Total Collision Cross Sections for the Interaction of Atomic Beams of Alkali Metals with Gases*†

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Total collision cross sections (Q) for the interaction of atomic beams of K and Cs with a number of molecules were measured with an apparatus of $30''$ angular resolution. Although absolute determinations of Q are difficult, relative values are readily obtained ($\pm 3\%$). Results are reported as the ratio (Q^*) of the cross section for a given molecule to that of argon for the same beam atom. Seventy-seven molecules (of varied complexity and reactivity) were studied with K and 16 with Cs beams. Q^* ranged from 0.29 to 2.8.

The data were correlated using the Massey-Mohr theory, assuming an attractive intermolecular potential $V(r) = -C/r^6$. For this case $Q = b(C/v_r)^{2/5}$, where v_r is the relative velocity and b a known constant. C was estimated from standard formulas for the London dispersion and dipole-induced dipole forces, using known refraction and dipole moment data. The theoretical values of Q differ by a nearly constant factor from the experimental results; thus values of Q^* are predicted with good accuracy. The deviation between Q_{calc}^* and Q_{obs}^* was $<\pm 3\%$ for 57% (and $<\pm 10\%$ for 87%) of the molecules. Most of the large deviations occurred for the light gases.

INTRODUCTION

CONSIDERABLE information about intermolecular forces may be obtained from studies of the scattering of a beam of molecules by a gas. The molecular beam method allows for the detection of very small angle deflections; thus the total collision cross section is a measure of the "maximum interaction sphere" of the two molecules.

The results of earlier investigations[1-6] have suggested the need for quantum theory in any proper description of the experimental phenomena. Massey and Mohr[7] have obtained an expression which relates total *elastic* collision cross sections with the intermolecular attractive potential.

Most previous molecular beam cross-section measurements have been confined to a few scattering gases (mainly inert gases and homonuclear diatomic molecules). For these cases, the attractive intermolecular interaction is identified with the London dispersion force only. There appears to be little information in the literature on the general applicability of the theory to scattering by molecules. A number of additional features must be considered in connection with molecular scattering, including:

(1) dipole-induced dipole (and dipole-dipole) forces if one (or both) of the molecules possess a dipole moment,

(2) possible anisotropy of the intermolecular potential,

(3) inelastic scattering involving, e.g., vibrational transitions, chemical reaction,[8] etc.

It was thought to be of interest to examine a large number of molecules, both simple and complex, chemically inert as well as reactive, to investigate the general applicability of the theory and the possible importance of inelastic scattering. The effect of the direct-dipole-dipole and the dipole-induced dipole molecular interactions as well as the dispersion forces ought to be observable.

In the present paper, results are presented for the scattering of beams of K and Cs by a variety of scattering molecules. The total collision cross sections were obtained and compared with values predicted theoretically for elastic scattering. A forthcoming paper will report results for CsCl beams, with particular emphasis on the direct dipole-dipole forces.

APPARATUS†

The schematic arrangement of the main components of the apparatus is presented in Fig. 1. Not shown is the vacuum envelope (8 in. diam., 24 in. long), which is divided by a bulkhead at C into separately pumped regions (the "oven chamber" and the "detector chamber"). Typical operating pressures were 5×10^{-7} and 1×10^{-7} mm Hg in the respective chambers. Large liquid nitrogen traps and baffles were located in each chamber.

The oven A (of Monel) was similar to that of Miller and Kusch,[9] employing their "ideal slit," whose width was 0.0025 ± 0.001 cm. The oven temperature was measured with a Chromel-Alumel thermocouple in a suitable well.

The scattering chamber was somewhat similar to

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† For further details, see Ph.D. dissertation, E. W. Rothe, University of Michigan (1959), available from University Microfilms, Ann Arbor, Michigan.

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[1] W. Mais, Phys. Rev. **45**, 773 (1934).

[2] S. Rosin and I. Rabi, Phys. Rev. **48**, 373 (1935).

[3] P. Rosenberg, Phys. Rev. **55**, 1267 (1939).

[4] I. Rabi, Rev. Sci. Instr. **6**, 251 (1935).

[5] Jawtusch, Schuster, and Jaeckel, Z. Physik **141**, 146 (1955).

[6] K. Kodera and T. Tamura, Bull. Chem. Soc. Japan **31**, 206 (1958).

[7] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A144**, 188 (1934).

[8] E. H. Taylor and S. Datz, J. Chem. Phys. **23**, 1711 (1955).

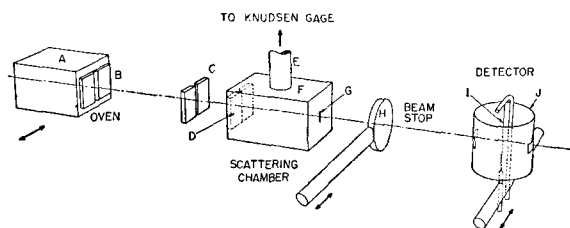[9] R. Miller and P. Kusch, Phys. Rev. **99**, 1314 (1955).

FIG. 1. Schematic view of the molecular beam scattering apparatus.

that of Estermann *et al.*[10] Its collimating slit (D) was similar to the oven slit (B); its width was identical. The inlet and exit channels were each 1.27 cm long, 0.38 cm high and 0.028 cm wide; the central cavity was 2.53 cm in length. The effective scattering path d was taken to be: $1.27+2.53+1.27/2=4.44$ cm.

