Total Cross Sections for the Scattering of Potassium by He, Ne, Ar, Xe, and H_2 in the Thermal Energy Range*

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Absolute values of the cross sections for the scattering of potassium by helium, neon, argon, xenon, and molecular hydrogen have been determined in the thermal energy range. The atomic beam was velocity-selected using a Stern-Gerlach magnet with a resolution of approximately 10%. A capillary flow method was used to determine the target-gas density with reasonably high accuracy. Temperature effects of the target gas were taken into account, using the tables of Berkling *et al.*, and the target-gas temperature was varied to extend the relative-velocity range employed. The potential constants for K-A and K-Xe are in reasonable agreement with those obtained from the cross-section measurements of Rothe and Bernstein, and Helbing and Pauly. The values obtained for K-A, K-Xe, and K-H_2 are 571.6, 1024, and 106.2×10^{-60} erg cm^6, respectively; K-Ne exhibits an approximate $v^{-2/3}$ velocity dependence over the range 400 to 1450 m/sec; while the K-He cross section is essentially velocity-independent over the range 650 to 2000 m/sec.

INTRODUCTION

During recent years, many measurements have been made on the velocity dependence of the collision cross sections for alkalis on rare-gas atoms in the thermal energy range.[1,2] Absolute values of these cross sections, nevertheless, remain somewhat uncertain because of the difficulties which arise in beam experiments, where absolute values of densities and temperatures, and precise knowledge of geometry are required. Since interatomic potential constants are usually a sensitive function of the collision cross section, the errors in these determinations may be quite high. In addition, there have been persistent discrepancies between experimentally and theoretically obtained Van der Waals potential constants.[2]

We discuss here measurements of the scattering of a velocity-selected potassium beam by helium, neon, argon, xenon, and molecular hydrogen. A capillary flow method was used to determine the target-gas density with reasonably high accuracy. Effects due to the finite temperature of the scattering gas were taken into account, and the temperature was varied in order both to verify the method for correcting for the target-gas velocity distribution, and to extend the range of relative velocities.

EXPERIMENTAL METHOD

Source and Detection

Figure 1 is a schematic diagram of the apparatus and includes relevant dimensions. The potassium oven is a modified Kusch design, fabricated from nickel. A hole 0.125 in. in diameter connects the slit end of the oven with the potassium well. The slit width is 0.003 in. A nickel spiral was inserted in the channel near the slit to insure that the effusing atoms are at the slit temperature. Two thermocouples, inserted into recessed wells close to the slit, were employed to measure the slit temperature, which could be kept constant to within $\pm0.1°$ during the course of a run. The surface ionization detector was a 0.002-in. S. Cohn alloy No. 479 platinum-tungsten wire, which was aged sufficiently to produce an ion background of less than 10^{-14} A. An Ecko vibrating-reed electrometer, type N616A, was used. It was found to be linear to within 1% of full scale reading over the entire range of inputs employed.

Using the Kusch 50% criterion,[3] the angular resolving power of the apparatus is found to be approximately 60 sec of arc (assuming an infinitesimal detector).

Velocity Selector

The use of an inhomogeneous magnet as a velocity selector or analyzer was first discussed by Cohen and Ellett.[4] Bederson and Rubin[5] analyze a velocity selector similar to that used in the present work, consisting of an offset oven and an inhomogeneous magnet followed by two collimating slits. They show that the resolution $\Delta v_B/v_B$ is proportional to the parameter w/s, where Δv_B is the range of transmitted velocities, centered at v_B, w is the oven slit width, and s is the oven displacement from the beam axis. That is,

$$\Delta v_B/v_B = Gw/s\,, \tag{1}$$

where G is a constant which depends upon apparatus geometry and magnet characteristics. The transmitted velocity is varied by changing the magnet current with the oven at a fixed position. The velocity resolution

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† From part of a thesis submitted by K. Lulla in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Department of Physics, New York University.

[1] For a comprehensive review and bibliography of recent low-energy atom-atom collision experiments see R. B. Bernstein, Science 144, 141 (1964).

[2] R. B. Bernstein, in *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland Publishing Company, Amsterdam, 1964).

