifshitz formula that Q is proportional to $v_r^{-2/5}$). Then $Q(v_r)$ can be removed from the integral sign in Eq. (19). The validity of this approximation is discussed further in Appendix C. Integrating over v_r and then v_g , one obtains

$$P_{v_b} = \frac{2kT_g}{m_g v_b} \frac{n_g Q}{\pi^{3/2}} \psi(x) , \quad (20)$$

where

$$\psi(x) = x \exp(-x^2) + (2x^2 + 1) \int_0^x \exp(-y^2) dy , \quad (21)$$

and

$$x = \left(\frac{m_g v_b^2}{2kT_g} \right)^{1/2} . \quad (22)$$

Define a free path length λ_{v_b} and a probability of collision per unit path length k_{v_b} for the beam atom of speed v_b . Then,

$$\lambda_{v_b} = \frac{1}{k_{v_b}} = \frac{v_b}{P_{v_b}} = \frac{\pi^{\frac{1}{2}} x^2}{n_g Q \psi(x)}. \quad (23)$$

Let $f_b(v_b)$ represent the Maxwellian beam distribution of speeds. Then, by definition of average value,

$$\bar{\lambda}_{v_b} = \int_0^{\infty} f_b(v_b) \lambda_{v_b} dv_b. \quad (24)$$

Substituting the beam speed distribution and λ_{v_b} from Eq. (23) into Eq. (24), one obtains

$$\bar{\lambda}_{v_b} = \frac{2(\pi)^{\frac{1}{2}}}{n_g Q} \left[z^2 \int_0^{\infty} \frac{x^5}{\psi(x)} \exp(-zx^2) dx \right], \quad (25)$$

where $z = m_b T_g / m_g T_b$. The quantity in brackets in Eq. (25) is called $J(z)$ and is tabulated in the literature (Rosenberg 1942) for various values of z .

The chance that a beam atom of speed v_b will pass a distance d through the scattering gas without collision is given by

$$p(v_b) = \exp\left(-\frac{d}{\lambda_{v_b}}\right). \quad (26)$$

The ratio I/I_0 of the beam intensities with and without the scattering gas is then equal to the probability $p(v_b)$ averaged over all beam velocities with the aid of $f_b(v_b)$. Thus,

$$I/I_0 = \overline{p(v_b)} = \overline{\exp(-\frac{d}{\lambda v_b})} . \quad (27)$$

An approximation that is often used next is obtained by taking (see Appendix C)

$$I/I_0 \simeq \exp(-\frac{d}{\bar{\lambda} v_b}) . \quad (28)$$

Hence, with this approximation,

$$\bar{\lambda} v_b = \frac{d}{\ln(I_0/I)} . \quad (29)$$

Eliminating $\bar{\lambda} v_b$ from Eqs. (25) and (29), and using the perfect-gas law, $p_g = n_g k T_g$, one obtains

$$Q = \frac{2(\pi)^{\frac{1}{2}} k T_g}{d} J(z) \frac{\ln(I_0/I)}{p_g} . \quad (30)$$

This is the so-called Rosin-Rabi formula. To calculate Q one needs only the masses and temperatures of the colliding atoms, the effective scattering path length d and the slope of the semi-logarithmic graph of the net beam intensity I versus the scattering gas pressure p_g .

B. Problem of Angular Resolution in Molecular-Beam Scattering Experiments

The principal goal of the present experiments was to determine the effect of the angular resolution of the experimental apparatus upon the elastic scattering partial cross sections. Thus, it is important to understand the meaning of angular resolution and, particularly, the definition which is employed here. In this section the role of resolution in molecular-beam research is discussed and some criticism of the use of the molecular-beam technique for determining intermolecular potential parameters which appears in the literature is also indicated.

1. Definition of Angular Resolution in Terms of Apparatus Parameters. Kusch 50% Criterion

Until fairly recently the definition of angular resolution employed in molecular-beam scattering experiments of the present type was merely the angle $\theta = 2a/l$, where $2a$ was the diameter of the hot wire detector and l was the distance from the center of the scattering region to the detector wire. Thus, θ was the angle subtended by the detector wire at the center of the scattering chamber. This was not, however, a very satisfactory measure of the "ability" to detect scattered particles because of the following reason; particles scattered through an angle greater than θ

could still strike the detector if the azimuthal angle of deflection was such as to scatter them onto the vertical wire which lies in a plane perpendicular to the beam direction.

In the past, literature dealing with total cross section measurements used this poorly defined statement for the definition of angular resolution. Kusch (1964) proposed a criterion which is related to the minimum scattering angle that can be detected. He suggested a reasonable definition of resolution as the minimum scattering angle for which the efficiency of the detection of scattering was 50%. This quantity, $\theta_{50\%}$, has since been adopted by many workers in the field of molecular-beam total scattering cross section research and is more fully discussed in the following paragraphs. It must be emphasized that the Kusch 50% criterion does not depend on the details of the scattering process, but depends only on the geometry of the apparatus.

As was mentioned in the introduction, in the current type of molecular-beam work the beam is formed by a vertical source slit (on front of the oven), further defined by a vertical collimating slit and detected by a vertical hot wire detector. The detector is placed in the center of the beam image. The beam shape at the detector position is determined by (i) the width of the source and collimating slits, (ii) the distance between the source slit and

collimating slit and (iii) the distance between the collimating slit and detector.

As shown in Ramsey (1956, p. 17) the shape of the unscattered beam in the plane of the detector is trapezoidal. The umbra (region of uniform intensity) extends from $x = -d$ to $x = +d$, where x is perpendicular both to the length of the detector and to the direction of the beam. The intensity drops linearly to zero from $x = \pm d$ to $x = \pm c$. Consider now an "equivalent rectangular image", i.e., the intensity of the beam is uniform within the interval $x = \pm b$, where $b = \frac{1}{2}(c + d)$, and is zero elsewhere. Assume the diameter of the detector wire extends from $x = -a$ to $x = +a$, where $a \leq b$.

Assume next that the height of the beam, $2h$, is large compared to the width of the beam, i.e., $h \gg b$. Also assume that the scattering of the beam takes place in a plane which is perpendicular to the beam direction and between the collimating slit and the detector wire. Let l be the distance from this scattering plane to the detector. Actually, of course, the scattering takes place over a finite length which is assumed to be much less than l . Also it is assumed that the slits which enclose the scattering region are sufficiently wide so that they do not change the beam image described above.

Suppose that a certain number of particles scattered through a specific polar angle φ contribute an intensity $I'(\varphi)$, whereas without scattering they contributed a greater intensity I . The efficiency of detection is given by $\eta_0 = I'/I$. A scattering process is not detectable when $\eta_0 = 1$.

When scattering occurs, the intensity that was originally in an element of area $dx dy$ within the beam image is placed on the circumference of a circle of radius $r = l\varphi$ and with its center on the element of area. I' is calculated from the integral of the portion of the circumference of the circles intercepted by the detector wire. The results for a rectangular image vary for different ranges of values of ρ , defined by $\rho = r/b = l\varphi/b$, and appear in the literature (Kusch 1964).

Let $\alpha = a/b = \frac{\text{detector width}}{\text{beam width}}$, so that $\alpha \leq 1$ and assume $h = \infty$. Then if η_0 is set equal to 0.5 (so that the efficiency of detection is 50%), the calculations yield

$$\eta_{50\%} = \rho(\alpha)b/l, \quad (31)$$

where $\rho(\alpha)$ is equal to $(2)^{\frac{1}{2}}$, 1.486, and $\pi/2$ for α equal to 0, 0.5, and 1.0, respectively. Hence, it is seen that the width of the detector has only a very slight role in the determination of this criterion for resolution.

The relation for $\epsilon_{50\%}$ given in Eq. (31) has been obtained using the assumption of a rectangular beam shape instead of the actual trapezoidal beam shape. The effect of the penumbra on the resolution has been shown to be very small in Kusch's paper. The results for a trapezoidal beam and an infinitesimal detector can be written from the results for a rectangular beam and a finite detector by the proper transformation. The effect of the penumbra changes $\epsilon_{50\%}$ the same way as changing the width of the detector in the equivalent rectangular beam case, and this change has already been quoted as small.

The assumption of $h \gg b$ (i.e., the beam height is much greater than its width) was also made in deriving Eq. (31). Without this assumption a significant change could occur in the efficiency of detection. However, this assumption is certainly justified in the present experiments, since $h/b \geq 20$ for all runs.

Thus, for all practical purposes, $\epsilon_{50\%}$ is nearly proportional to the beam width $2b$. This fact enables one to easily change the effective angular resolution of the apparatus by simply tilting the source slit to bring about misalignment of the various elements that define the beam. This misalignment yields a greater value for the beam width and, hence, changes the angular resolution of the apparatus. This was the method employed in the present experiments to

vary the resolution in order to measure the partial cross sections at various values of resolution.

It must be remembered that the above criterion for resolution is based on the use of vertical elements for defining the beam. It should be pointed out that the apparatus of Estermann, Foner and Stern (1947) employed horizontal elements for defining and detecting the beam in connection with a gravity deflection method for an attempt to determine the velocity dependence of the total cross section. They used the measured values of the gravity deflected beam width and l to calculate the stated resolution of approximately one minute of arc quoted in Table I. However, it is not clear to the present investigator how an application of the Kusch criterion can be made to their experimental set-up, since different velocity atoms are gravity deflected by different amounts and, hence, the beam profile they encountered has a different significance than that of the equivalent rectangular beam used in the derivation of Eq. (31). Nevertheless, their stated resolution of one minute of arc is quoted in the literature (Helbing and Pauly 1964) and reference to that value is continued here.

Other attempts to indicate the angular resolution required to give meaningful results in molecular-beam scattering experiments have been developed. A discussion of these, along with a previous resolution study by other investigators, is given next.

2. Massey-Burhop Criterion for Necessary Angular Resolution

For the rigid sphere model of intermolecular interactions, Massey and Mohr (1933) have developed a quantum mechanical angular distribution calculation for the scattering intensity as a function of the scattering angle. Classically, this angular distribution is merely a straight line graph whose intensity $I(\theta)$ is equal to $\frac{1}{4} r_0^2$ for all values of θ from 0 to π , where r_0 is the sum of the atomic radii. However, for the quantum calculation of $I(\theta)$, the Massey-Mohr result yields an approximation which can be described as (i) a linear variation in $I(\theta)$ at small angles between the value $\frac{1}{4} k^2 r_0^2$ at $\theta = 0$ and the classical value which is taken to fail at the angle $\theta' = \pi/k r_0$ and (ii) $I(\theta) = \frac{1}{4} r_0^2$ for $\theta > \pi/k r_0$, where k has its usual significance of being the wave number. In other words, the quantum calculation favors an increase in small angle scattering which leads to the familiar result that the quantum mechanical total cross section is twice the classical value for rigid spheres whenever $k r_0$ is large.

Massey and Burhop (1952) suggested a possible definition for necessary angular resolution which is given by

$$\beta = \frac{\int_{\theta_{mc}}^{\pi} I(\theta) \sin \theta \, d\theta}{\int_0^{\pi} I(\theta) \sin \theta \, d\theta}, \quad (32)$$

where β can be made as near unity as desired by making θ_{mc} (subscript c refers to center of mass system) small enough. If θ_{mL} is the minimum angle of deviation in degrees in the laboratory system (recall that $\cot \theta_L = \cot \theta_c + (m_b/m_g) \csc \theta_c$ for elastic collisions), and β is set equal to 0.9 so that the cross section determined is within 10% of the true value, it is found (using the Massey-Mohr rigid sphere angular distribution for $I(\theta)$) that

$$\theta_{mL} = 277/r_o(MT)^{\frac{1}{2}}, \quad (33)$$

where M is the atomic mass of the incident particle, T the equivalent temperature ($^{\circ}\text{K}$) of the incident particles and r_o is measured in \AA . For the case of Cs-He scattering, $\theta_{mL} = 0.27$ degrees for $T = 300^{\circ}\text{K}$, or $\theta_{mL} = 0.15$ degrees for $T = 1000^{\circ}\text{K}$ (Massey and Burhop 1952, p. 391). With this definition for the necessary angular resolution, all the investigators in Table I should have been well within the 10% limit. It might be commented that one obvious flaw in this criterion for necessary resolution (at least for the case of alkali beam-inert gas scattering) is the assumption of rigid sphere interactions.