A conventional Langmuir-Taylor surface ionization detector was used. The tungsten[11] filament (I) was 0.0025 ± 0.0005 cm in diameter and *ca* 5 cm long. It was heated to about 1500°K by 75 ma dc and was biased by $+90$ v relative to the ion collector (J). A preamplifier containing a Victoreen 5800 electrometer tube with a 2×10^{10}-ohm grid resistor was followed by a standard inverse feedback dc amplifier and a 10-mv strip chart recorder. Typical ion currents were in the range of 10^{-10} amp, corresponding to a beam intensity of 6×10^{8} atoms/sec.

The distance from the slit (B) to slit (D) was 11.12 cm; from the latter to the detector (I) was 19.68 cm. The calculated half-width of the unscattered beam at the detector is thus 0.007 cm; the observed value was about twice this value. The angle subtended at the midpoint of the scattering path by the detector wire is about 30″, taken as the nominal resolution of the apparatus.

The scattering gas inlet manifold included a high-vacuum pumping system, a needle valve for controlled leak of the gas from a reservoir into the scattering chamber, and a Knudsen gauge. The gauge and chamber were placed so that the pressure drop in the tubing between them was due only to the very small flow effusing from the scattering chamber, and was therefore negligible. The Knudsen gauge[12] was of the Klumb and Schwartz[13] design. Its calibration was linear (by comparison with an ionization gauge) and virtually independent of the gas composition; its sensitivity was 6.6×10^{-6} mm Hg/mm scale deflection (by calibration with a McLeod gauge). The working range of pressure

in the scattering chamber[14] was from 1×10^{-6} to 2×10^{-4} mm Hg; although the absolute value of the pressure was uncertain by $\pm10\%$, relative values were known to $\pm2\%$.

EXPERIMENTAL PROCEDURE

Optical alignment of the components of the beam apparatus with a telescope preceded final alignment with the beam. The oven contents were degassed about 2 days at *ca.* 125°C. After a period of 20 to 30 min at the desired operating point the oven temperature and beam intensity had stabilized and measurements were begun.

The beam intensity was measured for 10 to 20 values of scattering gas pressures corresponding to 5–95% attenuation of the beam. The beam was interrupted frequently to check the zero line; the 100% transmittance line was recorded before and after each series of points during evacuation of the scattering chamber. Plots of log (I/I_0) *vs* P were usually linear for $I/I_0>0.1$. A typical plot of primary data is shown in Fig. 2.

From the slope S of such lines the total cross section Q may be calculated, using the Rosin-Rabi[2] equation[15]

$$Q=2(\pi)^{\frac{1}{2}}J(z)\ \ln(I/I_0)/n_1d, \qquad (1)$$

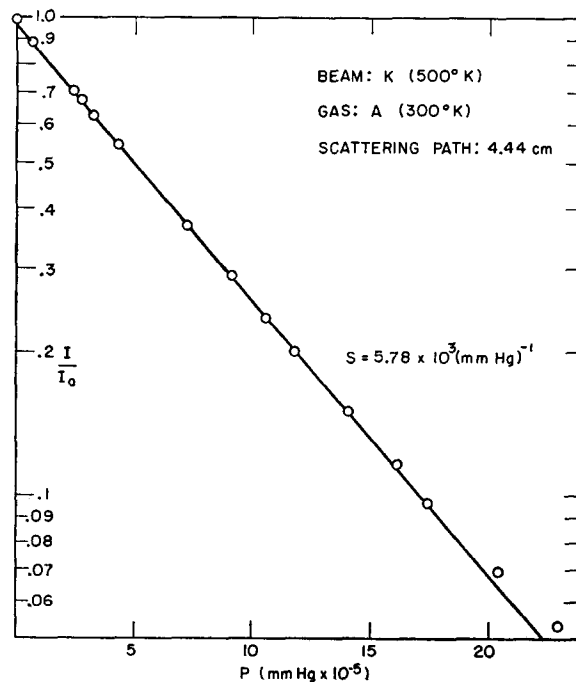
FIG. 2. Typical primary data.

[10] Estermann, Foner, and Stern, Phys. Rev. **71**, 250 (1947).

[11] For some poly-halogen scattering gases (e.g. CCl₄) it was necessary to oxidize the filament (poisoning of the original oxygen-free surface gradually lowered the ionization efficiency).

[12] The gauge was constructed and kindly provided by Dr. G. A. Miller.

[13] H. Klumb and H. Schwarz, Z. Physik **22**, 418 (1944).

[14] A pressure of 5×10^{-4} mm Hg in the scattering chamber yielded no detectable increase (i.e. $<2\times10^{-8}$ mm Hg) in the pressure in the detector chamber.

[15] As pointed out by Rosin and Rabi,[2] this equation is an approximation to the accurate one which involves a tedious numerical integration. Appendix I summarizes a number of calculations which show the validity of the approximation in the present case.

where

$$J(z) = z^2 \int_0^\infty [x^5/\psi(x)] \exp(-zx^2) dx,$$

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

$$z = m_2 T_1/m_1 T_2 \quad \text{and} \quad x = v_2/(2kT_1/m_1)^{\frac{1}{2}}.$$

Here Q is the cross section (cm^2); m_1, m_2 are molecular masses of the scattering gas (1) and beam atoms (2); T_1, T_2 are temperatures (°K) of the gas (1) and beam (2); v_2 is the speed of the beam atom (cm sec^{-1}); $n_1 =$ concentration of scattering gas (molecules cm^{-3}) and d is the scattering path length (cm). For the present measurements $T_1 = 300°$K and $d = 4.44$ cm; thus

$$Q = 5.709 \times 10^{-19} J(z) S, \tag{2}$$

with S in units of (mm Hg)$^{-1}$. $J(z)$ was obtained by graphical interpolation of Rosenberg's[16] table.