[3] P. Kusch, J. Chem. Phys. 40, 1 (1964).

[4] V. W. Cohen and A. Ellett, Phys. Rev. 51, 65 (1937).

[5] B. Bederson and K. Rubin, U.S.A.E.C. Tech. Rept. NYO-10117, New York University, 1962 (unpublished).

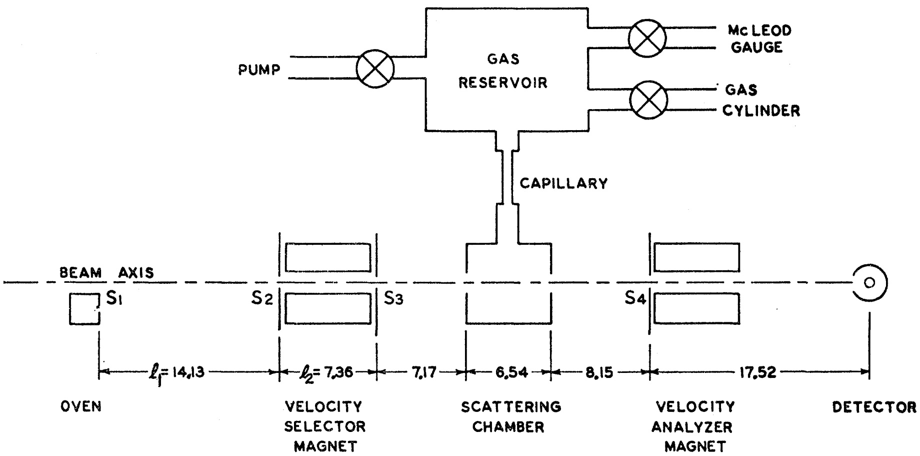

FIG. 1. Schematic diagram of the apparatus, not to scale. Dimensions are in inches, $S_1=0.003$ in., $S_2=0.005$ in., $S_3=0.002$ in., and $S_4=0.002$ in.

of the selector of the present apparatus is estimated to be about 10%, and the analyzer magnet was used to verify this estimate. Note that the resolution is independent of velocity, for a given oven position. Final confirmation of the reliability of the selector was obtained by plotting the transmitted beam as a function of magnetic field in the selector magnet.

If we assume a modified (v^3) Maxwellian distribution in the unselected beam, then $I(v_B)$, the transmitted beam intensity, is approximately given by

$$I(v_B)=Cv_B^3\exp(-\beta^2v_B^2)\Delta v_B\,,$$

provided $\Delta v_B \ll v_B$, where C is a geometric and normalization constant, and $\beta^2=m_B/2kT$ with m_B the mass of the beam particle and T the source temperature. Because of Eq. (1) this becomes the modified (v^4) distribution

$$I(v_B)=(GwC/s)v_B^4\exp(-\beta^2v_B^2)\,. \tag{2}$$

The transmitted velocity can be expressed as a function of the current i in the selector magnet coils by the relation

$$v_B=Ki^{1/2}\,,$$

where

$$K=[\mu_0 a l_2(l_2+2l_1)/2Ms]^{1/2}\,, \tag{3}$$

with μ_0 the Bohr magneton, a the ratio of magnetic field gradient to current, l_1 the distance from source to magnet, and l_2 the length of the magnet (see Fig. 1). At higher fields, a is not constant because of magnet saturation. Saturation effects were taken into account by direct field measurements using a Bell 120 gauss-