3. Pauly Criterion for Necessary Resolution.

Helbing and Pauly's Resolution Study

Helbing and Pauly (1964) used the method of crossed beams to make a resolution study on the total cross section for various scattering gases colliding with primary beams of Cs and K. They measured the intensity of the scattered primary beam at various angles of deflection θ_L in the lab system. By integration of the intensity versus θ_L curve from some specific value of $\theta_L = \theta_{mL}$ to $\theta_L = \pi$, they obtained the percentage of the cross section corresponding to this value of θ_{mL} . In other words all scattering through an angle greater than θ_{mL} , which they take as the criterion for minimum angular resolution in the lab system, contributes to the partial cross section corresponding to θ_{mL} . They quoted their results by plotting the percentage of the total cross section so determined against the angle of resolution θ_{mL} in minutes of arc. They emphasized the case of Cs-He scattering also. Their results show that the difference between the values listed in Table I cannot be explained by the difference in resolution employed by the different researchers. Incidentally, Helbing and Pauly's graph actually shows about 13% drop for the Cs-He total cross section as the "resolution" is varied between one and five minutes of arc instead of 3% as quoted in the text of their article.

As a byproduct of their work it was possible to set a limit on the amount ΔQ by which values of the partial cross section (for a given angle of minimum resolution θ_m) are smaller than the true values, Q_0 , corresponding to $\theta_m = 0$. Pauly (1959) has shown, for the van der Waals attraction, that

$$\Delta Q/Q_0 = 0.02(\theta_m/\theta')^2, \quad (34)$$

where θ' is the angle at which classical mechanics breaks down in the description of scattering (Pauly used $\theta' = 2/kr_0$ whereas Massey and Burhop (1952) used $\theta' = \pi/kr_0$). However, the angles θ_m and θ' in Eq. (34) are center of mass angles. Consequently, this expression is not applicable to the present case of heavy beam atoms and relatively lighter scattering gas atoms. The Pauly criterion, Eq. (34), could only be expected to yield meaningful results for velocity selected light beam atoms and heavy scattering gas atoms considered at rest, in which case the angles of scattering in the center of mass system and lab system are not materially different.

4. Literature Criticism of Molecular-Beam Method

Dalgarno and Kingston (1959) have made a study of the attractive intermolecular potential parameter (van der Waals constant) by using theoretical and experimental values

of the electric dipole oscillator strengths which are used to calculate the coefficients of the leading terms in the series representations of the long-range interactions between pairs of atoms. They conclude that the cross sections derived from molecular-beam measurements are unreliable, and suggest that the normal van der Waals interaction does not suffice to explain the observations at very low scattering angles. They deduce, if the lack of agreement shown in Table I is accepted, that an interaction must be occurring other than the normal van der Waals forces. A tentative explanation has been proposed by Dalgarno and McCarroll (1957). They showed that the inclusion of spin angular momentum in the discussion of intermolecular forces introduced a coupling term which varies as the inverse square of the distance of separation. They suggested that this may resolve the anomaly between the measurements shown in Table I.

At the present time, however, no satisfactory explanation for the discrepancies listed in Table I has been offered by theoretical or experimental work appearing in the literature.

C. Summary of Goals of Present Experiments

In summary, the measured value of the "total" (actually partial) scattering cross section depends on the resolution of the apparatus, that is, the minimum scattering

angle that may be detected. If the molecular-beam method for measuring cross sections (and subsequent inference of potential parameters) is to be considered a valid technique, one must attain sufficient angular resolution so that no further significant increase in the cross section results when the resolution is improved.

The disagreement in absolute cross section determinations for Cs-He of the investigators given in Table I was thought possibly to be due to the resolution differences. This was one of the factors that prompted the present set of experiments. However, since absolute cross sections are very difficult to obtain (due to numerous systematic errors in theory and/or experiment), the explanation might not lie in the resolution problem (Helbing and Pauly's result seems to substantiate this).

The primary goal of the present experiments was to make a study of the measured values of relative "total" cross sections as a function of the resolution $\approx 50\%$ for a cesium beam scattered by inert gases. Hence, absolute determinations of Q (and, thus, of C) were actually of secondary interest. The item of primary interest was to settle the question of whether the apparent variation in the measured cross section with resolution was real. Also, the question of necessary resolution to determine meaningful results from molecular-beam scattering experiments was of

interest. In addition, it must be remembered that the measurements listed in Table I were all performed on different molecular-beam machines; thus, it appeared to be a good idea to investigate this apparent anomaly using one machine.

In general, it must be admitted that the problem of resolution, along with the Rosin-Rabi formula and other theoretical and experimental aspects must be more thoroughly investigated before the results of this type of research are to be accepted without caution.

EXPERIMENTAL SET-UP AND PROCEDURE

The present chapter contains brief descriptions of the apparatus and the procedure used in the performance of the experiments. Typical raw data curves, from which the cross sections were calculated, are also presented. The brief, rather qualitative description of the apparatus is presented in this chapter merely to clarify the discussion of experimental procedure. A more complete discussion of the apparatus is presented in Appendix A.

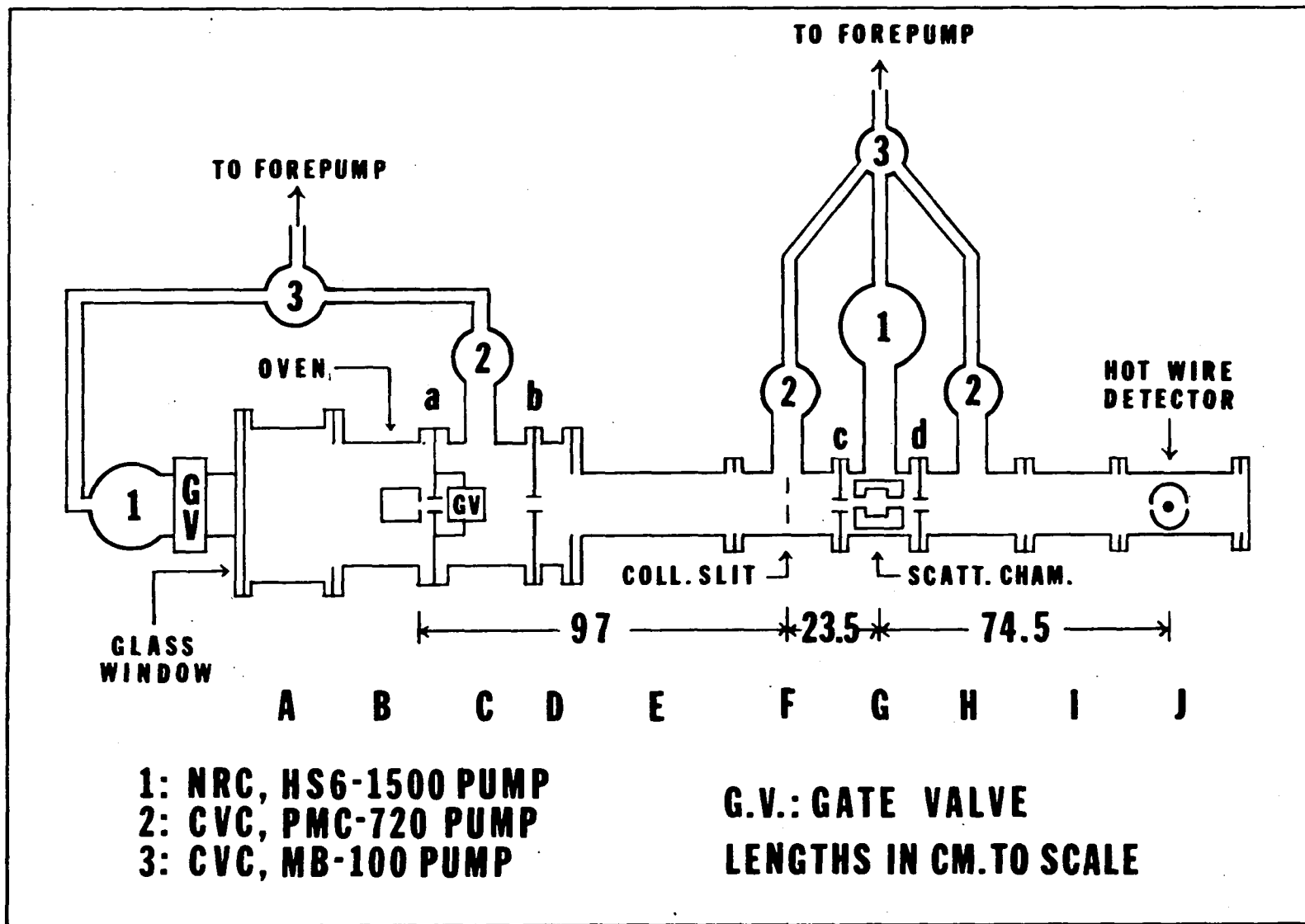
I. Apparatus

The arrangement of the main features of the molecular-beam apparatus is shown in Figure 1. The description of this machine can be presented in three sections: (A) the vacuum system, (B) the components necessary for obtaining, scattering and detecting a beam and (C) the auxiliary equipment used for measuring the scattering gas pressure and the beam intensity.

A. Vacuum System

The vacuum system was designed to provide a high vacuum (from 2 to 8×10^{-8} mm Hg) over the major portion of the long (two meters) beam path in order to reduce spurious

Figure 1. Diagram of Vacuum System
Showing Essential Features.



scattering of the beam by the background gas to a negligible amount. The chambers D-J of Figure 1 were made of stainless steel, coupled together using copper gasket seals and were bakeable to 500°C. This feature, plus the freon baffles (-35°C) and liquid nitrogen cold traps above the three large oil diffusion pumps, allowed the attainment of the necessary vacuum.

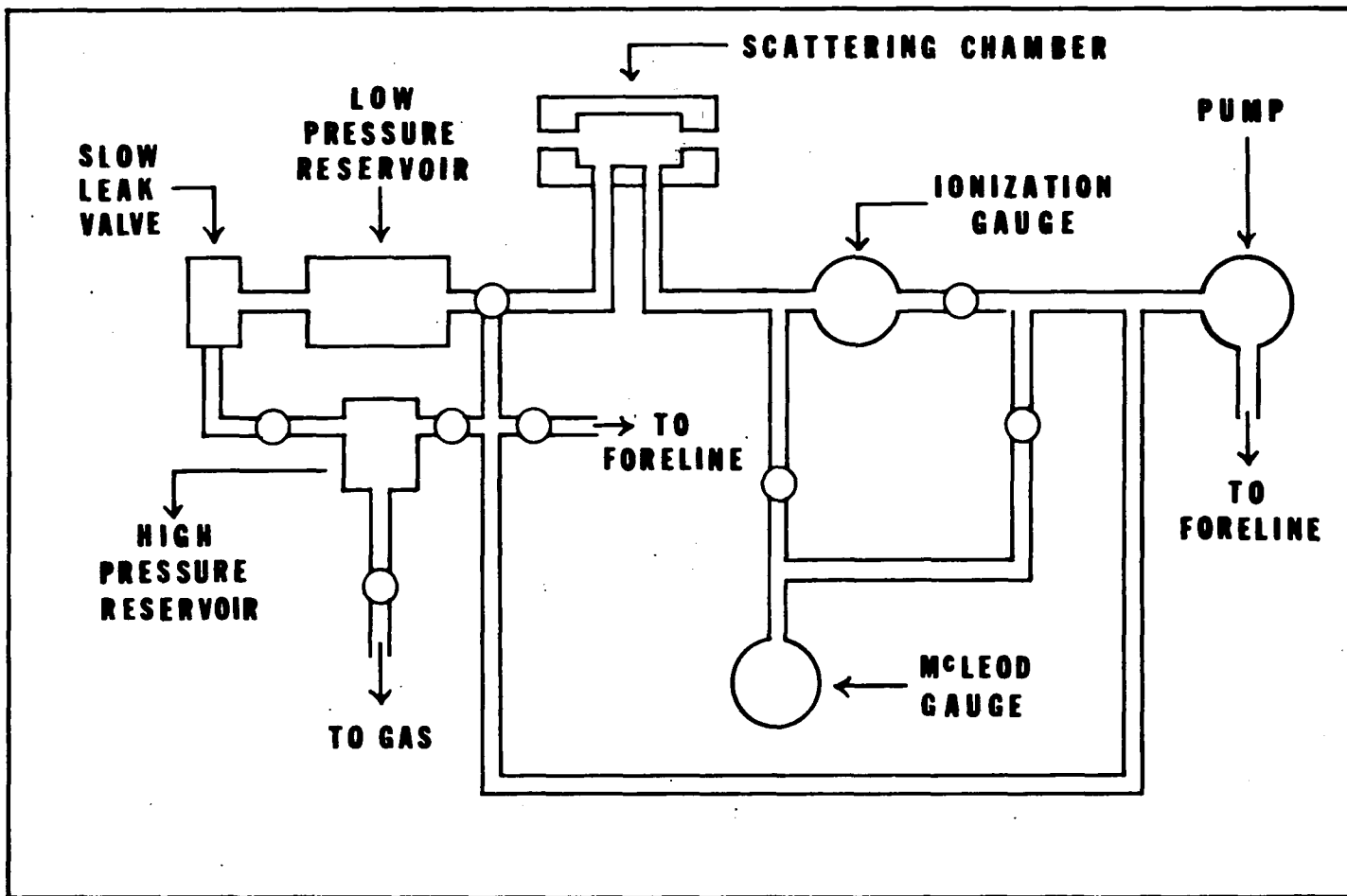
B. Components for Obtaining, Scattering and Detecting a Beam

Cesium beam atoms, vaporized in the heated oven shown in chamber B of Figure 1, effused through a vertical slit in the front of the oven, passed through the vertical collimator slit in chamber F, passed through the scattering chamber in chamber G and struck the vertical surface ionization detector wire in chamber J. The oven and collimator slits defined the beam. The neutral cesium atoms which struck the detector wire came off the wire as positive ions (with almost 100% efficiency). The beam intensity was determined by measuring this positive ion current.