It was found that values of Q were not accurately reproducible over long intervals. In a one-year period the apparent cross section of K–A, for example, varied[17] over an extreme range of $\pm 10\%$. However, the ratio of the cross sections of two gases was readily reproduced with a probable erorr of $\pm 3\%$. Data are therefore reported in terms of relative cross sections $Q^* = Q_{12}/A_{A2}$ where Q_{12} and Q_{A2} are the total collision cross sections for beam 2 with gas 1 and with argon, respectively. All values of Q^* represent an average of at least two measurements on different days. To minimize systematic errors due to possible adsorption "memory" effects, different sequences of molecules were used in replicate experiments.

Materials

All scattering gases were purified and characterized before use. Details of purification and physical properties are reported elsewhere,† together with data on the K and Cs used for the beams.

RESULTS

The absolute cross sections for K–A and Cs–A are subject to an overall uncertainty of perhaps $\pm 15\%$, based on a consideration of the numerous systematic errors (including, e.g., the problem of the absolute value of the scattering gas pressure, the scattering

TABLE I. Comparison of Q^* with literature data.

	Present results	Reference 1	Reference 2	Reference 3
K—H$_2$	0.321	0.307	0.302	0.336
K—D$_2$	0.360		0.393	0.430
K—He	0.292	0.283	0.284	0.291
K—Ne	0.40	0.45	0.45	
K—N$_2$	0.97	0.94		1.04
Cs—H$_2$	0.310		0.313	
Cs—D$_2$	0.380		0.383	
Cs—He	0.310		0.283	
Cs—Ne	0.44		0.50	

path length, and the influence of imperfect resolution upon the cross section). The results are as follows:

	Q_{mean}(A^2)	Q_{max}(A^2)
K–A	734	767
Cs–A	857	895,

where Q_{mean} represents the average of all observed values and Q_{max} is the largest observation. These differ significantly from previous results; e.g., Rosin and Rabi[2] found Q_{K-A} and Q_{Cs-A} to be 580 and 572 A^2, respectively. The resolution (30″) of the present apparatus is only slightly better than that (ca 1′) of the earlier investigators;[2] the origin of the discrepancy is not clear. However, the relative cross sections are in fair agreement with previous results. Table I shows a comparison of present values of Q^* with those from three investigations in which results with argon were reported.

The results for all molecules studied are listed in Table II following a description of the procedure used for the theoretical estimation of Q^*.

THEORETICAL ESTIMATION OF Q^*

Massey and Buckingham[18] have applied the Massey-Mohr theory to data[2] on the scattering of alkali beams by He, Ne, and A. From the experimental cross sections they evaluated the attractive potential constant defined on the basis of an inverse sixth-power potential

$$V(r) = -C/r^6, \tag{3}$$

and compared these values of C with theoretical estimates based on the Hellmann[19] formula for the London dispersion force. The discrepancies between calculated and observed values of C ranged from 5–70%.

For the potential function of Eq. (3), the Massey-Mohr expression for the total elastic cross section becomes

$$Q = b(C/v_r)^{2/5}, \tag{4}$$

where v_r is the average relative velocity of the colliding

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[16] P. Rosenberg, Phys. Rev. **61**, 528 (1942).
[17] The changes in Q were probably due primarily to changes in resolution. The largest effects were noted when the slits were cleaned or reset. When the slits began to clog, Q increased (presumably on account of the narrower beam); after cleaning the slits, Q decreased. Improper beam alignment also led to decreased values of Q.

[18] H. S. Massey and R. A. Buckingham, Nature **138**, 77 (1936).
[19] H. Hellmann, Acta Physicochim. U.R.S.S. **2**, 273 (1935).

TABLE II. Summary of results for K.