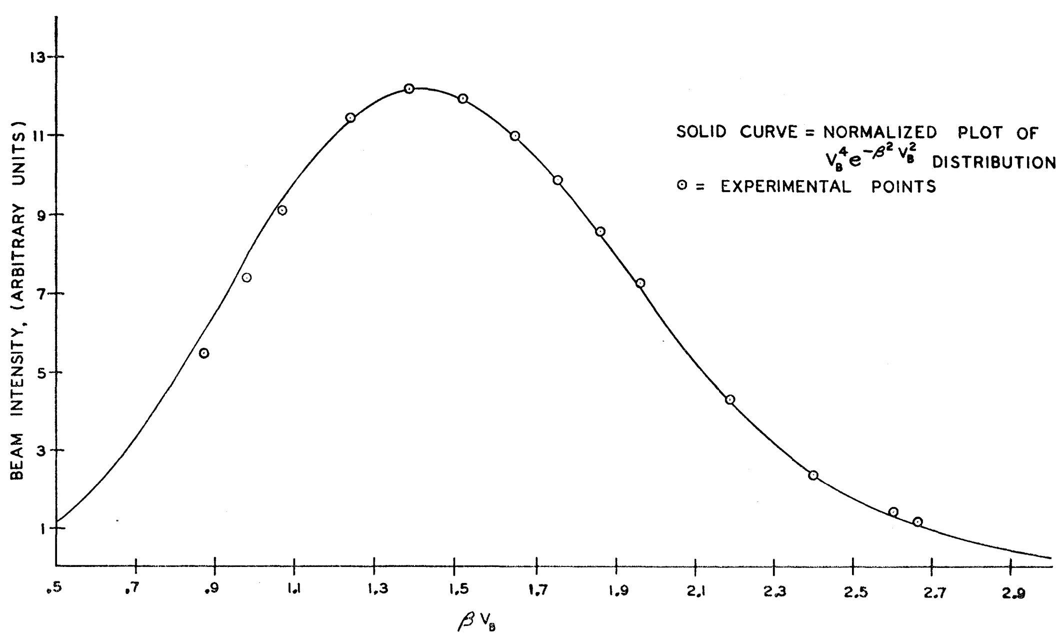

FIG. 2. Beam intensity versus beam speed normalized to the most probable oven speed.

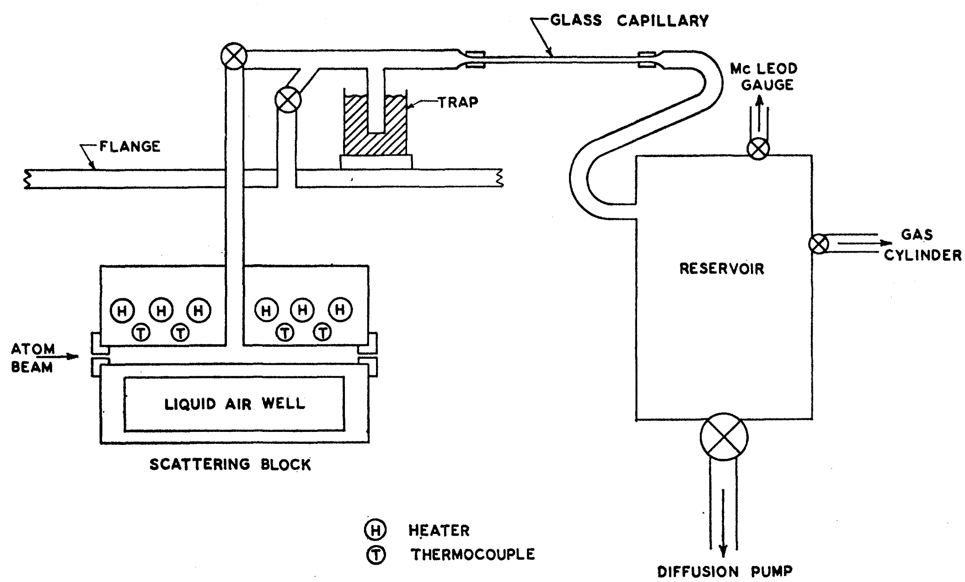

FIG. 3. Scattering block and gas handling systems.

meter. Figure 2 is an experimental plot of $I(v_B)$ versus βv_B for a potassium beam emerging from an oven with a slit temperature of about 280°C. K is obtained by normalization rather than by direct calculation, using the relation

$$K=(1/\beta)[2/i(\max)]^{1/2},$$

where $i(\max)$ is the value of i at which $I(v_B)$ is a maximum [note that $\beta v_B(\max)=\sqrt{2}$]. The solid curve in Fig. 2 is a calculated plot of Eq. (2) normalized at the maximum. The agreement with the data is seen to be excellent, although there is some deficiency of particles with lower velocities.