C. Auxiliary Equipment

The gas handling system, used for admitting scattering gas into the scattering chamber, is shown in Figure 2. The pressure of the gas in the scattering chamber was measured using the ionization gauge (Veeco RG-75). The

Figure 2. Schematic of Gas Handling System.



ionization gauge was then calibrated using the McLeod gauge (Dresser Vacuum Corp., model DMG 103). The work with He and Ne scattering gases was done on the 10^{-6} mm Hg scale of the ion gauge control panel and this scale was measured to be linear within 1.2% over its entire range. The work with Ar, Kr and Xe was done on the 10^{-5} mm Hg scale and this scale was measured to be linear within 0.6% over its entire range.

An E-H Research Laboratories, Inc. Electrometer (model number 201 C) was used to measure the positive ion current put out by the hot wire detector. A Varian strip-chart recorder (model number G-11A) recorded the electrometer current readings. There was no way to calibrate the electrometer-recorder combination on the scales that were used for measurements of beam intensity (3×10^{-12} and 10×10^{-12} ampere scales) due to the lack of a method for inserting such a small input current without experiencing noise difficulties. However, calibration was done on the higher current scales. Calibration on the 3×10^{-11} ampere scale showed that the detection system was linear within 3% over the entire scale. Calibration on the 10×10^{-11} ampere scale showed approximately 1% non-linearity and calibration on the 3×10^{-10} ampere scale showed only a small fraction of 1% non-linearity. Undoubtedly, the deviations from linearity were primarily due to the noise problem. Since the only difference between these higher current scales and

the scales used in the experiments was the value of the electrometer input resistor, it was assumed that the electrometer-recorder combination was at least as linear on the scales actually used as the scales on which calibration was possible.

Figure 3 is a schematic diagram depicting the essential features of the beam components and shows the apparatus necessary for the measurements that were taken in the experiments.

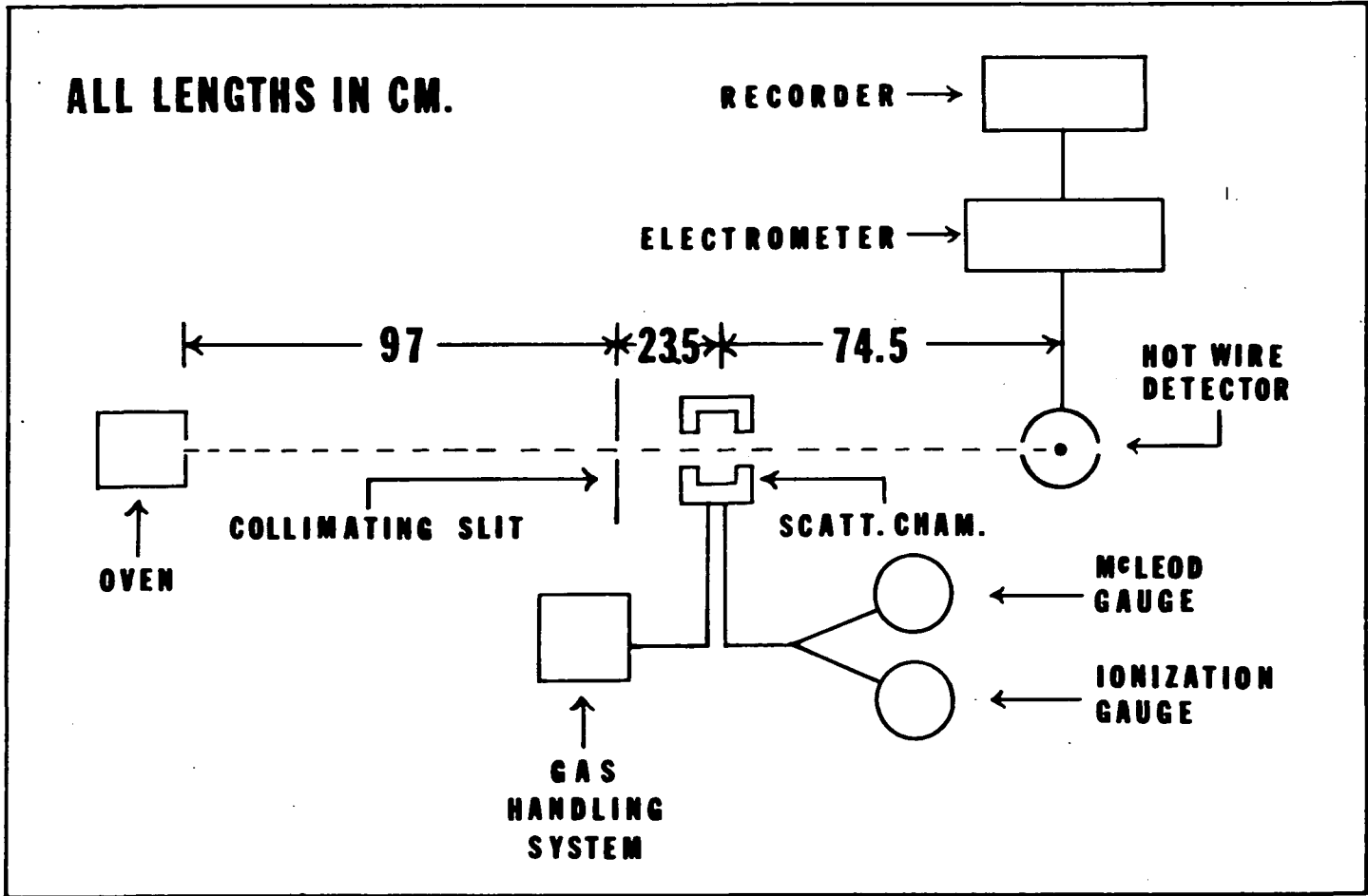
II. Experimental Procedure

A. Preparation for Experiments

The hot wire detector, scattering chamber, collimating slit and the buffer slits were optically aligned with the aid of a telescope before the end flange on chamber J of Figure 1 was used to seal the vacuum system. Final alignment of the slits and detector was accomplished by the use of the beam itself.

A capsule, containing two grams of cesium, was warmed to liquify the contents. The capsule was then broken in a dry nitrogen atmosphere (using a glove bag) and the contents poured into the oven well. The well was sealed by a copper gasket and a threaded plug screwed into the oven. The oven was placed in the apparatus by removal of the glass window shown in Figure 1, pumped down by opening the gate

Figure 3. Schematic of Apparatus.



valves shown in Figure 1 after replacing the window and its contents were outgassed by slowly heating them for approximately two days, raising the oven temperature every twelve hours until the final operating temperature was reached (approximately 420°K).

The gas handling system was evacuated and the inert scattering gas was connected to the high pressure reservoir as shown in Figure 2. With this preliminary work completed, the machine was ready for operation.

B. Raw Data Determinations

1. Beam Profiles

The oven was translated and rotated (by means of sliding O-ring vacuum seals) as necessary to "peak in" the beam. The collimating slit, scattering chamber and detector were also adjusted (by stainless steel bellows arrangements) to aid in finding and "peaking in" the beam.

The oven was translated far to one side and a beam profile was run by translating the oven in small increments (the oven positioning was reproducible to 0.1 mil) through the position corresponding to maximum intensity and far to the other side. According to the formula derived geometrically in Ramsey (1956, p. 17), it should have been possible to obtain a beam profile whose width at half maximum intensity was 2.0 mils using a one mil oven slit and a one

mil collimating slit. It was possible to obtain many beams whose half-widths were approximately 2.2 mils. This discrepancy was caused by slight misalignment of the slits and detector wire. Using the one mil oven slit and the one mil collimating slit, it was possible to obtain half-widths from approximately 2.2 to 12 mils. The larger half-width beams were achieved by merely tilting the oven (to bring about misalignment of the oven slit with the collimating slit and detector wire) and running a new beam profile. The limit to the largest half-width obtainable was set by the decrease in beam intensity caused by the misalignment. Using an eight mil oven slit and the one mil collimating slit, it was possible to obtain half-widths from approximately 8.5 mils to 25 mils. Thus, the two different oven slit widths were sufficient to give a large overlap in the values of beam half-widths used and, as was seen earlier, this gives a good overlap in the values of $\approx 50\%$ encountered with the two different oven slit widths.

Figure 4 represents a typical beam profile taken with a one mil oven slit corresponding to fairly good alignment. The calculation of the beam half-width corresponding to this fairly symmetric beam was obtained by merely measuring the width at half maximum intensity. Figure 5 represents a typical beam profile taken with an eight mil oven slit corresponding to poor alignment (i.e., a tilted

Figure 4. Typical Beam Profile for One
Mil Oven Slit Width.