Molecule	μ	α	C_{disp}	C_{ind}	$10^{-5}\bar{v}_r$	Q_{calc}*	Q_{obs}*
A. Inert gases.							
He	0	0.206	28.7		1.396	0.339	0.292
Ne	0	0.408	57.7		0.826	0.553	0.400
A	0	1.64	223		0.727	(1.00)	(1.00)
Kr	0	2.48	333		0.669	1.21	1.26
Xe	0	4.02	526		0.649	1.47	1.45
B. Diatomic molecules.							
H_2	0	0.806	107		1.874	0.509	0.321
D_2	0	0.796	105		1.393	0.571	0.360
O_2	0	1.57	217		0.753	0.974	0.96
N_2	0	1.74	238		0.771	1.00	0.97
CO	0.1	1.94	264		0.771	1.05	1.04
NO	0.16	1.70	234	1	0.762	1.00	1.06
HCl	1.03	2.58	344	36	0.737	1.23	1.21
HBr	0.79	3.49	460	21	0.671	1.40	1.35
C. Triatomic molecules.							
CO_2	0	2.59	356		0.717	1.21	1.23
CS_2	0	8.08	1057		0.674	1.92	1.80
H_2O	1.84	1.45	199	115	0.848	1.08	0.97
N_2O	0.17	2.92	399	1	0.717	1.27	1.28
H_2S	1.02	3.61	475	35	0.745	1.38	1.31
SO_2	1.62	3.78	514	89	0.686	1.52	1.50
D. Spherical top molecules.							
CF_4	0	2.82	394		0.666	1.30	1.32
SiF_4	0	3.32	462		0.658	1.39	1.40
SF_6	0	4.48	625		0.645	1.58	1.54
CCl_4	0	10.24	1369		0.644	2.17	2.18
$SiCl_4$	0	11.27	1501		0.641	2.25	2.19
$SnCl_4$	0	13.71	1809		0.631	2.44	2.28
E. Hydrocarbons.							
CH_4	0	2.56	342		0.873	1.10	0.97
C_2H_4	0	4.10	547		0.771	1.40	1.30
C_2H_6	0	4.39	587		0.761	1.45	1.31
C_3H_6	0.34	6.04	806	4	0.721	1.68	1.57
C_3H_8	0	6.23	835		0.717	1.70	1.61
$trans$-C_4H_8-2	0	7.87	1051		0.696	1.89	1.79
n-C_4H_{10}	0	8.00	1073		0.693	1.91	1.80
i-C_4H_{10}	0	8.00	1072		0.693	1.91	1.80
cis-C_4H_8-2	0	7.87	1051		0.696	1.89	1.81
C_4H_8-1	0.37	7.82	1046	5	0.696	1.89	1.82
i-C_4H_8	0.49	7.87	1051	8	0.696	1.90	1.82
$cyclo$-C_5H_{10}	0	8.94	1200		0.680	2.01	2.00
n-C_5H_{12}	0	9.77	1310		0.678	2.09	2.03
C_6H_6	0	9.99	1335		0.673	2.11	1.98
$cyclo$-C_6H_{12}	0	10.75	1442		0.669	2.18	2.05
n-C_6H_{14}	0	11.59	1554		0.667	2.25	2.22
$C_6H_5CH_3$	0.37	11.81	1578	5	0.664	2.27	2.26
F. Chlorinated C_2 hydrocarbons.							
C_2H_5Cl	2.02	6.30	843	139	0.685	1.85	1.78
$1,2$-$C_2H_4Cl_2$	1.12	8.12	1088	43	0.661	1.99	2.01
$1,1$-$C_2H_4Cl_2$	2.07	8.16	1092	146	0.661	2.06	2.03
C_2HCl_3	0.94	9.55	1278	30	0.649	2.12	2.11
$1,1,2$-$C_2H_3Cl_3$	1.25	9.97	1335	53	0.648	2.17	2.21
$1,1,1$-$C_2H_3Cl_3$	1.79	10.12	1355	109	0.648	2.22	2.20
C_2Cl_4	0	11.61	1553		0.642	2.28	2.30
s-$C_2H_2Cl_4$	1.36	11.84	1585	63	0.641	2.34	2.34
G. n-Alkyl bromides.							
CH_3Br	1.79	5.44	722	109	0.663	1.75	1.77
C_2H_5Br	2.02	7.33	975	139	0.656	1.98	1.93
C_3H_7Br	2.04	9.13	1216	141	0.651	2.15	2.16
C_4H_9Br	2.04	10.93	1458	141	0.648	2.30	2.28
$C_6H_{13}Br$	1.97	14.51	1939	132	0.642	2.56	2.56
$C_8H_{17}Br$	1.96	18.15	2427	131	0.638	2.79	2.80

TABLE II.—*Continued*.

Molecule	μ	α	C_{disp}	C_{ind}	$10^{-5}\bar{v}_r$	Q_{calc}^*	Q_{obs}^*
H. Halomethanes.							
CH_3F	1.79	2.57	351	109	0.745	1.32	1.27
CH_2F_2	1.96	2.69	371	131	0.702	1.40	1.34
CHF_3	1.64	2.77	384	91	0.680	1.39	1.37
CH_3Cl	1.87	4.44	594	119	0.704	1.61	1.60
CH_2Cl_2	1.62	6.32	847	89	0.668	1.83	1.83
$CHCl_3$	1.02	8.32	1113	35	0.653	2.01	2.01
CCl_4	Listed in D.				0.644	2.17	2.18
CH_3Br	Listed in G.				0.663	1.75	1.77
CH_3I	1.65	7.29	952	93	0.646	1.94	1.90
CF_4	Listed in D.				0.666	1.30	1.32
$CClF_3$	0.46	4.65	640	7	0.658	1.59	1.58
$CBrF_3$	0.65	5.65	774	14	0.645	1.74	1.72
CH_2FCl	1.79	4.51	611	109	0.681	1.64	1.57
CHF_2Cl	1.29	4.44	608	57	0.667	1.60	1.58
$CHFCl_2$	1.29	6.39	865	57	0.659	1.83	1.87
CF_2Cl_2	0.51	6.34	865	9	0.652	1.80	1.81
CH_2ClBr	1.53	7.27	967	80	0.650	1.94	1.97
$CHFClBr$	1.32	7.44	1000	59	0.645	1.95	2.10
I. Miscellaneous molecules.							
NH_3	1.47	2.16	291	73	0.860	1.14	0.99
H_2CO	2.31	2.81	381	181	0.761	1.42	1.28
CH_3OH	1.70	3.25	440	98	0.753	1.40	1.38
CH_3NH_2	1.27	3.92	527	55	0.757	1.44	1.28
$(CH_3)_2CO$	2.85	6.11	826	276	0.693	1.93	1.89
C_3H_5Cl	2.02	7.84	1048	139	0.674	2.01	1.97
C_6H_5Br	1.70	12.89	1716	98	0.643	2.43	2.32

atoms (cm sec^{-1}), and $b=4.662\times10^{11}$ for C in units of erg cm^6. For the present case of beam scattering by molecules one requires an estimate of C.