Scattering Block and Gas Flow System

A diagram of the scattering block and gas handling system is shown in Fig. 3. The scattering block is fabricated of annealed stainless steel and contains a cylindrical cavity of 0.501(1)-in. diameter, which serves as the scattering region. The block is 6.001(1) in. long, 4 in. wide, and 2.5 in. deep, and is gold-plated. An 0.5-in.-diam tube and a high-conductance valve connect the block to the capillary leak. The block is attached to a liquid-nitrogen reservoir, and is capable of being heated to temperatures of up to 250°C by means of six Vulcan heaters contained in recessed wells. Four thermocouples (two Chromel-Alumel and two copper-Constantan) are also contained in wells to measure the block temperature.

Two low-conductance plugs at the ends of the scattering region serve as the entrance and exit holes for the potassium beam. These are 0.742(1) in. and 0.599(1) in. long, respectively, and the inside diameters are 0.090(1) in. and 0.091(1) in., respectively. The pressure in the reservoir, called the primary pressure, is measured on a laboratory standard CVC McLeod gauge, type GM-100A. A liquid-air reservoir, in series with the filling system, is used to trap out condensables.

A capillary tube connects the reservoir and the scattering region. This arrangement makes it possible to maintain reasonably high primary pressures ($\sim 200\mu$), which can be measured with a fair degree of accuracy with the McLeod gauge, and which should also minimize errors due to diffusion of McLeod-gauge mercury.[6] The pressure P_0 at the center of the scattering chamber is then given to a good degree of accuracy by the expression

$$P_0=F_CT_BP_RY/F_BT_R, \tag{4}$$

where F_C and F_B are the conductance of the capillary and the effective conductance of the scattering block, respectively, P_R is the primary pressure, and T_R and T_B are the absolute temperatures of the reservoir and the block, respectively. The quantity Y is a correction factor to take into account deviations from pure molecular flow through the capillary. Negligible error has been introduced in Eq. (4) by assuming that the pressure is zero on the scattering-block side of the capillary in calculating the gas flow through the capillary. The conductances were calculated using the Clausing equation,[7]

$$F=3638KA(T/M)^{1/2}\ \mathrm{cm^3\,sec^{-1}},$$

where K is the corrected Clausing factor, A is the cross-sectional area, and T is the temperature. The quantity $\int ndl$, representing the total effective product of target-gas density and length, is then obtained by

[6] H. Ishii and K. Nakayama, *Transactions of the Eighth Vacuum Symposium and Second International Congress* (Pergamon Press, Ltd., Oxford, 1962), Vol. I, p. 519.

[7] S. Dushman, *Scientific Foundations of Vacuum Technique*, edited and revised by J. M. Lafferty *et al.* (John Wiley & Sons, Inc., New York, 1962), 2nd ed., pp. 93–111.

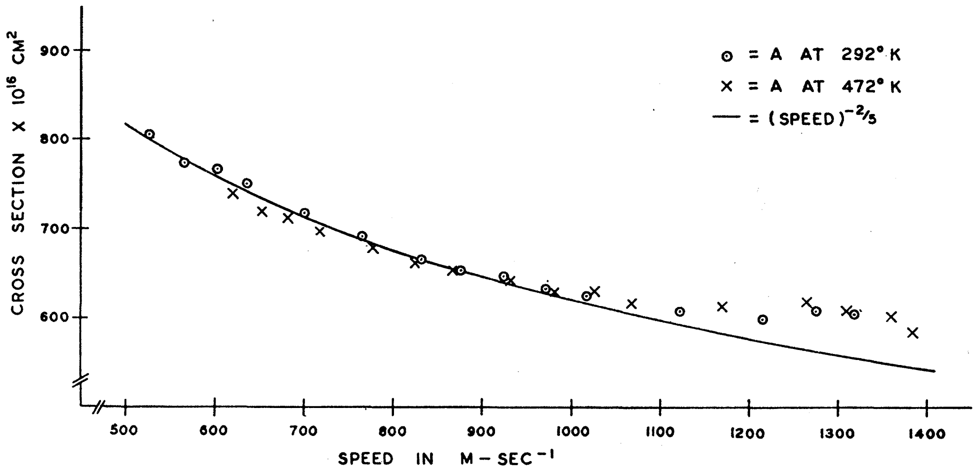

FIG. 4. K-A cross section versus average relative speed.