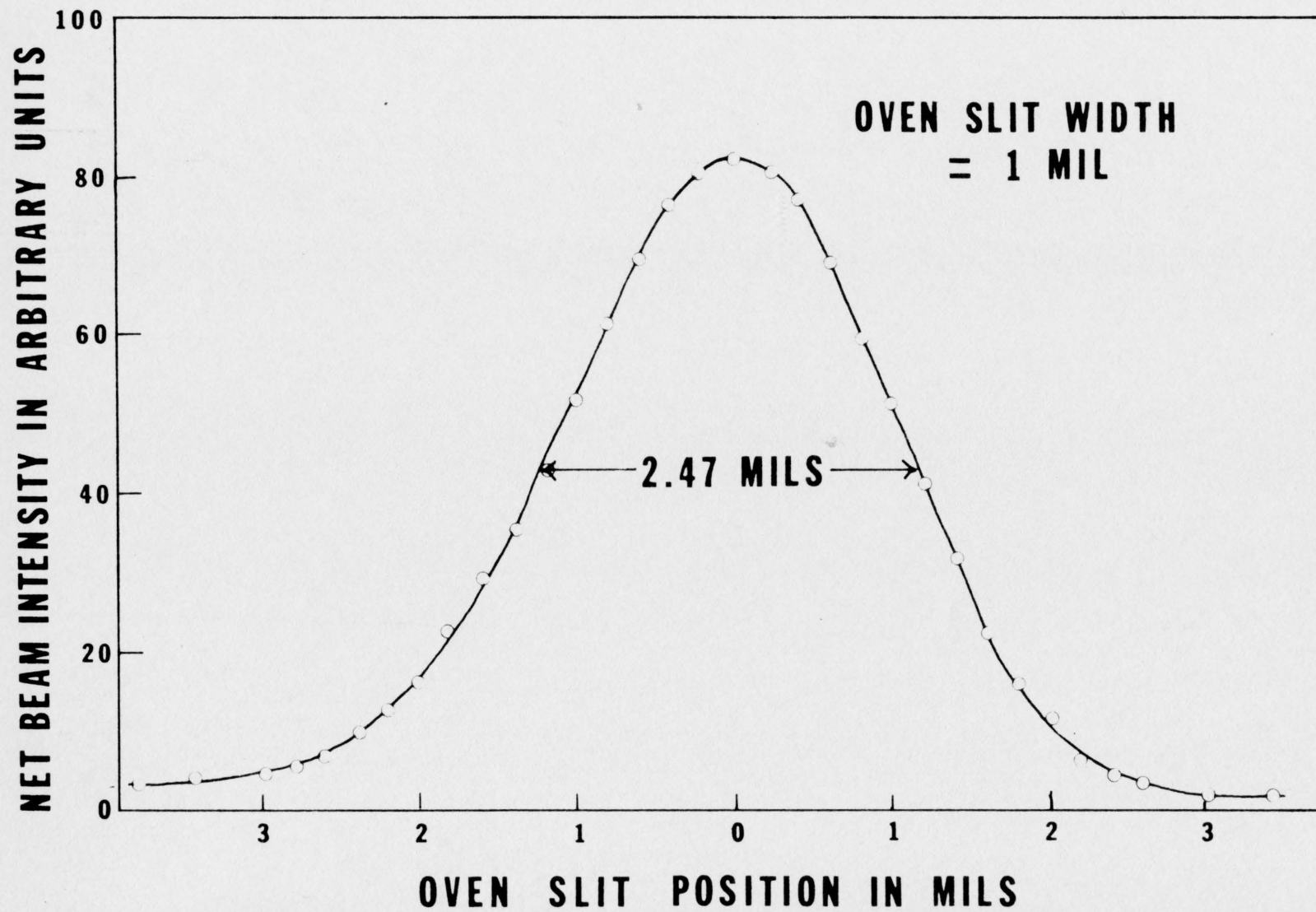
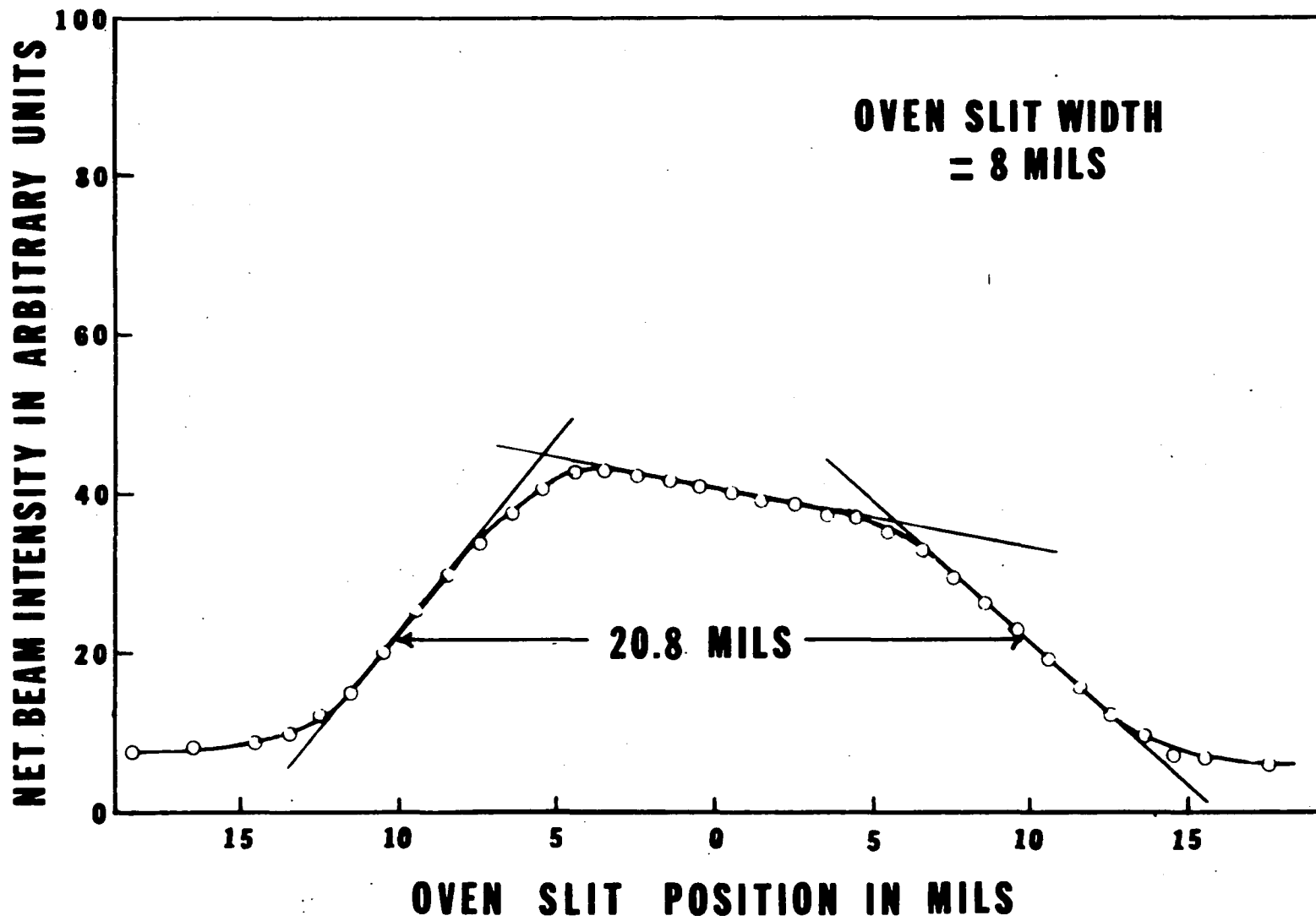


Figure 5. Typical Beam Profile for Eight
Mil Oven Slit Width.

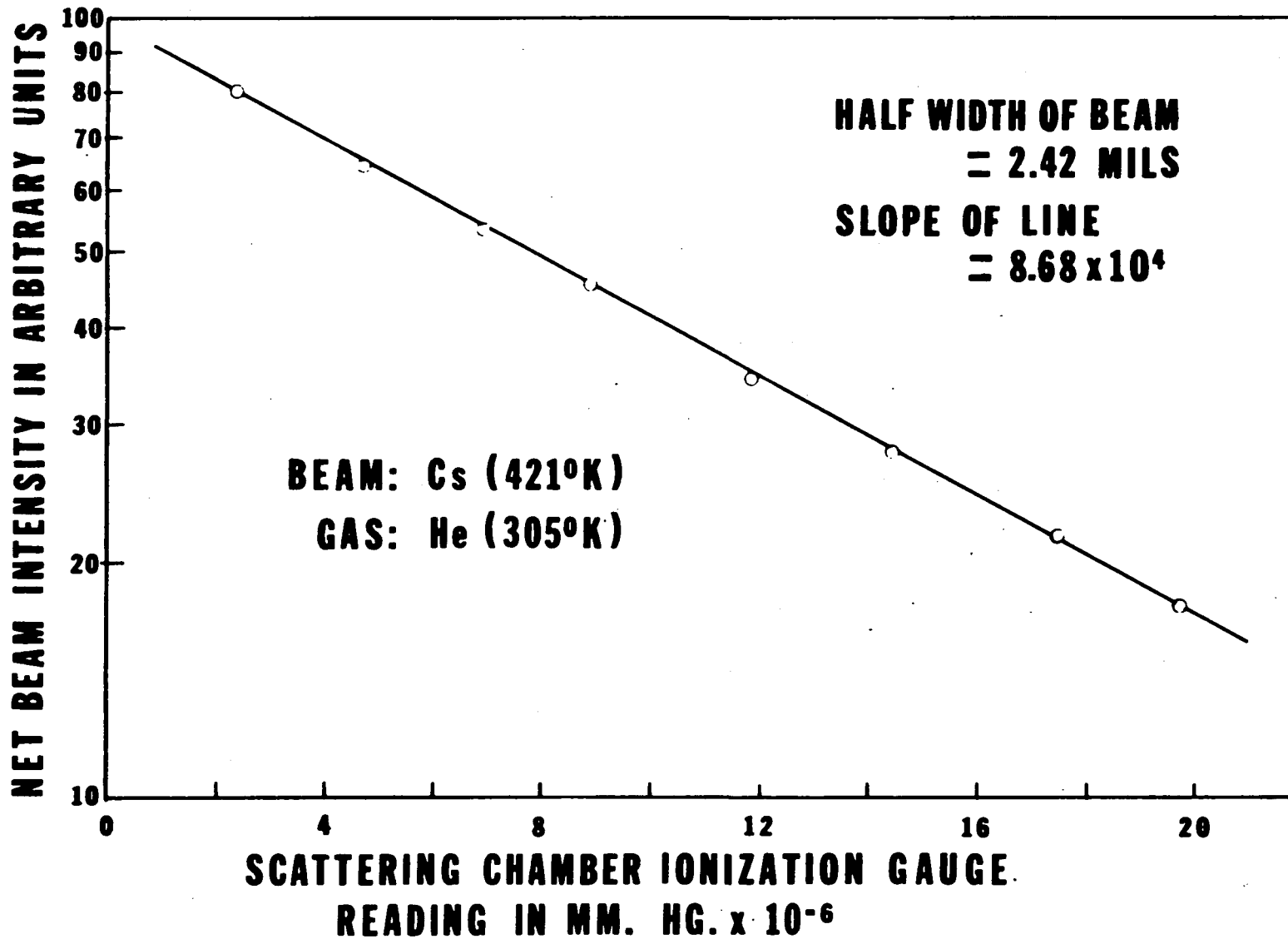


oven). The calculation of the half-width corresponding to this asymmetric beam required a different technique. The average maximum intensity was obtained by averaging the values of the intersection points of the line drawn across the "top" of the beam with the lines drawn along the "sides" of the beam; the beam half-width was then taken as the width at one-half of this average maximum intensity. This was a legitimate procedure, since it was just another method of obtaining the equivalent rectangular beam used in Kusch's 50% criterion for resolution.

2. Attenuation Runs

During an actual run, the beam was attenuated at approximately eight different pressures of scattering gas in the scattering chamber and the intensity at each pressure was plotted vs. pressure on semi-log paper. The beam intensity was attenuated by adjusting the slow leak valve (Figure 2) and the beam was allowed to pass through the scattering chamber approximately six minutes before the final equilibrium beam intensity and gas pressure were read. Figure 6 shows a graph of typical primary data. The background intensity which was subtracted was taken as the background value just prior to the beginning of a run. The gate valve in front of the oven (Figure 1) served as a beam stop. After waiting several minutes for the background to drop,

Figure 6. Typical Primary Data.



the gate valve was lifted and another run was started. The slope of the line in Figure 6 was the desired quantity (i.e., $1/p_g \ln(I_0/I)$ in the Rosin-Rabi equation).

C. Cross Section Determinations

In order to determine the cross section by means of the Rosin-Rabi equation, the following steps were also taken. A thermometer, capable of being read within $\pm 0.2^\circ\text{C}$ and in disagreement less than this amount by comparison with an A.S.T.M. standardized thermometer at room temperature, was placed directly under the chamber containing the scattering box at room temperature in order to measure T_g . The emf of the oven thermocouple as measured by a Minneapolis-Honeywell potentiometer (model number 2703), with a manufacturers stated accuracy of 0.05 mv ($= 1.25^\circ\text{C}$), was used to determine the beam temperature T_b . The slopes of approximately four distinct runs were averaged to give the best value of $1/p_g \ln(I_0/I)$ at each value of $\phi_{50\%}$. From all runs at a particular $\phi_{50\%}$ the average value of $T_g J(z)$ was used also. The effective scattering length, d , was calculated by an application of the formula found in the literature (Rothe et al. 1962). This approximation is discussed further in Appendix C. After determination of these quantities, the calculation of Q was made from the Rosin-Rabi equation.

The above procedure was sufficient to make the resolution study on the partial cross sections, which was the primary goal of these experiments. To obtain absolute cross sections, however, the McLeod gauge had to be employed to calibrate the scattering chamber ionization gauge for each gas. A discussion of this process is given in Appendix B.

RESULTS AND CONCLUSIONS

The discussion of the results of the current experiments is presented in two parts. First, a discussion of the variation of Q with $\phi_{50\%}$ is considered. Then a discussion of the absolute values of Q and C as determined by these experiments is presented. Some comments on the various possible errors encountered are also given in this chapter. Finally, a brief discussion of the general conclusions deduced from the present work is given at the end of this chapter.