The long-range molecular interactions may be divided into three types: (a) direct dipole-dipole, (b) dipole-induced dipole and (c) induced dipole-induced dipole (or London dispersion) interactions. To a first approximation all of these are expressible in terms of an inverse sixth-power dependence on the intermolecular distance (for large r). Thus in Eq. (3), $C=C_{d-d}+C_{ind}+C_{disp}$, where

$$C_{d-d}=2\mu_1^2\mu_2^2/3kT, \qquad (5)^{20}$$

$$C_{ind}=\alpha_2\mu_1^2+\alpha_1\mu_2^2, \qquad (6)^{21}$$

and

$$C_{disp}=\frac{3e\hbar}{2(m_e)^{\frac{1}{2}}}\frac{\alpha_1\alpha_2}{[(\alpha_1/N_1)^{\frac{1}{2}}+(\alpha_2/N_2)^{\frac{1}{2}}]}. \qquad (7)^{22,23}$$

Here μ, α, and N refer, respectively, to the dipole moment, the polarizability, and the number of outer shell electrons of each molecule: m_e and e represent the electronic mass and charge, and $\hbar$ and k have their usual meaning. For the molecular beam case Eq. (5)

must be somewhat modified.[24] With reference to the present experiments dealing with K and Cs beams, $C_{d-d}=0$; Eqs. (6) and (7) become

$$C_{ind}=D\mu_1^2, \qquad (8)$$

and

$$C_{disp}=E\alpha_1/[F+(\alpha_1/N_1)^{\frac{1}{2}}], \qquad (9)$$

with μ_1 in Debyes and α_1 in A^3. Evaluating[25] the constants to give C in units of 10^{-60} erg cm^6, one obtains

	D	E	F
K	34.0	855.8	5.832
Cs	42.0	1057.1	6.480.

It is not within the scope of the present paper to offer a critique of the validity of Eq. (7); its obvious advantage is that it requires only a knowledge of

[20] W. Keesom, Physik. Z. **22**, 129 (1921).
[21] P. Debye, Physik. Z. **22**, 302 (1921).
[22] F. London, Z. Physik **63**, 245 (1930).
[23] J. Slater and J. Kirkwood, Phys. Rev. **37**, 682 (1931).

[24] If T_1 and T_2 are the temperatures (°K) of the different species, the appropriate substitution† would be

$$T=2T_1T_2/(T_1+T_2).$$

It is to be noted that Eq. (5) is valid only for

$$r\gg r_{min}=(\mu_1\mu_2/kT)^{1/3};$$

thus for $\mu_1=\mu_2=1D$ and $T=300°K$, $r_{min}=2.9A$; for $\mu_1=1D$ and $\mu_2=10D$, $r_{min}=6.2$ A.

[25] The polarizabilities of K and Cs were taken to be 34.0 and 42.0 A^3, respectively [H. Scheffers and J. Stark, Physik. Z. **35**, 625 (1934)]. The units of μ_1 and α_1 are debyes and A^3, respectively. N is obtained by summing the periodic table group numbers for each constituent atom in the scattering molecule ($N=8$ for the noble gases, except for He, where $N=2$).

TABLE III. Summary of results for Cs.

Molecule	μ	α	C_{disp}	C_{ind}	$10^{-5}\bar{v}_r$	Q_{calc}^*	Q_{obs}^*
He	0	0.206	32.0		1.297	0.301	0.310
Ne	0	0.408	64.3		0.641	0.528	0.440
A	0	1.64	250		0.506	(1.00)	(1.00)
Kr	0	2.49	373		0.416	1.27	1.28
Xe	0	4.02	591		0.382	1.58	1.58
H_2	0	0.806	120		1.802	0.448	0.310
D_2	0	0.796	118		1.293	0.509	0.380
N_2	0	1.74	267		0.568	0.98	0.95
CO_2	0	2.59	398		0.491	1.22	1.21
H_2O	1.84	1.45	223	142	0.670	1.04	1.03
CH_4	0	2.56	383		0.701	1.04	0.98
CF_4	0	2.82	440		0.412	1.36	1.44
SF_6	0	4.48	698		0.376	1.70	1.72
$SiCl_4$	0	11.27	1684		0.368	2.44	2.30
H_2CO	2.31	2.81	426	224	0.555	1.41	1.30
$(CH_3)_2CO$	2.85	6.11	925	341	0.454	2.00	1.87

polarizability. Massey and Buckingham[18] used Hellmann's more complex equation; however this results[19] in no appreciable change in the numerical values for the energy. The denominator of Eq. (7) is nearly constant for all scattering gases with K and Cs (since α_2/N_2 is relatively large); thus C_{disp} is approximately proportional to the polarizability of the scattering molecule. The present results are therefore insensitive to the form of the denominator.[26]

Polarizabilities were obtained from literature data, usually by extrapolating molar refractions from the visible region to $\lambda = \infty$ to obtain P_E; then $\alpha(A^3) = 0.3963 P_E(cc)$. Tables II and III summarize the values of α and μ employed† in the present calculations.