summing over the various elements of the attenuation region, taking into account the variation of density with position. The pressure drop across each of the conductance elements is assumed to be linear. Contributions due to the scattering both inside the exit plugs and in the vacuum in the vicinity of the exit plugs are included. The value of this integral for the scattering block used in the present experiment is

$$\int ndl = 24.672\times10^{12} P_R Y (T_B T_R)^{-1/2}\ \mathrm{cm}^{-2},$$

with P_R in microns. Deviations from perfect molecular flow through the capillary are taken into account by using Knudsen's conductance formula.[7] The use of Knudsen's formula is only necessary at the highest pressures used ($\sim 280\,\mu$), and the corrections were always less than 4%. The corrections were checked experimentally by observing that the logarithm of the beam attenuation was linear with the calculated scattering-chamber pressure over all pressures employed.

EXPERIMENTAL PROCEDURE AND DATA

If we assume a monoenergetic beam and a Maxwellian target gas, the transmittance I/I_0 of the beam is given by

$$I/I_0 = \exp\left[-(1/v_B)\int vQ(v)f(\mathbf{v}_g)d\mathbf{v}_g \int ndl\right], \quad (5)$$

provided the target-gas velocity distribution function $f(\mathbf{v}_g)$ is independent of position along the beam path. I_0 and I are the unattenuated and attenuated beams, respectively. The quantities v_B, v_g, and v are the magnitudes of the beam, target, and relative velocities, respectively, and $Q(v)$ is the beam-target total-collision cross section. If $Q(v)$ is of the form

$$Q(v) = Q_0/v^{2/(n-1)},$$

then Eq. (5) can be written as

$$\ln(I/I_0) = -(Q_0/v_B^{2/(n-1)})F_{a0}(n,x)\int ndl, \quad (6)$$

where

$$F_{a0}(n,x) = (1/v_B)\int vf(\mathbf{v}_g)(v_B/v)^{2/(n-1)}d\mathbf{v}_g \quad (7)$$

and $x = v_B\beta_g$, with $1/\beta_g$ the most probable speed of a target particle.

The quantity $F_{a0}(n,x)$ has been evaluated for $n=6$ and $n=\infty$ (hard sphere) by Berkling *et al.*[8] For n and x sufficiently large, Eq. (6) can be approximated by

$$\ln(I/I_0) = -Q(v)F_{a0}(\infty,x)\int ndl. \quad (8)$$

The error from using this approximation is less than two parts per hundred for $n=6$, for the ranges of x employed in the present work. Equation (8) is, therefore, employed to obtain both the velocity dependence and the absolute values of Q_0, except for K-Ne, where Eq. (6) with $n=4$ is used. Where possible, data were obtained at room temperatures, 500°K and 80°K (liquid nitrogen). Because of the long time necessary to achieve equilibrium, the latter temperature was not employed for argon and xenon.

The data are presented in Figs. 4–8 for a potassium beam scattered by argon, xenon, neon, helium, and H_2, respectively. The scattering-block temperatures employed are stated in the figure legends. Note that runs for a particular target gas at various temperatures are in good agreement. Normalized $v^{-2/5}$ curves are also presented in the argon and xenon figures, and a normalized $v^{-2/3}$ curve is presented in the neon figure. It can be seen that xenon exhibits $v^{-2/5}$ behavior throughout the range studied, while argon deviates somewhat at the high end of the velocity range. The K-Ne cross

[8] K. Berkling, R. Helbing, K. Kramer, H. Pauly, Ch. Schlier, and P. Toschek, Z. Physik **166**, 406 (1962).

