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Collision Cross Sections of Hydrogen and of Deuterium

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Total collision cross sections have been measured for hydrogen atoms, with energies between 300 and 800 ev, scattered in room temperature hydrogen, and for deuterium atoms, with energies between 500 and 1150 ev, scattered in room temperature deuterium. The H-H₂ cross section has a pronounced maximum at 600 volts indicating the presence of inelastic scattering. In the case of D-D₂ there is a similar effect, less pronounced, at about 800 volts.

Classical theory has been used to evaluate the repulsive potentials for the two systems on the assumption that smooth curves through the experimental results represent elastic cross sections, and that the atoms and molecules are mass points whose interaction forces are spherically symmetrical. For H-H₂, the present potential has been combined with one previously obtained, and the results represented by

$$V(r) = [0.708 \exp(-29.9r^2) + 0.0607 \exp(-0.942r^2)] \times 10^{-10} \text{ erg}$$

for r between 0.27 and 0.68 Å. The relation for D-D₂ is

$$V(r) = 4.59 \times 10^{-11} \exp(-5.17r^2) \text{ ergs}$$

for r between 0.29 and 0.56 Å. The D-D₂ potential is considerably larger than that for H-H₂ for r between 0.29 and 0.56 Å, but the difference decreases markedly as r increases. It is suggested that the apparent difference in the potentials may result from the assumption of spherical symmetry which, even on a relative basis, does not exist in the present case because of the difference in the nuclear statistics of H₂ and D₂.

HYDROGEN atoms, with energies in the range 200-800 ev, have been previously scattered in room temperature hydrogen¹ and the total collision cross sections so determined used to evaluate the repulsive potential at small separation distances for the H-H₂ system.² In order to ascertain if the approximate equality of intermolecular and intramolecular forces which exists for hydrogen and deuterium at large separation distances, persists at small distances, it was decided to measure the collision cross sections of high velocity deuterium atoms scattered in room temperature deuterium. It was considered desirable to repeat the measurements on hydrogen to ensure that the present cross-section determinations for the two systems were under comparable conditions, as well as to check the earlier work.

The apparatus and experimental procedure was the same as that used in the scattering of high energy argon atoms in argon.³ Since the geometry and, therefore, the angular aperture of the present scattering system differed from that originally used,¹ the present values for the total collision cross sections of hydrogen atoms scattered in hydrogen would not be expected to agree with those previously determined. The repulsive potentials evaluated from the two sets of results, however, might be expected to agree.

Total collision cross sections were determined, as previously, from ratios of beam intensities at two different pressures of scattering gas, and the usual tests were applied for the absence of multiple scattering. A total of 112 cross sections, from 7 to 18 at each voltage, were measured for 300 to 800 ev hydrogen atoms scattered

in hydrogen gas. In the case of the deuterium experiments, 65 cross sections, from 4 to 14 at each voltage, were measured for 500 to 1150 ev deuterium atoms scattered in deuterium gas. Hydrogen and deuterium of 99.9 percent purity were used in the experiments. The final results are summarized in Tables I and II which contain values of \bar{S} , the arithmetic average of all total collision cross sections measured at a given voltage, S , elastic collision cross sections as read from the smooth curves which eliminate the maxima near 600 and 800 volts as shown in Fig. 1, and \bar{L} , the average mean free path at 1 mm of Hg and 0°C computed from the relation

$$\bar{L} = 1/(n\bar{S}), \quad (1)$$

where n is the number of scattering molecules per cm³ at 1 mm of Hg and 0°C. The maxima in Fig. 1 are similar to those previously observed in the scattering of hydrogen atoms by hydrogen, and of argon atoms by argon, and are probably due to inelastic scattering processes such as excitation or ionization. The tabulated values of S satisfy the relations

$$\mu v^2/S^{\frac{1}{2}} = [7.48 \times 10^{-5} \exp(-34.39S) + 8.58 \times 10^{-9} \exp(-4.72S)] \text{ ergs/A} \quad (2)$$

for the H-H₂ system, and

$$\mu v^2/S^{\frac{1}{2}} = [3.04 \times 10^{-8} \exp(-12.60S) + 5.28 \times 10^{-9} \exp(-1.73S)] \text{ ergs/A} \quad (3)$$

for the D-D₂ system, where μ is the reduced mass, and v , the relative initial velocity of the scattering system. These expressions were derived for use in evaluating the repulsive potential, $V(r)$, as a function of the separation distance, r , by a combination of the methods previously used for the case where the potential cannot be represented by $V(r) = K/r^n$ over the required range of r ,^{2b}

¹ I. Amdur and H. Pearlman, J. Chem. Phys. 8, 7 (1940).

² (a) I. Amdur, J. Chem. Phys. 11, 157 (1943); (b) 17, 844 (1949).

³ Amdur, Davenport, and Kells, J. Chem. Phys. 18, 525 (1950).

and where the aperture geometry is determined by several openings in the scattering path.³ The percentage errors in the last column of each table are the probable errors of the \bar{S} and \bar{L} values.