For the evaluation of the average relative velocity Massey and Buckingham[18] used[27] a spherical average of $v^{-2/5}$, in terms of average Maxwellian velocities for the gas and beam particles, respectively. In the present work $\bar{v}_r$ was obtained by averaging all relative velocities of the gas and the beam molecules. The resulting equation [see Appendix II, Eq. (e)] gives values which differ, however, by less than 5% from those obtained using average velocities for gas and beam particles together with the standard formulas[28] for the relative velocity:

$$\bar{v}_r = \bar{v}_2 + (\bar{v}_1^2/3\bar{v}_2) \quad \text{for} \quad \bar{v}_2 > \bar{v}_1;$$

$$\bar{v}_r = \bar{v}_1 + (\bar{v}_2^2/3\bar{v}_1) \quad \text{for} \quad \bar{v}_1 > \bar{v}_2;$$

where

$$\bar{v}_1 = (8kT_1/\pi m_1)^{\frac{1}{2}} \quad \text{and} \quad \bar{v}_2 = (9\pi kT_2/8m_2)^{\frac{1}{2}},$$

respectively. Since Q [according to Eq. (4)] is relatively insensitive to v_r, no important errors result in any case. Tables II and III summarize the results of all experiments and calculations for beams of K and Cs at 500°K and 450°K, respectively. The columns list (for each scattering gas) $\mu(D)$, $\alpha(A^3)$, C_{disp} and C_{ind} (10^{-60} erg cm⁶), $\bar{v}_r$ (cm sec⁻¹), Q_{calc}^* and Q_{obs}^*.

DISCUSSION OF RESULTS

It is of interest to compare absolute values before proceeding to a discussion of relative cross sections. The results are summarized in Table IV.

The experimental values are significantly higher than Q_{calc}. The very high-resolution (5″) experiments of Estermann, Foner, and Stern[10] on the cross section for Cs—He yielded experimental values still higher than the present results. Recent high-resolution experiments of Pauly[29] gave cross sections for K–N₂ and Cs–N₂ of 679 and 908 A², respectively, in fair agreement with the present values.

From an experimental viewpoint the question of resolution certainly needs further attention; at the same time the theoretical estimation of C_{disp} is also in need of refinement.

As seen in Tables II and III, relative cross sections Q_{calc}^* and Q_{obs}^* are in good agreement generally. Points of interest are noted below. In Appendix III a brief theoretical correlation of the data of two other investigations is given.

[26] The same conclusion results from substituting for the denominator a term proportional to $1/I_1 + 1/I_2$ (where the I's are the first ionization potentials of the two species).

[27] R. A. Buckingham (private communication), March 17, 1959.

[28] See, for example, L. Loeb, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1934), p. 95.

[29] H. Pauly, Z. angew. Phys. **9**, 600 (1957).

TABLE IV. Comparison of absolute cross sections (A²).

	$(Q_{obs})_{mean}$	Exptl. ratio K—A/Cs—A	Q_{calc}	Calc. ratio K—A/Cs—A
K—A	734		461	
Cs—A	857	0.86	558	0.83

(A) Inert Gases

The observed values of Q^* are in good agreement with Q_{calc}^* (for both K and Cs), except for Ne, for which the Q_{calc}^* is appreciably higher than Q_{obs}^*. The present value of Q_{obs}^* for Ne is also lower than results obtained by previous workers (Table I), but even these are lower than Q_{calc}^*. No explanation of this discrepancy is offered.[30]

(B) Diatomic Molecules

Good agreement between Q_{obs}^* and Q_{calc}^* is noted for both K and Cs beams, with all scattering molecules except H_2 and D_2, where Q_{calc}^* is seen to be considerably higher than Q_{obs}^*. It may be noted, however, that the *ratios* of the cross sections of H_2 and D_2 for both K and Cs agree closely with the calculated ratios. The potential constants of H_2 and D_2 are virtually identical, so C_{calc}^* is nearly the same for both molecules. Thus the difference in the cross sections is explainable entirely in terms of the relative velocity factor in Eq. (4).

(C) Triatomic Molecules

Q_{obs}^* for H_2O is considerably lower than Q_{calc}^* with K. Because of experimental difficulties with H_2O the experimental results should be accepted with caution.

(D) Spherical Top Molecules

Good agreement of observed and calculated Q^*'s is found for all spherical top molecules. Only for $SnCl_4$ is the discrepancy greater than the $\pm 3\%$ uncertainty in Q_{obs}^*.

(E) Hydrocarbons

A comparison of Q_{obs}^* and Q_{calc}^* for the *n*-alkanes is shown in Fig. 3. The deviations are greatest for the lighter hydrocarbons. Reference to Table II shows no significant differentiation between isomers of hydrocarbons.

(F) Chlorinated C_2 Hydrocarbons

Good agreement between Q_{obs}^* and Q_{calc}^* is noted. Again, isomers are seen to be experimentally indistinguishable.

(G) *n*-Alkyl Bromides

The results are shown in Fig. 3. Agreement is good throughout.

FIG. 3. Comparison of observed and calculated Q^*. K Beam.

(H) Halomethanes

Most of the results are plotted in Fig. 4. Agreement is generally good. The fluoromethane series illustrates the effect of the induction term, C_{ind}. The polarizability increases only slightly in the series from CH_4 to CF_4. CH_4 and CF_4 are non-polar, while the intermediate compounds are polar, giving rise to a C_{ind} term. A maximum in the cross section is thus found for CHF_3. The analogous effect in the chloride series is not observable because the small induction term is masked by the large effect of the polarizability increase.