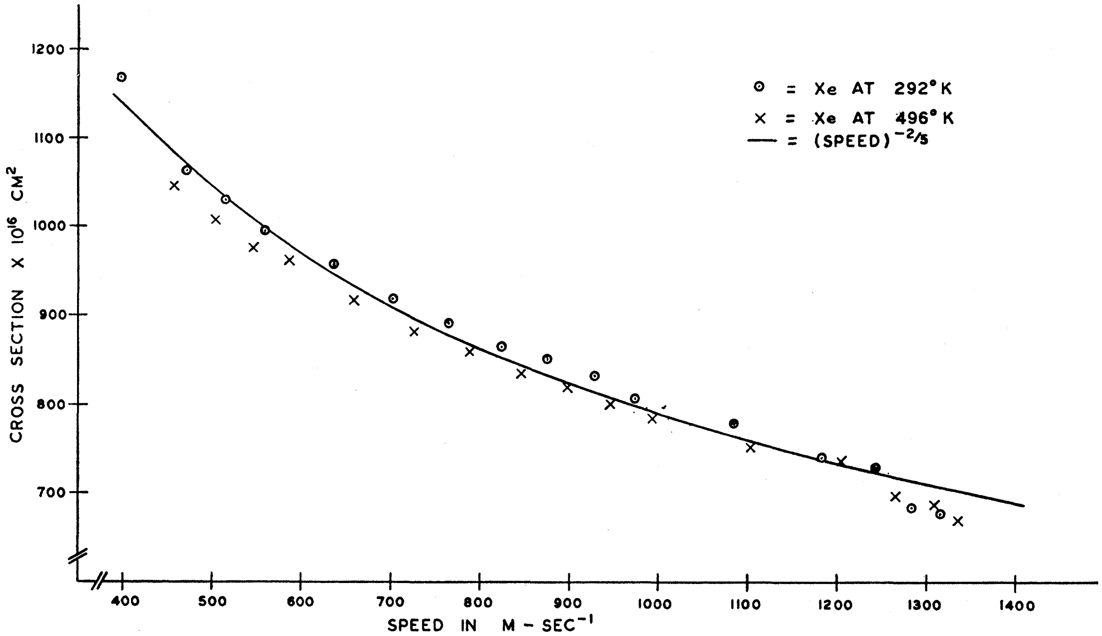

FIG. 5. K-Xe cross section versus average relative speed.

section varies approximately as $v^{-2/3}$, with the dependence being somewhat steeper than this in the low velocity range. The K-He cross section exhibits an extremely slow velocity dependence. The K-H_2 cross section varies as $v^{-2/5}$ in the upper half of the velocity range studied.

DISCUSSION OF RESULTS AND EXPERIMENTAL ERROR

If the interatomic potentials for K-A, K-Xe, and K-H_2 are assumed to be of the form

$$V(r)=-C/r^6,$$

TABLE I. Interatomic potential constants $C=4\epsilon\sigma^6$ for potassium (in units of 10^{-60} erg cm^6).

Element	Relative velocity range	Q_0	C Present experiment	C Rothe and Bernstein[a]	C Helbing and Pauly[b]
Xe	500–900 m/sec	$80\,011\times10^{-16}$	1024	1320	1070
A	550–850 m/sec	$63\,207\times10^{-16}$	571.6	600	410
H_2	1800–2500 m/sec	$32\,261\times10^{-16}$	106.2		

[a] See Ref. 10.
[b] See Ref. 11.