The repulsive interaction potentials derived from the variation of elastic cross section with energy as given in Eqs. (2) and (3) may be represented as follows:

(a) for the system, H-H₂,

$$V(r) = [4.38 \times 10^{14} \exp(-361r^2) + 0.236 \exp(-10.8r^2)] \times 10^{-10} \text{ ergs}(r \text{ in } \text{\AA}) \quad (4)$$

for r in the range 0.32–0.39A;

(b) for the system, D-D₂,

$$V(r) = 4.59 \times 10^{-11} \exp(-5.17r^2) \text{ ergs}(r \text{ in } \text{\AA}) \quad (5)$$

for r in the range 0.29–0.56A.

Recently,^{2b} a relation was obtained for the average H-H₂ repulsive potential,

$$V(r) = [0.567 \exp(-24.9r^2) + 0.215r \exp(-2.40r^2)] \times 10^{-10} \text{ ergs}(r \text{ in } \text{\AA}) \quad (6)$$

for r in the range 0.27–0.68A. Since the range of separation distance for which Eq. (4) is valid is so much smaller than that of Eq. (5), the present results will be combined with those of Eq. (6) to obtain a relation, based on two separate investigations, which is valid over a range of separation distance comparable to that of the D-D₂ system. This relation may be expressed as

$$V(r) = [0.708 \exp(-29.9r^2) + 0.0607 \exp(-0.942r^2)] \times 10^{-10} \text{ ergs}(r \text{ in } \text{\AA}) \quad (7)$$

for r between 0.27 and 0.68A. Equation (7) gives $V(r)$ values which, over the appropriate ranges of r , show an average absolute deviation of 12 percent from values computed from Eq. (4) or Eq. (6). This deviation which

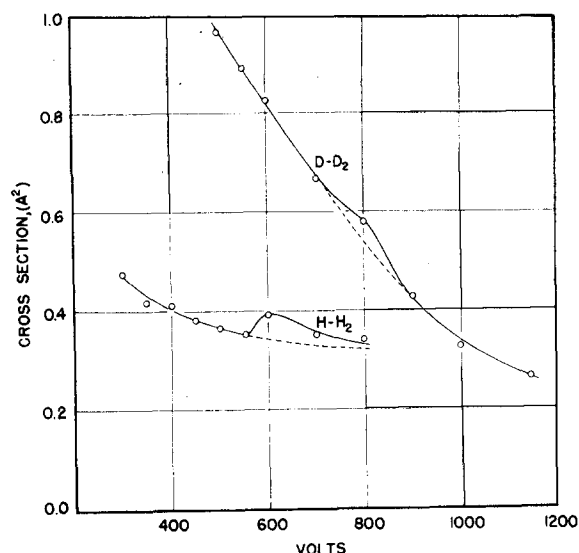


FIG. 1. Total collision cross sections.

TABLE I. Summary of collision cross section results for H-H₂.

Voltage	\bar{S} A ²	S A ²	\bar{L} cm	Percent error (±)
300	0.477	0.472	0.593	1.9
350	0.419	0.432	0.675	1.4
400	0.408	0.404	0.693	1.0
450	0.383	0.383	0.738	1.3
500	0.366	0.367	0.773	1.4
550	0.355	0.356	0.797	1.1
600	0.392	0.346	0.721	0.8
700	0.352	0.332	0.803	1.1
800	0.341	0.323	0.829	2.6

TABLE II. Summary of collision cross section results for D-D₂.

Voltage	\bar{S} A ²	S A ²	\bar{L} cm	Percent error (±)
500	0.967	0.970	0.292	0.8
550	0.898	0.892	0.315	1.0
600	0.827	0.817	0.342	0.6
700	0.669	0.670	0.423	1.2
800	0.579	0.536	0.488	0.7
900	0.428	0.421	0.661	0.7
1000	0.325	0.338	0.870	4.6
1150	0.265	0.263	1.067	3.5

may be due to possible differences in beam composition in the present experiments (arc pressure, 0.23 mm) and in the earlier experiments (arc pressure, 0.3–0.4 mm), is small in comparison with the difference between the $V(r)$ values for H-H₂ and D-D₂ at a given separation distance, as shown graphically in Fig. 2.

For separation distances much greater than those involved in the present experiments, the intermolecular and intramolecular forces for hydrogen and deuterium are nearly equal. Wooley, Scott, and Brickwedde⁴ have summarized the evidence for this conclusion in reviewing experimental measurements and theoretical treatments of viscosity, thermal conductivity, and compressibility of H₂ and D₂, and Hurlburt and Hirschfelder⁵ have shown that band spectra measurements are in accord with the assumption of approximately equal intramolecular forces. In the case of intramolecular forces, evidence is supplied by measurements of the recombination rates of atomic hydrogen and of atomic deuterium.⁶

In the present case, the separation distances between nearest atoms in both systems are smaller than the radius of the first Bohr orbit, 0.53A, as seen in Fig. 2 where r is the distance between the center of the beam atom and the center of gravity of the scattering molecule. Yet, it is somewhat surprising to find the large departure from the approximate equality of interaction potentials observed at larger distances, since widely different potentials have been reported previously only in connection with nuclear interactions, where separa-

⁴ Wooley, Scott, and Brickwedde, J. Research Nat. Bur. Stand. 41, 379 (1948) RP1932.