(I) Miscellaneous Molecules

Fair agreement is noted for most cases. However, apparent cross sections for NH_3, CH_3NH_2, and CH_2O are lower than Q_{calc}^*. Part of the discrepancy may be due to experimental difficulty (similar to the case of H_2O).

SUMMARY OF DEVIATIONS

Of the molecules studied with K and Cs beams, 57% showed deviations (calculated *vs* observed) less than $\pm 3\%$ (the estimated experimental uncertainty). For 18% the deviations were from $\pm 3\%$ to $\pm 6\%$; for 12% the range was from ± 6 to $\pm 10\%$. For 13%

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[30] Any impurity in the neon would lead to a greater apparent cross section, since Ne is the least effective molecule for beam scattering of those studied. Molecules with lower cross section are known, but these have smaller mass (and thus higher speeds), making them more efficient scatterers.
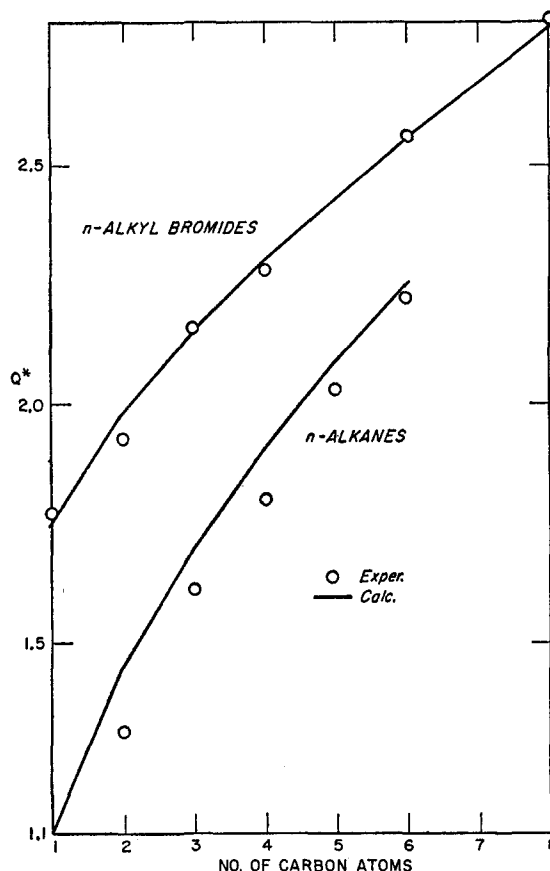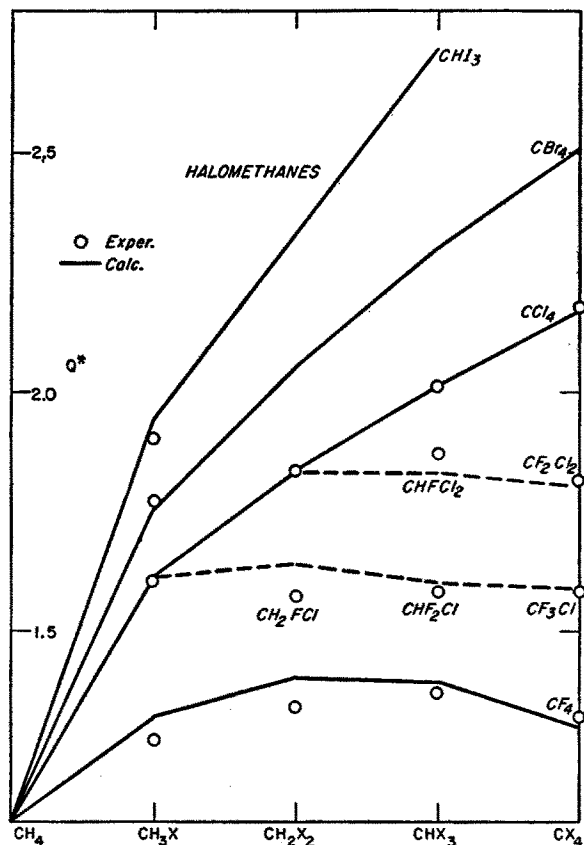
FIG. 4. Comparison of observed and calculated Q^*. K Beam.

deviations were greater than $\pm 10\%$. Most of the large discrepancies occur with the relatively low molecular weight molecules.

CONCLUSIONS

It appears that (1) the principal contribution to the total cross section is that due to elastic scattering, (2) the Massey-Mohr approach represents a sound theoretical basis for discussion of the elastic scattering cross sections, (3) studies of elastic scattering give a rather direct measure of the long-range intermolecular attractive forces and (4) the Slater-Kirkwood approximation for the London force and the Debye equation for the induction force are sufficiently accurate to make useful predictions of potential constants, at least on a relative basis.

ACKNOWLEDGMENTS

APPENDIX I. ACCURACY OF APPROXIMATION FORMULA [EQ. (1)] FOR Q

A number of values of the transmittance I/I_0 have been[†] back-calculated using both the approximate formula [Eq. (1)] and the "exact formula" of Rosin and Rabi.[2] The numerical integrations were carried out using an IBM 650 computer. Values were obtained for K (500°K) scattering in H_2, He, CH_4, A, and $SiCl_4$ (all at 300°K); results were plotted as percent deviation between "approximate" and "exact" transmittance vs the transmittance. In the region normally used for the determination of $Q(I/I_0$ from 1.0 to 0.1) the extreme deviation of I/I_0 is about 5% for H_2 (the worst case). Since the average of the deviations in the desired range is less than this and since a partially compensating correction is needed for argon, the net correction would increase Q^* by ca 1%.