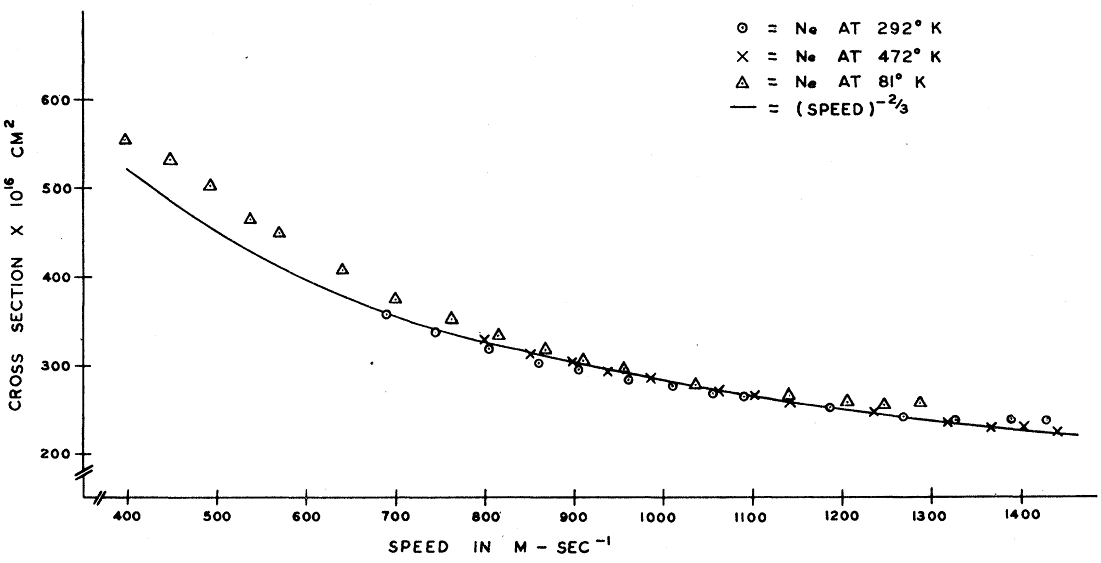

FIG. 6. K-Ne cross section versus average relative speed.

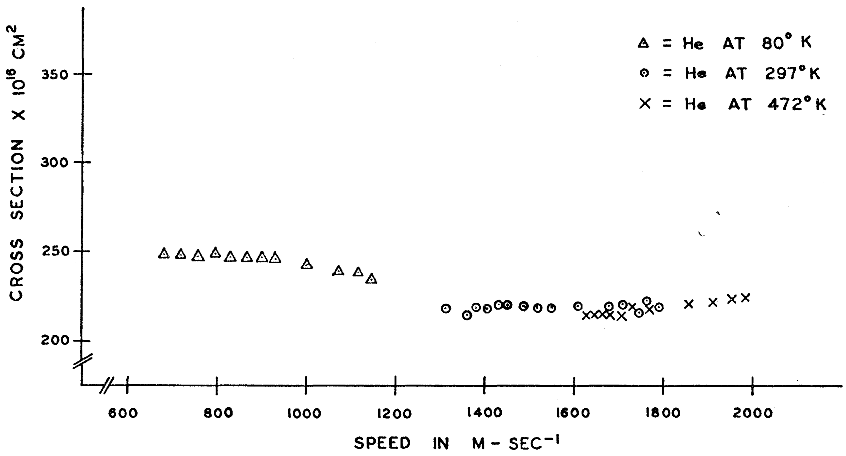

FIG. 7. K-He cross section versus average relative speed.

then the C's can be calculated (using the Landau-Lifshitz formula)[9] from the relation

$$C = (\bar{Q}_0/4.992\times10^{11})^{5/2},$$

where $\bar{Q}_0$ is the average value of Q_0 obtained from experiment. These values are presented in Table I, which also includes the values of C calculated from the cross sections measured by Rothe and Bernstein[10] and Helbing and Pauly.[11] Both groups used thermal beams without velocity selection.

In obtaining absolute values for Q and C, the principal sources of error are the following: (1) uncertainty in the McLeod-gauge measurements; (2) effects of the angular resolutions; (3) errors in $\int ndl$ due to errors in the conductance formulas used. We estimate about 5% error for (1) and (2) combined, and a 5% error for (3). The bias introduced by the finite angular resolution θ_0 can be estimated, using a small-angle formula for $\sigma(\theta)$. To order of θ_0^2, the bias ΔQ is[12]