I. Variation of Q with $\phi_{50\%}$

A. Graphs of Present Results

In Figures 7-11 the partial total cross section was plotted as a function of the resolution for each of the five scattering gases used. In this section of this chapter, consider the Q axes of Figures 7-11 as plotted in arbitrary units. The use of an absolute scale for the Q axes is discussed later. The curves for Cs-He, Cs-Ne and Cs-A were extrapolated (shown by dotted lines) to zero resolution in order to yield the value of Q corresponding to 100% of the true total cross section. The curves for Cs-Kr and Cs-Xe

Figure 7. Partial Cross Section vs. Angular
Resolution for Cs-He.

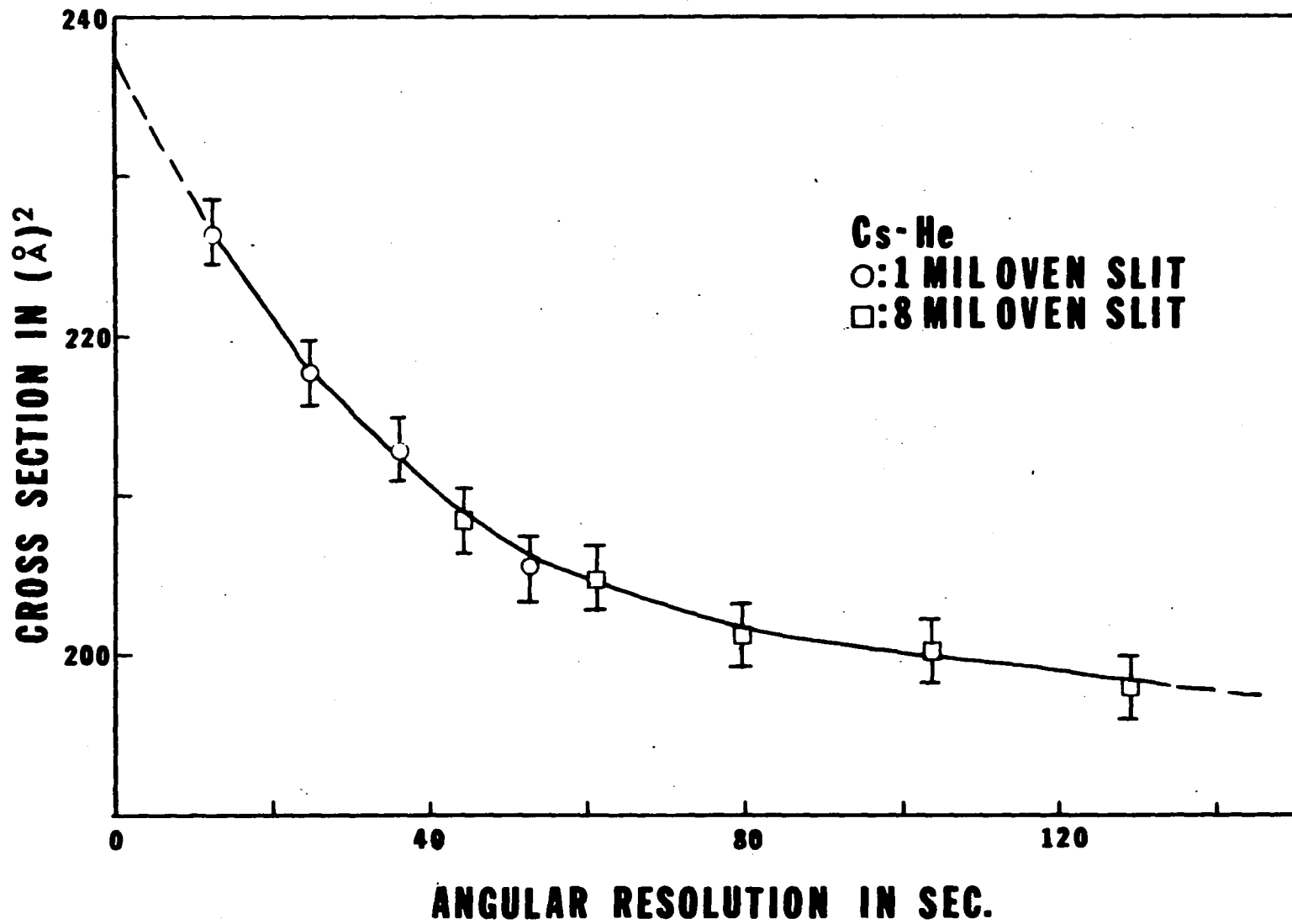


Figure 8. Partial Cross Section vs. Angular
Resolution for Cs-Ne.

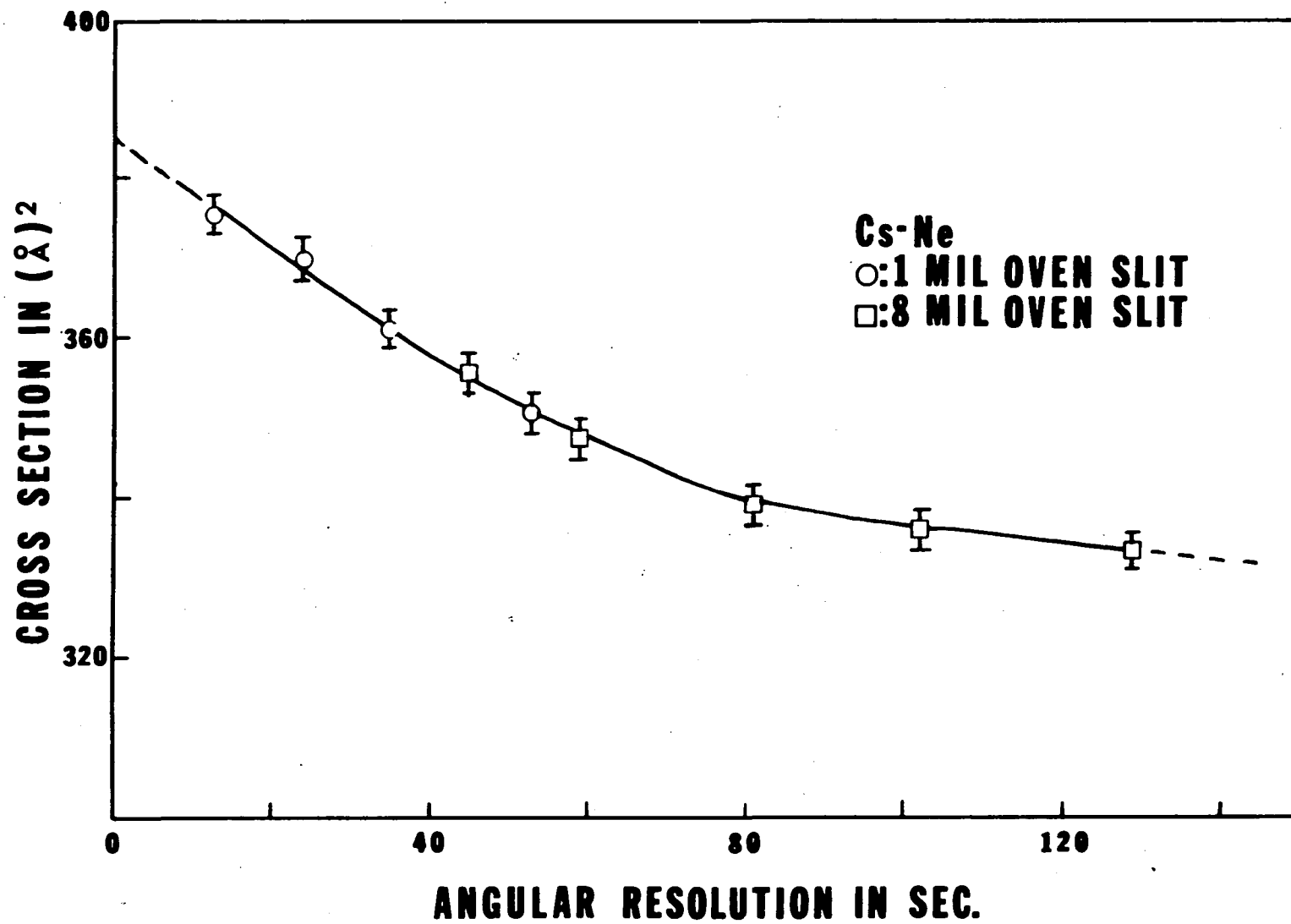


Figure 9. Partial Cross Section vs. Angular
Resolution for Cs-A.

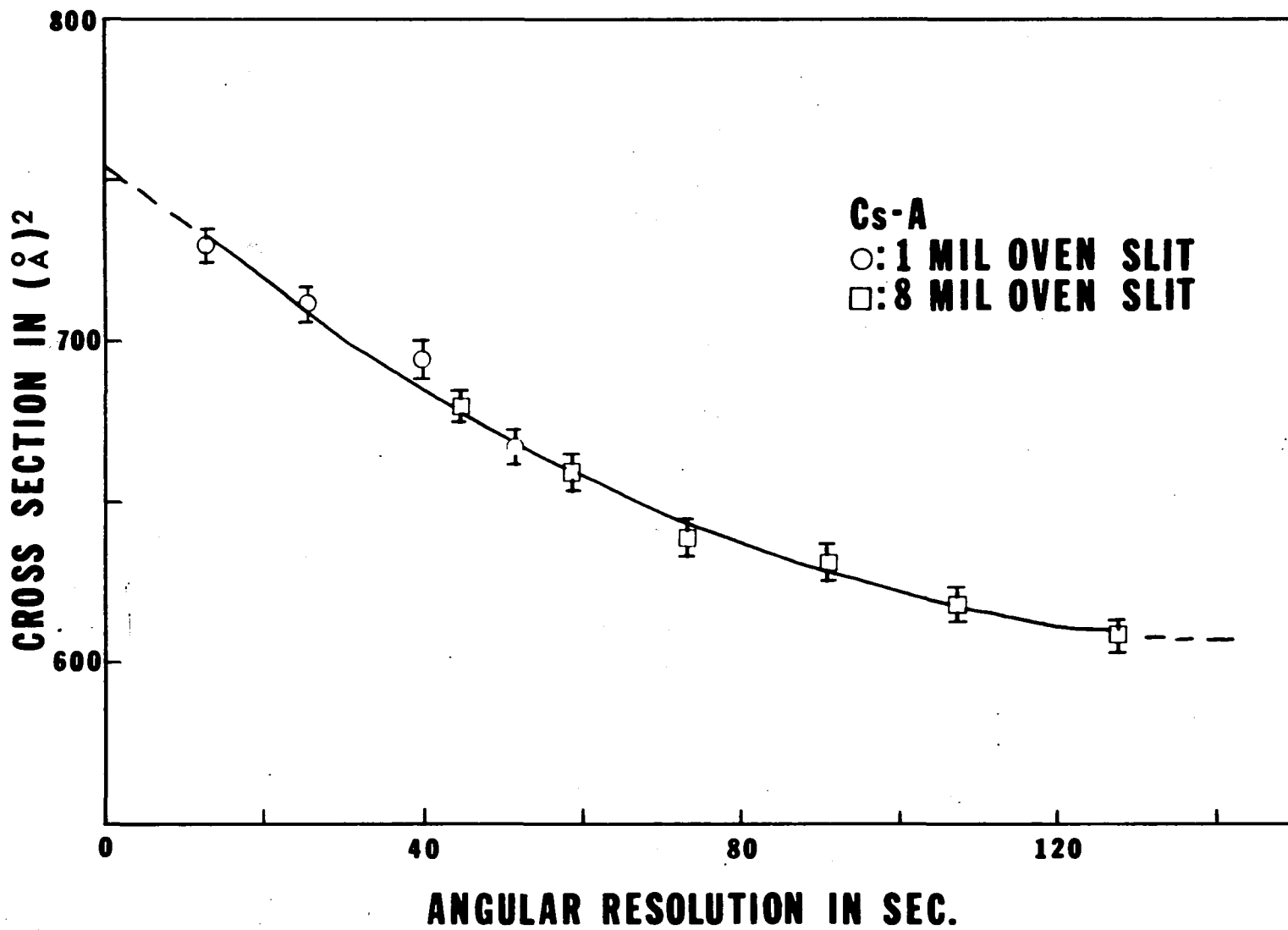


Figure 10. Partial Cross Section vs. Angular
Resolution for Cs-Kr.