It may be noted, however, that the error would become much more serious at very high attenuations; e.g. at $I/I_0 = 0.02$, errors in transmittance up to 40% may result in some cases.

APPENDIX II. AVERAGE RELATIVE VELOCITY OF BEAM AND GAS MOLECULES

The calculation of $\bar{v}_r$ given below is similar to that[28] for a homogeneous gas except that the different velocity distribution of molecules in the beam must be taken into account.

Consider a molecule of type 2, of speed v_2, moving in a random gas whose molecules (type 1) have a uniform speed v_1. The relative velocity v_r of a molecule of type 2 with respect to type 1, averaged over all directions of molecule 1 is given[28] by

$$v_r = v_2 + (v_1^2/3v_2) \quad \text{for} \quad v_2 > v_1;$$

$$v_r = v_1 + (v_2^2/3v_1) \quad \text{for} \quad v_1 > v_2. \quad \text{(a)}$$

To obtain $\bar{v}_r$, the average v_r obtained from the consideration of all beam and scattering molecule velocities, one makes use of the two velocity distribution functions,

gas: $\quad df_1 = (4/\pi^{\frac{1}{2}}\alpha_1^3) v_1^2 \exp(-v_1^2/\alpha_1^2) dv_1,$ $\quad$ (b)

beam: $\quad df_2 = (2/\alpha_2^4) v_2^3 \exp(-v_2^2/\alpha_2^2) dv_2,$ $\quad$ (c)

where α_i is $(2kT_i/m_i)^{\frac{1}{2}}$.

The average v_r is obtained by substituting these fractions into Eq. (a) and integrating over all velocities,

giving

$$\bar{v}_r = (8/3\pi^{\frac{1}{2}}\alpha_1{}^3\alpha_2{}^4) \left[\int_0^\infty v_2{}^2 \exp(-v_2{}^2/\alpha_2{}^2) dv_2 \right.$$

$$\cdot \int_0^{v_2} [(3v_2{}^2+v_1{}^2)/v_2] v_1{}^2 \exp(-v_1{}^2/\alpha_1{}^2) dv_1$$

$$+ \int_0^\infty v_2{}^3 \exp(-v_2{}^2/\alpha_2{}^2) dv_2$$

$$\left. \cdot \int_{v_2}^\infty [(3v_1{}^2+v_2{}^2)/v_1] v_1{}^2 \exp(-v_1{}^2/\alpha_1{}^2) dv_1 \right]. \quad (d)$$

The result of the integration is†

$$\bar{v}_r = [3/(\pi)^{\frac{1}{2}} \{ (\alpha_2{}^4/2\beta^2\alpha_1{}^3) + (\alpha_2{}^4/\beta^3\alpha_1{}^3)$$

$$+ (\alpha_2{}^2/\beta^3\alpha_1) + (\alpha_1/2\beta^2)$$

$$+ [(\alpha_2/2) + (\alpha_1{}^2/6\alpha_2)][\tan^{-1}(\alpha_2/\alpha_1)] \}, \quad (e)$$

where $\beta = 1 + (\alpha_2{}^2/\alpha_1{}^2)$.

APPENDIX III. THEORETICAL CORRELATION OF Q^* FOR CERTAIN OTHER INVESTIGATIONS

Rosin and Rabi[2] measured total collision cross sections for the scattering of alkali beams in H_2 and D_2; they suggested that the difference in cross sections between H_2 and D_2 is connected with the excitation of rotational levels. From the Discussion (B), the differ-

TABLE V. Ratio of cross sections (Q_{K_2}/Q_K).

Scattering molecule	Est. (a)	Est. (b)	Observed[3]
H_2	1.33	1.26	1.26
D_2	1.35	1.28	1.36
He	1.34	1.28	1.21
A	1.44	1.35	1.20
N_2	1.42	1.35	1.21

The uncertainty in the data is[3] ca. ±5%.

ence in cross section of H_2 and D_2 should be attributable primarily to the velocity dependence of Q. This view is made plausible by the small difference between the $Li-H_2$ and $Li-D_2$ cross sections; here v_r is largely determined by the comparatively high Li speed. The speeds of the H_2 and D_2 are predominant in the v_r calculation for the other alkalis, however. The ratios of Q's for H_2 and D_2 from Reference 2 and as estimated from Eq. (4), respectively, are: Li 1.02, 1.05; Na 1.18, 1.10; K 1.30, 1.12; Rb 1.25, 1.13; Cs 1.22, 1.14. The error in the cross sections was[2] ±4% for Li, Na and K; ca. ±8% for Rb and Cs.

Rosenberg[3] measured the cross section of K and K_2 in a number of gases. A reasonable explanation of his results may be obtained from Eq. (4). Only an assumption about the polarizability of K_2 is needed. Two estimates of this value have been used for this calculation: (a) $\alpha_{K_2} = 2\alpha_K$ and (b) $\alpha_{K_2} = 2^{\frac{3}{2}}\alpha_K$. The resulting ratios of Q's are given in Table V.