$$\Delta Q \approx 0.027 Q^2 k^2 \theta_0^2,$$

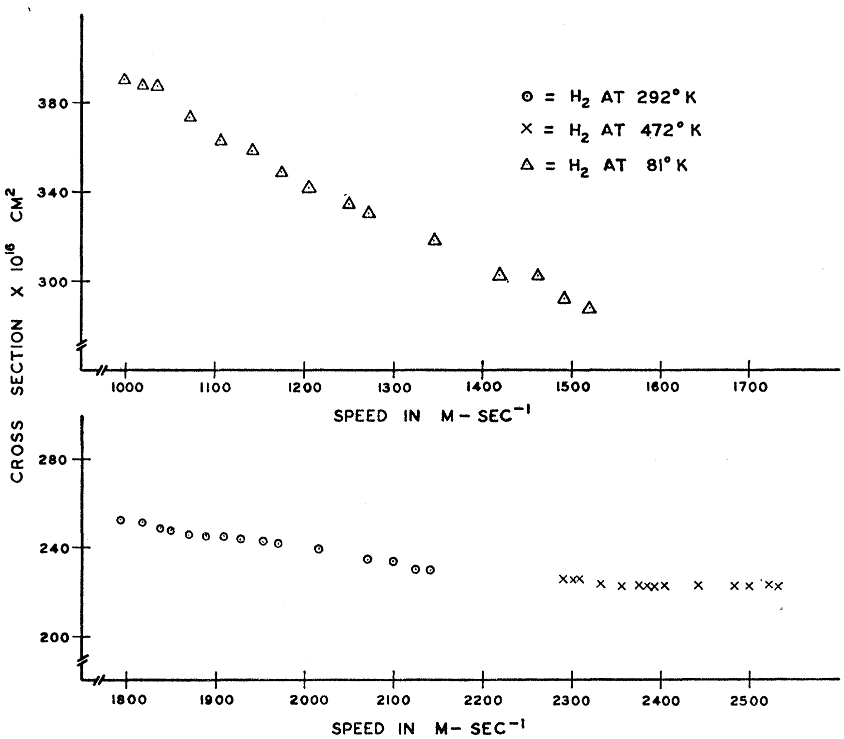

FIG. 8. K-H_2 cross section versus average relative speed.

[9] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press Ltd., London, 1958), p. 416.
[10] E. W. Rothe and R. B. Bernstein, J. Chem. Phys. **31**, 1619 (1959).
[11] R. Helbing and H. Pauly, Z. Physik **179**, 16 (1964).
[12] H. Pauly, Z. Physik **157**, 54 (1959).

where $k=Mv/\hbar$. Using our estimate of 60 sec of arc for θ_0, we obtain values of $\Delta Q/Q$ which for the worst case of the present work (K-He) is approximately 0.5%, and is therefore insignificant. This was verified experimentally by observing the dependence of the cross section upon slit width S_4, which was varied from the original value of 0.002 in. up to 0.016 in. We make an over-all error assignment of $\pm 10\%$ on the absolute values of the cross section measurements.

If the more realistic Lennard-Jones potential with parameters ϵ and σ is assumed, and if reasonable values of σ (between 2×10^{-8} and 6×10^{-8} cm) are chosen, undulations of these cross sections about the $v^{-2/5}$ dependence[2] should occur for K-A and K-Xe. The lack of observable undulations is probably due to inadequate velocity resolution, in the case of K-Xe, and to an insufficient velocity range for K-A.

All of the experimental values of C for K-Xe and K-A of Table I are significantly higher than recent theoretical estimates. Dalgarno and Kingston,[13] for example, have estimated C for K-Xe and K-A to be 651 and 268×10^{-60} erg cm^6, respectively, or roughly half the experimental values, and this discrepancy therefore remains unexplained. (Fontana[14] has considered the effects of the dipole-quadrupole interaction, and of retardation, on C for A-A, and shows that at thermal energies neither of these corrections is significant.)

The K-He cross section for our velocity ranges lie in the "high-velocity" region, where the repulsive core is being probed. The K-Ne data are in an intermediate velocity range, where the cross section falls off more steeply than $v^{-2/5}$. This might explain the discrepancy noted by Rothe and Bernstein. They observed that ratios of cross sections were predicted rather well by the theoretical formulas for the dispersion force except for K-Ne, where the predicted cross section was too high. On the other hand, the predicted ratios of cross sections involving K-He should also be in error, but are not. This may be due to the fact that if the $v^{-2/5}$ dependence is extrapolated beyond the region where it applies, it will at some point intersect the rather flat dependence of the high-velocity region. If this intersection fortuitously coincides with the region being measured, cross section ratios in agreement with theory will be obtained.

ACKNOWLEDGMENTS

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[13] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **73**, 455 (1959).

[14] P. R. Fontana, in *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland Publishing Company, Amsterdam, 1964).