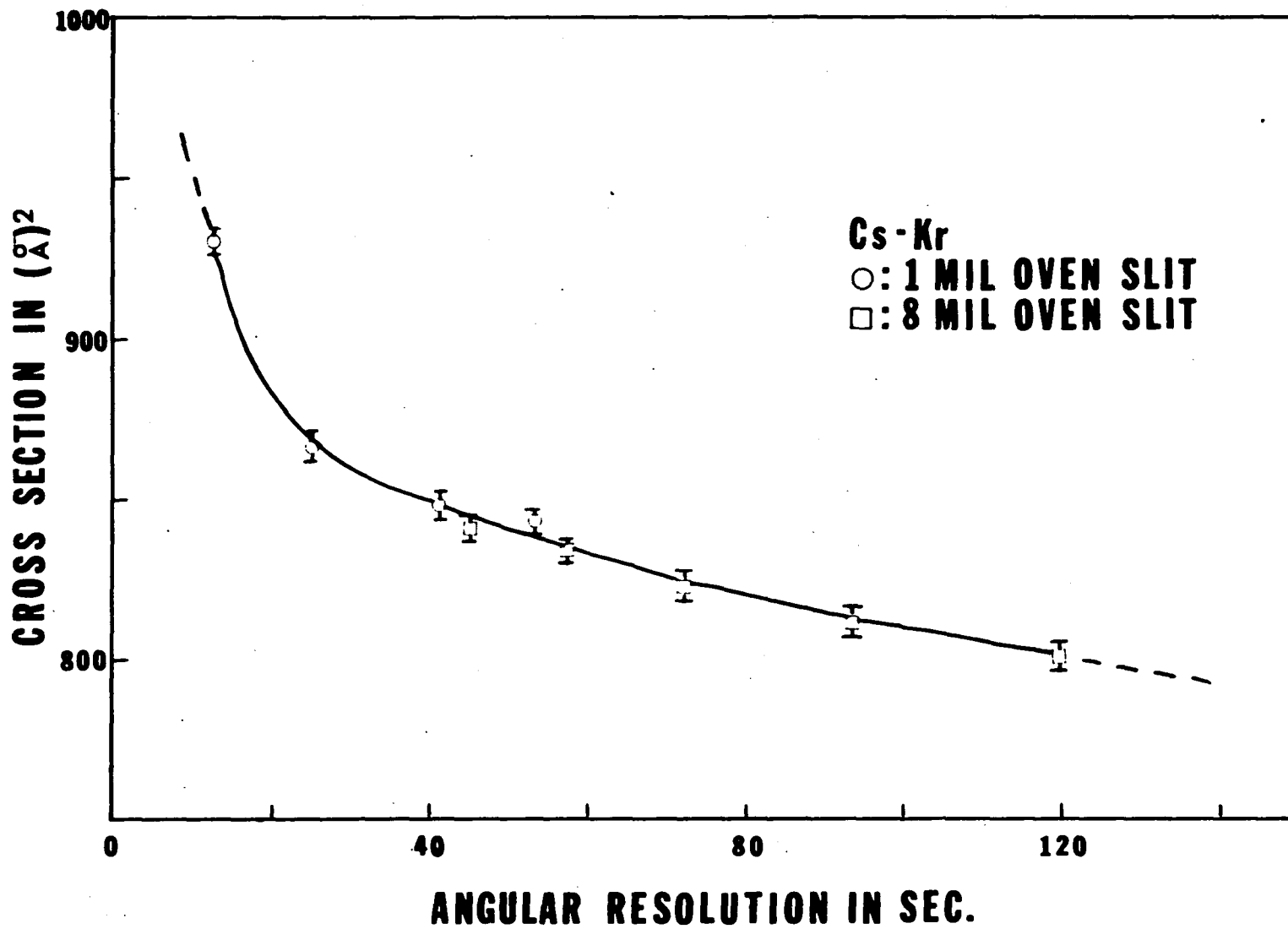
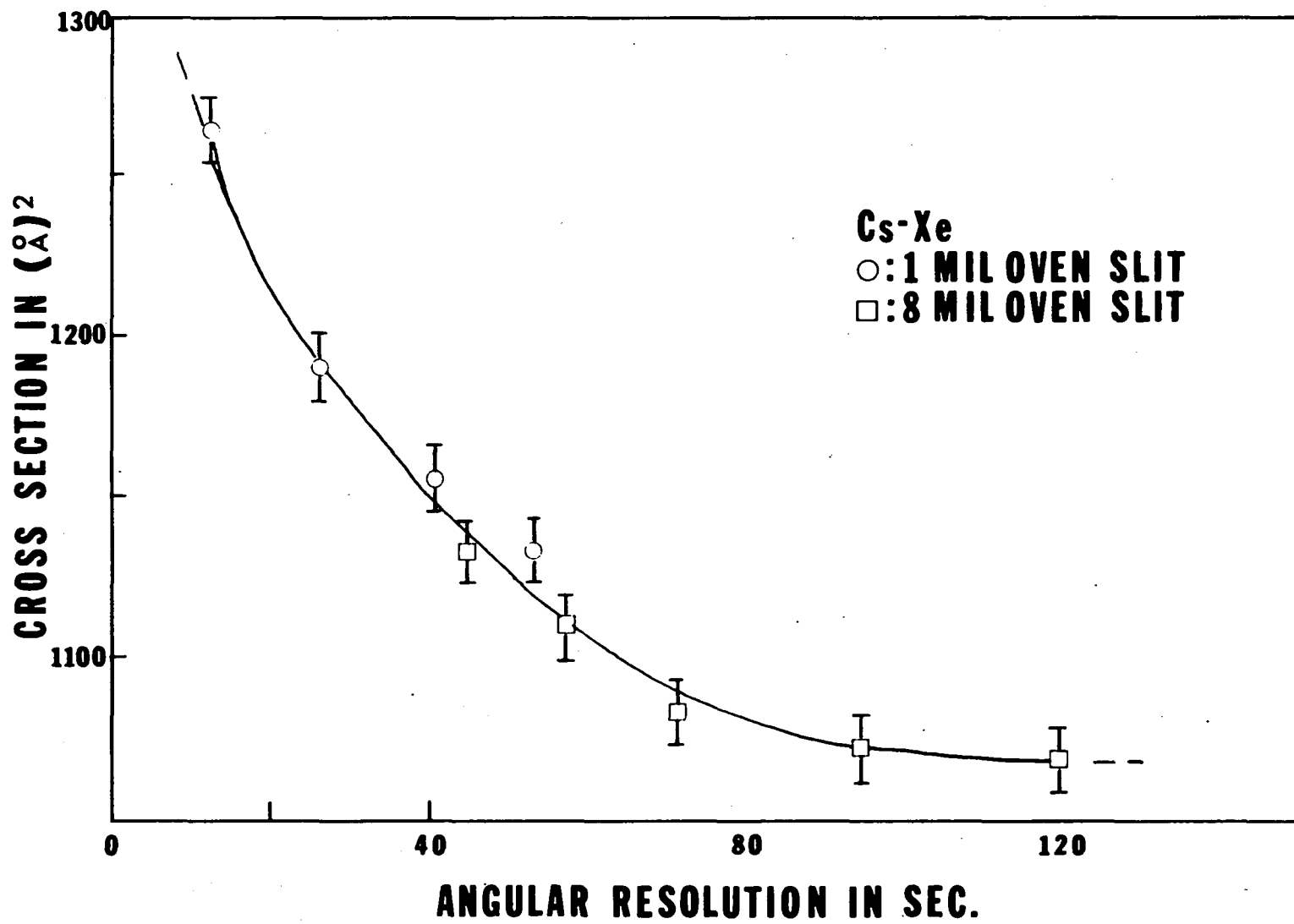


Figure 11. Partial Cross Section vs. Angular
Resolution for Cs-Xe.



were not extrapolated. The steep slopes near zero resolution in these two cases made extrapolation difficult and quite arbitrary.

In order to give an estimate of the reproducibility that can be expected, an error analysis was made and the results are shown by the standard error flags on the data points in Figures 7-11. This standard error (standard deviation of the mean value) was calculated by use of the method of inefficient statistics, since the number of distinct runs at each value of $\phi_{50\%}$ constituted a rather small sample. As described in Evans (1955, p. 904), the standard error in such cases is given approximately by

$$\text{standard error} \simeq \frac{\text{range}}{n}, \quad (35)$$

where n is the number of independent trials (i.e., number of runs at one value of $\phi_{50\%}$). The flags shown in each particular figure were, however, calculated for only one point represented on each graph. The point was taken as the one which corresponded to the largest range encountered; thus, it is felt that the standard error flags shown are very liberal. This type of statistical fluctuation has the effect of only being able to change the shapes of the curves. The types of errors which can raise or lower uniformly the entire curves of the reported cross sections are discussed later.

A brief discussion of the present results and the results of Helbing and Pauly's resolution study is presented next.

B. Comparison with Helbing and Pauly's Work

For the three cases in which extrapolation to zero resolution was felt sufficiently justified, it was possible to calculate the percentage of the true total cross section at any value of resolution. Figure 12 depicts graphically this information for Cs-He, Cs-Ne and Cs-A.

Helbing and Pauly (1964) reported the results of their resolution study in the same manner as that shown in Figure 12. Thus, a comparison of the present results with their results for Cs-He and Cs-A (the only two cases common to both the present experiments and Helbing and Pauly's work) is possible. But, since their graph is not spread out in the range of resolution in which the present work was done, the comparison is not entirely justifiable. Also, their method was completely different from the present experiments, since they used crossed beams and made a resolution study by a piecewise integration of the observed small angle scattering. At one minute and two minutes of resolution, the present values for $Q_{\text{Cs-He}}$ and $Q_{\text{Cs-A}}$ have dropped off faster than their corresponding drops. Table II shows the comparison.

Figure 12. Percentage of True Cross Section as
Function of Resolution for Cs-He,
Cs-Ne, Cs-A.

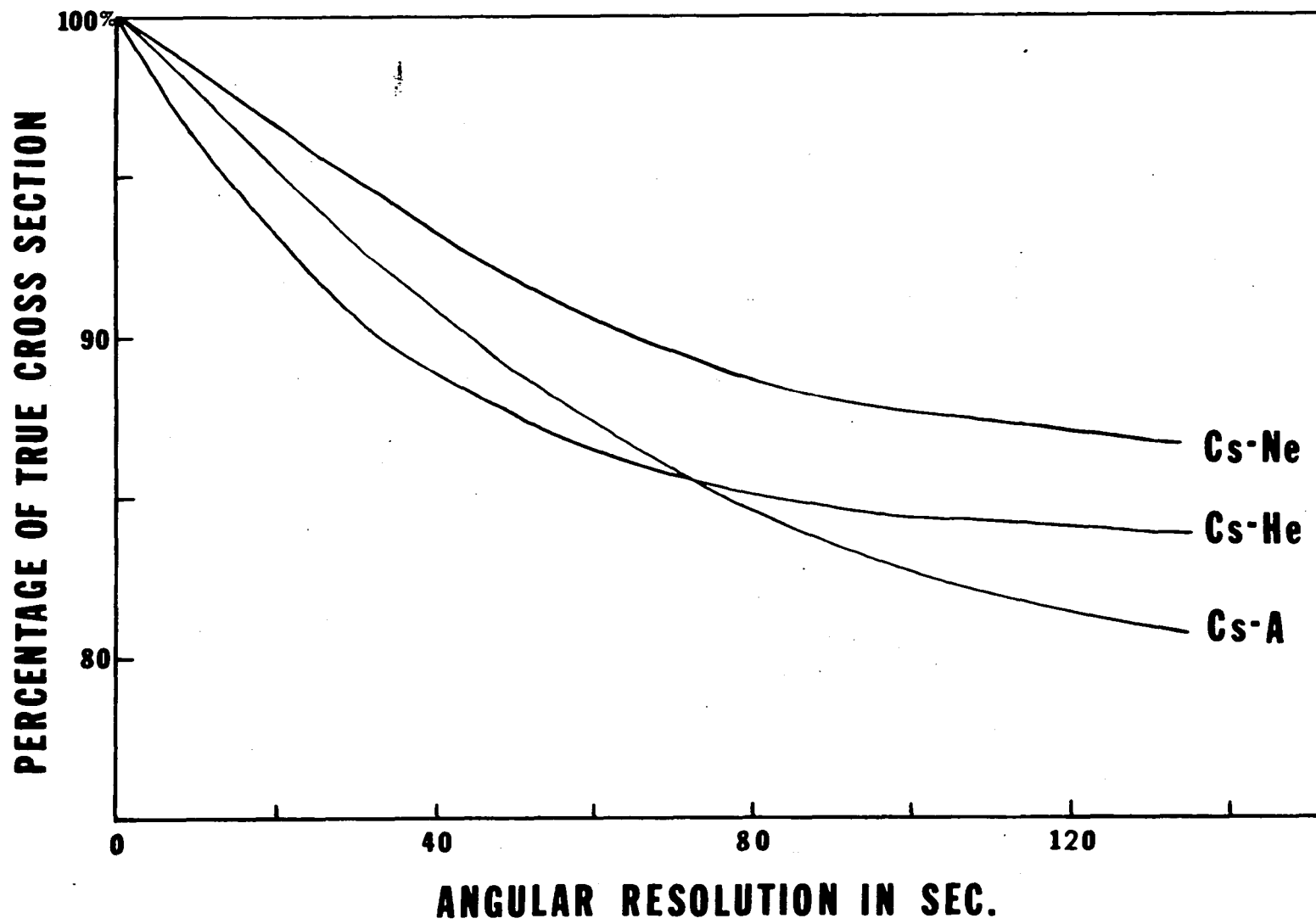


TABLE II

Comparison of Q_{Cs-He} and Q_{Cs-A} as a Function of Resolution With the Results of Helbing and Pauly