⁵ H. M. Hurlburt and J. O. Hirschfelder, J. Chem. Phys. 9, 61 (1941).

⁶ I. Amdur, J. Am. Chem. Soc. 57, 856 (1935).

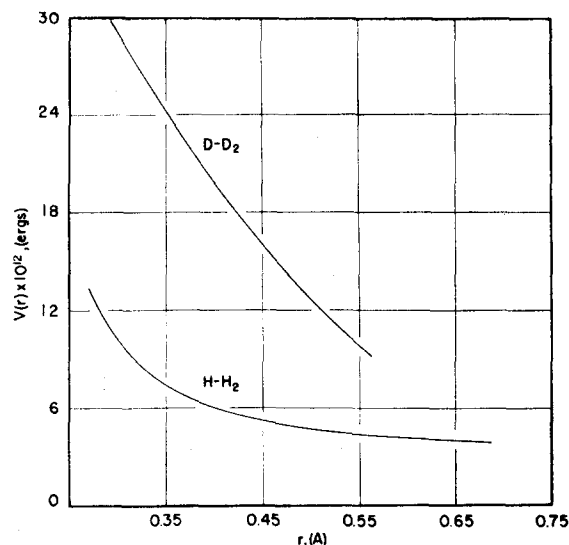


FIG. 2. Average repulsive potentials based on assumption that the atoms and molecules are mass points.

tion distances are extremely small, of the order of 10^{-4} Å. There is the possibility that the difference in potentials shown in Fig. 2 may have its origin in apparatus geometry. For example, the condensers which deflect ions from the partially neutralized beam are located near the detector end of the scattering path and may therefore be relatively inefficient in removing ions from the portion of the scattering path near the atom gun. If the cross section for "umladung" or charge transfer for H^+ in H_2 were appreciably greater than that for D^+ in D_2 , the observed total cross sections for $H-H_2$ could be smaller than those for $D-D_2$ because of greater enhancement of the intensity of the beam of H atoms, relative to that of the D atoms, during passage through the region scattering path above the condensers. Although possible, this explanation does not seem likely for the following reasons: first, at all voltages, the observed total cross sections were found to be independent of scattering pressure, whereas the presence of a significant amount of enhancement of scattered beam intensity resulting from charge transfer would cause a decrease of cross section with increasing scattering pressure, as in the case of multiple scattering; second, results obtained for He scattered in He (to be published later) in a second apparatus where the scattering gas is restricted to a region into which ions cannot penetrate, are in accord with results previously obtained in the present apparatus for the He-He system; finally, the difference between the two potentials in Fig. 2 dimin-

ishes, as anticipated, with increasing separation distance. For example, the $D-D_2$ potential is greater than the $H-H_2$ potential by 18.3×10^{-12} ergs at 0.29 Å, by 12.3×10^{-12} erg at 0.43 Å, and by 4.6×10^{-12} erg at 0.56 Å. If a short extrapolation of the curves is valid, the potentials would appear to coalesce at about 0.69 Å.

The authors suggest that the apparent difference in the two potentials might result from assuming spherically symmetrical force fields in calculating values of $V(r)$ from values of elastic cross sections as functions of voltage. Although this assumption cannot be true in an absolute sense for the systems under discussion, it might, if the systems behaved completely classically, be expected to give correct relative values of the potential, since, at a given voltage, the ratio of the angular velocity of the room temperature molecules to the linear velocities of the high energy beam atoms is the same for the $D-D_2$ and the $H-H_2$ systems. Under these conditions, both D_2 molecules and H_2 molecules would appear to present all orientations (on a number average basis) to the D atoms and H atoms, respectively, during the time in which the particles were within ranges of separation distance where mutual interactions were significant. However, the nuclear statistics of D_2 and H_2 are different, and at room temperature these molecules do not have exactly equal rotational energies as demanded by classical theory.⁷ Thus, the ratios of angular velocity to linear velocity differ slightly and the average configuration in the $D-D_2$ system need not be strictly the same as that in the $H-H_2$ system. Margenau⁸ has shown that at small separation distances, different orientations of the H_2 molecule with respect to the H atom produce very large changes in the magnitude of the interaction potential. It therefore seems possible for a relatively small difference in average orientation in the two systems to be responsible for the marked difference in the apparent potentials at small distances. As the separation distance is increased the effect of orientation would be expected to be of less significance and the assumption of spherical symmetry could lead to correct values of the average interaction potential. If a method could be found for analyzing the experimental results without assuming spherical symmetry, it is conceivable that, even at small distances, the interaction potentials for the two systems would turn out to be the same when referred to the same average orientation or to the same specific orientation.

⁷ A. Farkas, *Orthohydrogen, Parahydrogen, and Heavy Hydrogen* (Cambridge University Press, London, 1935), pp. 17 and 163.

⁸ H. Margenau, *Phys. Rev.* **66**, 303 (1944).