Resolution (min)	Scattering Gas	Present Results (% of Q_0)	Helbing and Pauly (% of Q_0)
1	He	86	95
1	A	87	90
2	He	84	93
2	A	80	83

Moreover, it must be remembered that not only was their method of varying the "resolution" different from the present experiments, but also their very meaning of "resolution" has a completely different significance from that of the present experiments. Their criterion stated that all particles scattered through a given angle equal to or greater than θ_{mL} contributed to the measured cross section, i.e., these particles would miss the detector. The Kusch criterion employed in the present work states that a particle deflected by the angle $\phi_{50\%}$ still has 50% probability of striking the detector. Hence, these two resolution studies cannot be expected to yield the same results, since they were not exactly the same type of investigation.

C. Conclusions Concerning Effect of Resolution

The present results have demonstrated the fact that the measured cross sections depended rather markedly on the resolution employed for all the cases encountered here. There is a statement in the literature (Rothe et al. 1962) that, at 1.5 minutes of arc, 99% of the total cross section was obtained for the scattering of beams of He, Ne, A, Kr and Xe by A. On the basis of the present experimental results, one could argue that 99% of the true cross section at that resolution was not very likely.

The interpretation of Figures 7-11 has an interesting possible explanation. A rough estimate of the extrapolated Q_0 for Cs-Kr and Cs-Xe showed that the Cs-Kr cross section dropped faster than Cs-A and Cs-Xe dropped faster than Cs-Kr. Thus, with the exception of Cs-He, the cross sections for cases with higher reported values of the van der Waals constants (Rothe and Bernstein 1959) drop off respectively faster. It seems reasonable to assume that, the larger C is, the more forward scattering predominates. Consequently, a faster decrease in Q as $\phi_{50\%}$ was increased can be expected for cases with increasing C, because a larger percentage of the forward scattered atoms can no longer be measured as scattered. Cs-He does not follow the predictions of this possible explanation at all. Also, future work at even higher resolution for Cs-Kr and Cs-Xe

is obviously necessary before such an explanation should be considered too seriously.

With respect to the Cs-He results, the present experiments have yielded the same conclusion reached by Helbing and Pauly (1964). Namely, the discrepancies listed in Table I cannot be explained by the differences in resolution employed by the different workers. For example, Rothe and Bernstein's (1959) result with a stated resolution of two minutes of arc is approximately 60% of Estermann, Foner and Stern's (1947) result at a stated resolution of one minute of arc. But, according to the present results, there is only approximately a 2% difference between the values of $Q_{\text{Cs-He}}$ at one minute and two minutes of arc. It was deduced, therefore, that another explanation is necessary to resolve the anomaly indicated by Table I.

II. Absolute Cross Sections

A. Results of Present Experiments

If one now uses the Q axes in Figures 7-9 as an absolute scale as labeled, it is possible to evaluate the true total cross section and the van der Waals constant for Cs-He, Cs-Ne and Cs-A as determined by the present experiments. Table III contains a summary of the results for the present experiments. Q_0 is the extrapolated true cross section in square Angstroms, Q_{12} is the partial cross section

TABLE III

Summary of Present Work for Cesium Beam

Scattering Gas	Q_0 (\AA^2)	Q_{12} (\AA^2)	\bar{v}_r (cm/sec)	C erg cm ⁶
He	237	227	13.0×10^4	63.8×10^{-80}
Ne	384	377	6.39×10^4	105×10^{-80}
A	753	733	4.99×10^4	441×10^{-80}
Kr		(935)		
Xe		(1265)		

at a resolution of 12 seconds (approximately the highest resolution at which measurements were actually taken), \bar{v}_r is the average relative velocity of the colliding atoms and C is the van der Waals constant as calculated from the Schiff-Landau-Lifshitz formula, Eq. (16), using the values of Q_0 and \bar{v}_r . Since extrapolation to zero resolution was not done for Cs-Kr and Cs-Xe, values of Q_0 and C for these cases are not reported. Also, the values of Q_{12} for these two cases are very doubtful (and, thus, appear in parentheses) because of the great uncertainty in the calibration procedure of the scattering gas pressure using the McLeod gauge for Kr and Xe gases. Appendix B discusses this problem in greater detail.

There were several sources of statistical and systematic errors which affected the results shown in Table III. These are discussed next.

B. Error Analysis of Results

The discussion of the effect of errors upon the absolute values reported are presented in two parts; errors in the semi-log curves of beam intensity versus scattering gas pressure and various other errors which effect the value of Q calculated from the Rosin-Rabi formula.

1. Errors in Raw Data Curves

The error in the determination of the slope of the I vs. p_g curves due to the slight non-linearity of the ionization gauge was found by direct calculation (by applying the necessary correction factor to the pressure readings) to be negligible in comparison to the human error involved in drawing and measuring the slope.

The error due to the slight non-linearity of the electrometer-recorder detection system for the beam intensity likewise had a negligible effect upon the determination of the slope of the raw data curves. A typical correction for the intensity corresponding to half scale deflection of the recorder was less than $\pm 1\%$, if the detection system were as high as 3% non-linear.

Another possible error which was considered was the actual precision with which one was able to read the instruments. Let $F = 1/p_g \ln(I_0/I)$. Then ΔF was calculated by inserting typical expected values of Δp_g and ΔI at various values of I_0 . ΔF was approximately $\pm 4\%$ for all cases at the lowest scattering gas pressures used and it dropped with increasing scattering gas pressures. This meant that an individual point on one I vs. p_g curve was subjected to what appeared to be a substantial uncertainty. But, it must be remembered that it is the slope determined by all the points on the I vs. p_g curve that was of interest and this was determined by constructing the best straight line through all the points (recall Figure 6). Consequently, no great concern was necessary whenever one point did not fit too well on the I vs. p_g graph, as long as there were enough other "good" points to enable a determination of the slope.

In summary, there was enough human uncertainty involved in constructing and measuring the slopes of the I vs. p_g curves to wash out the effects of the non-linearity of the ionization gauge, non-linearity of the detection system and the precision with which the instruments were read. This human error manifested itself in the range of slopes determined at each value of resolution and this primarily accounts for the error flags shown on Figures 7-11.

The remaining possible errors are of a systematic nature and are discussed next.

2. Possible Systematic Errors in Q and C

The use of the entire Rosin-Rabi equation for determination of absolute cross sections by the molecular-beam technique must be questioned (this is discussed further in Appendix C). In particular, the value of the effective path length used and the McLeod gauge calibration have large effects on the reported absolute cross sections. An estimate of these uncertainties was approximately 10% each, and are discussed further in Appendices B and C.

The problem of temperature measurements for both the beam and scattering gas atoms had very little effect on the results. The error due to uncertain scattering gas temperature was a maximum of 0.2°K out of approximately 305°K or less than $\pm 0.07\%$ (recall that Q is proportional to the scattering gas temperature). As for the beam temperature, an error as much as 5°K as determined from the emf of the oven thermocouple would only produce a change in Q of less than 0.5% in the case of Cs-Ne, for example, since $J(z)$ in the Rosin-Rabi formula is a very slowly varying function of the beam temperature.

If the background subtraction for the beam intensity were chosen as that background which existed approximately

six minutes after the beam was cut off, instead of using the lower background that existed just prior to an actual run, a calculation showed that Q was approximately 3-4% higher for a typical run.

It was felt that the absolute cross sections for Cs-He, Cs-Ne and Cs-A so determined were subject to an overall uncertainty of perhaps $\pm 25\%$, based on a consideration of these numerous systematic errors. No estimate of the absolute error for Cs-Kr and Cs-Xe was possible due to the McLeod gauge difficulty mentioned earlier.

Since $Q \propto C^{2/5}$, it is seen that $\Delta C/C = 5/2 \Delta Q/Q$. Hence, an overall uncertainty on the van der Waals constant for the Cs-He, Cs-Ne and Cs-A cases is perhaps $\pm 65\%$. This, incidentally, points out the importance of accurate determinations for Q if one uses the current molecular-beam method for calculations of C .

C. Comparison of Present Results with Literature Data

It is not intended here to present an exhaustive survey of the various other values of Q and C reported by other investigators. However, a brief comparison of the cross sections and van der Waals constants for Cs-He, Cs-Ne and Cs-A is given next.

1. Comparison of Total Cross Sections

Due to the large discrepancies in the absolute total cross section determinations reported by other workers, it has become customary in the literature to report values as Q^* , equal to the ratio of the cross section for the case considered to the cross section for Cs-A. Table IV lists some values of Q^* for comparison with the present results.

TABLE IV

Comparison of Q^* with Literature

Scattering Gas	Present Work	Rosin and Rabi	Rothe and Bernstein	Theoretical
He	.315	.283	.310	.298
Ne	.510	.502	.440	.527
A	(1.00)	(1.00)	(1.00)	(1.00)

Listed are the experimental results of Rosin and Rabi (1935) and Rothe and Bernstein (1959) who also used thermal beams and scattering chambers. Listed also are the theoretical values of Q^* which were obtained from Eq. (16) by the application of Eq. (9) for C and the use of Eq. (17) for \bar{v}_p using the present beam and scattering gas temperatures. For comparison of the experimental values with one another, it must be remembered that the current resolution was not only much

better than the others, but the present experiments showed that the cross sections neither dropped off linearly with resolution nor dropped off at the same rates. Thus, very good agreement among the experimentally reported Q^* 's is not actually expected.

2. Comparison of van der Waals Constants

Table V lists the values of the van der Waals constants determined from various molecular-beam experiments.

TABLE V

Comparison of C With Literature in Units
of 10^{-60} erg cm⁶

Scatter- ing Gas	Pres- ent Work	Rosin and Rabi	Estermann, Foner and Stern	Rothe and Bernstein	Helbing and Pauly	Theoret- ical Calc.
He	63.8	24.7	312	85	40	32
Ne	105	47.8		100		64.3
A	441	199		620	400	250

The results of Rosin and Rabi (1935) were obtained from their previously mentioned work; these were derived from their results and are given in Massey and Buckingham's (1936) paper. (The Schiff-Landau-Lifshitz formula, instead of the Massey-Mohr formula, produces a correction in these results, namely,

$C_{SLL} = 0.8425 C_{MM}$.) The experimental result of Estermann, Foner and Stern (1947) for Cs-He as reported in Ramsey (1956) using the Schiff-Landau-Lifshitz formula is included. Also, the experimental results of Rothe and Bernstein's (1959) previously mentioned work are included in Table V along with two values determined by Helbing and Pauly (taken from Helbing's dissertation), also using a thermal beam and a scattering chamber. These are reported in Bernstein's (1964) article. The theoretical calculations of C followed from the use of Eq. (9) and the quoted polarizabilities of the atoms; these are given in Rothe and Bernstein's (1959) paper. Here again, poor agreement among the results listed in Table V is not too surprising, since the discrepancies might possibly be due to the numerous experimental systematic errors in these various experiments.

With the exception of Rosin and Rabi, the remaining researchers all found the C 's determined by molecular-beam scattering experiments to be higher than the theoretical estimate. As mentioned in the introduction, this has been the case most often. An attempt to explain this situation is not made here, but reference to the theoretical paper of Dalgarno and McCarroll (1957) previously mentioned and the paper of Fontana (1964) is made. In particular, Fontana (1964) has considered the effect that other interactions, in addition to the $1/r^6$ intermolecular attraction, would

have on the value of C as determined from molecular-beam determinations of Q . He has shown that a small change in the power dependence of the interaction potential can effect the numerical value of C considerably. For example, letting $V = -C(\epsilon)/r^{6+\epsilon}$, and plotting C vs. ϵ , he shows that, for the A-A interaction, C changes from 180×10^{-60} for $\epsilon = 0$ to 50×10^{-60} for $\epsilon = 0.08$.

In summary, a comparison of the various experimental results listed in Table V shows that the present values for the van der Waals constants vary from a best agreement of 5% with Rothe and Bernstein's (1959) value for Cs-Ne to the worst agreement of more than a factor of two with all of Rosin and Rabi's (1935) results.

III. General Conclusions

The main significance of the present work was that it showed the very pronounced effect of angular resolution upon the measured cross sections. It has been demonstrated that, if one wishes to determine intermolecular potential parameters by the molecular-beam technique using the Schiff-Landau-Lifshitz formula (Eq. (16)), high apparatus resolution and high experimental accuracy are necessities for meaningful results.

With respect to Cs-He scattering, the case which was the primary motivation for this work, the present results

indicate that the question of resolution cannot explain the discrepancies listed in Table I.

It should be noted that the slopes of the Q vs. $\phi_{50\%}$ curves were always non-positive, i.e., Q always increased as the resolution was improved, as it must theoretically.

Future work at higher resolution is necessary in the cases of Cs-Kr and Cs-Xe, due to the sharp increase in Q as $\phi_{50\%}$ is reduced, before the nature of these variations is known.

The question of the resolution necessary in order that molecular-beam scattering experiments yield a prescribed fraction of the true total cross section for any specified pair of colliding atoms is still unanswered. Future work is necessary before a general statement concerning this problem can be made. Beams of potassium and lithium are now being used in the existing molecular-beam laboratory at the University of Arizona. It is hoped that the results of these experiments will cast more light on the general problem concerning the resolution needed to measure a given fraction of the true total cross section for colliding atoms.

APPENDIX A

Further Details of Apparatus and Materials

1. Vacuum System

The arrangement of the vacuum system is shown in Figure 1. Not shown in the diagram are freon 22 refrigerated baffles above all 720 and 1500 pumps, liquid nitrogen cold traps above the three baffles on the detector end of machine and ionization gauges on chambers A, C, D, G and H. All diffusion pumps used DC-704 fluid. Chambers A, B and C were made of brass and used O-rings for seals. The remaining chambers were all constructed from stainless steel (type 304) and used copper gaskets for seals. Viton O-rings were used for seals between the three pumps on the stainless steel section and their baffles. The entire vacuum system was fastened to a large aluminum I-beam (one foot wide by twelve feet long) which was shock-mounted on two large concrete pillars to minimize vibration.

2. Oven

The oven was also constructed from stainless steel and was similar in design to that shown in Ramsey (1956, p. 365). The slits on the front of the oven were set manually

and measured by a micrometer microscope. The oven heaters were constructed of ten mil tantalum wire wound into coils of seventy turns on a #55 drill and shielded from the oven itself by ceramic insulators. The oven sat on a base which was translated by means of a sliding O-ring attachment fastened to chamber B and its position was measured by a Starret gauge. The oven was rotated by means of a rod attached to the base and passing through the vacuum wall. A micrometer head was used to measure the amount of rotation.

The oven had two chromel-alumel thermocouples peened in it, one in the front and one near the well in the rear containing the cesium. The thermocouple in front typically gave a temperature 12°C higher than the rear thermocouple; this helped to keep the oven slit from clogging. The temperature of the beam, however, was taken as the reading corresponding to the rear thermocouple, since this was closer to the well and the flight of the atoms forming the beam originated in this vicinity.

3. Scattering Chamber

The scattering chamber was also made of stainless steel and had inlet and exit channels which were one-half inch long, one-half inch high and 0.030 inches wide. The central cavity was two inches long. Translation and rotation of the scattering chamber was achieved by means of a

stainless steel bellows arrangement attached to the side of chamber G of Figure 1.

4. Detector

A conventional Langmuir-Taylor surface ionization (hot wire) detector was used. A one mil tungsten filament was heated by 75 ma. d.c. and biased by +45 volts relative to the ion collector cup. The cup was a one inch long cylinder with $\frac{1}{2}$ inch outer diameter and $\frac{1}{32}$ inch walls. The beam was allowed to enter and exit by means of $\frac{3}{4}$ inch long and $\frac{1}{8}$ inch wide openings in the cup. The translation and rotation of the detector (also the collimating slit) were accomplished by means of stainless steel bellows arrangements attached to the vacuum wall and their positions measured by means of micrometer heads.

5. Purity of Materials

The cesium was obtained from United Mineral and Chemical Corp. and was stated to be 99.93% pure. The scattering gases were obtained from Air Reduction Company and were research grade. The He, Ne and Ar came in 250 lbs. pressure cylinders and Kr and Xe came in bottles at one atmosphere pressure.

6. Auxiliary Apparatus

- a. Sola constant voltage transformer for furnishing power to the oven variac and the entire detection system.
- b. Constant current power supply for the detector filament.
- c. Stokes microvac forepump (model 212F).
- d. Refrigeration system.
 - i. Brunner-Metic compressor (model WR-15LF, type A).
 - ii. Expansion valves.
 - iii. Heat exchangers.
 - iv. Filters, valves, strainers and pressure gauges.
- e. Safety system for diffusion pumps.
 - i. Shur-flo water interlocks.
 - ii. Thermocouple gauges and associated amplifier for closing relays to turn off pumps in event of forepressure rising too high.
- f. Minneapolis-Honeywell (model #2703) potentiometer for determining oven temperature.
- g. Veeco ionization gauge control panel and switching circuit.
- h. Thermocouple and associated circuitry for reading forepressure.
 - i. Forelines and ball valves.
- j. Water lines for cooling pumps.
- k. Leak detector (Veeco, model MS 9AB).

APPENDIX B

Use of McLeod Gauge for Calibration of Scattering Chamber Ionization Gauge

For absolute cross section determinations, it was necessary to calibrate the ion gauge which read the scattering chamber pressures with a McLeod gauge in order that absolute pressures were known. The McLeod gauge used had a manufacturer's stated practical working range to 10^{-6} mm Hg. Fifty pounds of triple distilled mercury were added to the gauge reservoir in an oxygen free atmosphere. A double dewar was placed between the tubing connecting the scattering chamber to the McLeod gauge in order to condense the mercury which otherwise would migrate into the scattering chamber. For the scattering gases He, Ne and A, liquid nitrogen was used to fill the double dewar. Kr and Xe gave considerable trouble, however, as the calibration data was not very reproducible for Kr and no reasonable results for Xe were obtained with liquid nitrogen in the double dewar. A warmer coolant (alcohol and liquid nitrogen mixture) was used to obtain the Xe calibration. When this same coolant was used for re-running the Kr calibration, a different result was obtained from that when liquid nitrogen was used.

(approximately 12% lower). Thus, the calibration results for Kr and Xe must be considered very doubtful.

The gases were slowly compressed by the mercury in the bulb of the McLeod and the final height of trapped gas in the capillary of the gauge was read with the aid of a cathetometer. The corresponding ion gauge readings (read just prior to compression of the gas by the mercury) and McLeod gauge readings were plotted on a linear graph. The equation of such a graph is

$$(I.G.) = \gamma(M.G.) + c, \quad (36)$$

where I.G. and M.G. represent the ion gauge and McLeod gauge readings, respectively, γ is the slope of the line and c is a constant. It can be shown that the actual non-background pressure of the scattering gas is merely given by $(I.G.)/\gamma$. Hence, the pressures in Figure 6 needed only to be divided by γ to convert them to absolute pressures. The value of γ used was determined by drawing the best fitting line through the points constituting the graph of the ion gauge readings vs. McLeod gauge readings. For the ion gauge employed in the present work, the values of γ used were 0.224, 0.414, 1.52, 1.85 and 3.04 for the gases He, Ne, A, Kr and Xe, respectively. The values of γ for Kr and Xe are extremely doubtful, since there was a question of whether or not enough gas was actually reaching the compression bulb of

the McLeod gauge. This was another reason why the graphs of Q vs. $\varphi_{50\%}$ for Cs-Kr and Cs-Xe were not extrapolated to obtain the true cross sections.

To obtain an estimate of the error involved in the calibration procedure using the McLeod, three reasonable lines were drawn through the points on the ion gauge vs. McLeod gauge graphs. The slopes of the two extreme lines (one too steep and one too flat) were used for the estimate of the error. In the three cases for He, Ne and A, the difference in the slopes of these extreme lines was 8% or less. Hence, an estimate of 10% accuracy in the use of the McLeod was felt to be liberal.

APPENDIX C

Validity of Rosin-Rabi Formula.

The usual expression for the total cross section, the Rosin-Rabi formula, was used for calculations. However, the validity of this equation is open for discussion due to a number of reasons. These are discussed in the following.

At high attenuations, multiple scattering must certainly occur and this is neglected in the derivation of the Rosin-Rabi equation. However, it must be pointed out that there was no definite evidence of multiple scattering in the experiments. It might be expected that the points on the beam intensity vs. scattering gas pressure curves would start to fall above the best straight line fit to the graph when multiple scattering occurred at high pressures due to the fact that deflected particles would undergo further scattering and be scattered back onto the detector. No definite effect of this nature was actually observed in the present work. However, Jawtusich, Schuster and Jaeckel (1955) and Kodera and Tamura (1957) have observed this phenomena in their respective experimental work at higher scattering gas pressures than were used here.

The step in the derivation of the Rosin-Rabi equation whereby Q was removed from under the integral sign has

been investigated by Rothe and Bernstein (1959). They have carried out numerical integrations using an IBM 650 computer and compared the "exact formula" of Rosin and Rabi (1935) with the approximate formula used here for the case of a K beam scattered by H_2 , He, CH_4 , A and $SiCl_4$. They concluded that, for these cases, the net correction in the relative cross sections would vary by approximately 1%. Beck (1962) also gives reference to the fact that Rosin and Rabi's method of averaging over the distribution of relative velocities assuming a velocity independent cross section varies by only approximately 5% with an exact numerical averaging over a $v^{-2/5}$ dependence of the cross section for the cases K-Kr and K-HBr.

Another approximation used was that expressed in Eq. (28). This step would be rigorous if the Maxwellian beam distribution were unchanged by the scattering phenomena. An attempt to justify this approximation has not been made here, but Rosin and Rabi (1935) have calculated that, after being scattered, the form of the original Maxwellian distribution is lost to some extent, since the lower velocity atoms have a smaller probability for passing through the scattering chamber without collision. This effect shifts the maximum of the distribution towards the region of higher velocities. Nonetheless, the approximation, Eq. (28), is felt to be of minor significance compared to the next criticism.

The final criticism is concerned with the effective scattering path used in the Rosin-Rabi equation. Rothe et al. (1962) have derived an expression which can be used to estimate the effective scattering path by consideration of the conductances in the various sections of the scattering chamber. Application of this formula to the present experimental situation yields an effective scattering length given by $d = \frac{1}{2}(\frac{1}{2}) + 2 + \frac{1}{2}(\frac{1}{2}) = 2\frac{1}{2}$ inches, i.e., the first and third terms represent one-half of the length of the entrance and exit channels, respectively, and the second term is the length of the central cavity. No consideration has been given to any cloud of scattering gas which may be present near the ends of the scattering chamber. If this approximation for d is assumed to be within 10%, it is estimated that the entire approximate Rosin-Rabi equation is accurate to $\pm 15\%$. This error and the estimated error of $\pm 10\%$ for the McLeod gauge calibration procedure were merely added to yield an estimated overall uncertainty of $\pm 25\%$ for the reported absolute cross sections in the present work.

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