

Argon Repulsive Potential from Collision CrossSection Measurements

I. Amdur, D. E. Davenport, and M. C. Kells

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occupied energy states, of the quantity

$$\frac{1}{|\text{grad}_k E|} \left\{ \frac{\partial^2 E}{\partial k_x^2} \frac{\partial^2 E}{\partial k_y^2} - \left(\frac{\partial^2 E}{\partial k_x \partial k_y} \right)^2 \right\},$$

where, within the confines of a given Brillouin zone, the values of energy (E) which may be assumed by a conduction electron are approximated as the range of a continuous function of the wave vector k , whose components are k_x , k_y , and k_z . (The magnetic field is parallel to the z direction.) It has been re-emphasized by Wallace¹¹ that the "Peierls diamagnetism" of the graphite is strongly dependent upon those electrons which are near the top of the first zone and those near the bottom of the second zone; in addition, Wallace

calculated that the number of electrons in the second zone is only a small fraction of 1 percent of the total number of conduction electrons. One would therefore expect that the removal of these electrons from the second zone would appreciably affect the diamagnetism of graphite; thus the formation of a relatively small number of carbon-bromine covalent or ionic bonds could account for the observed susceptibilities of the bromine-graphite mixtures. This point of view is supported by the fact that the gram susceptibility at room temperature of a bromine-graphite sample containing only 0.05 g Br/g C is 20 percent lower than the susceptibility of pure graphite.

Our data together with those of Rüdorff¹ indicate the possible presence of both molecular bromine and a small number of carbon-bromine bonds in bromine-graphite.

¹¹ P. R. Wallace, *Phys. Rev.* **71**, 622 (1947).

Argon Repulsive Potential from Collision Cross-Section Measurements

I. AMDUR, D. E. DAVENPORT, AND M. C. KELLS

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

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The total collision cross section has been measured for argon atoms, with energies between 300 and 1100 electron volts, scattered in room temperature argon. In the region between 700 and 1000 volts, the cross section shows a maximum indicative of inelastic scattering, probably due to ionization by the high energy atoms.

The repulsive potential between two argon atoms has been evaluated from elastic collision cross sections (deduced from observed values of the total collision cross section) using a method which takes account of the greater probability of small angle scattering by averaging the cross section over the length of the scattering path. The results may be expressed by

$$V(r) = 4.61 \times 10^{-11} / r^{4.38} \text{ ergs}$$

or

$$V(r) = 3.66 \times 10^{-8} \exp(-6.88r) \text{ ergs}$$

for values of r between 1.37 and 1.84 Å.

HIGH velocity argon atoms, with energies in the range 300–1100 electron volts, have been scattered in room temperature argon to obtain experimental values of the total collision cross section, as part of a program for the determination of repulsive potentials at close distances of interaction.

EXPERIMENTAL

The apparatus and experimental procedure were essentially those previously described¹ in connection with the measurement of total collision cross sections of high velocity hydrogen atoms scattered in room temperature molecular hydrogen. In the present experiments, the single-junction radiation thermocouple originally used as the detector was replaced by a forty-junction thermopile kindly supplied for the purpose by Professor L.

Harris.² The receiver surface of the new detector was square, 0.254 cm on a side, and was covered symmetrically with a circular mask, 0.132 cm in diameter. The geometric average angular aperture of the detector was 2.88°, and was computed by averaging linearly, with respect to distance along the beam axis, all half-angles subtended by the detector at its fixed position, 7.738 cm from the origin of the beam. The essential features of the scattering path which determine the geometric average angular aperture are shown in Fig. 1. In calculating the average aperture, it is necessary to take cognizance of the angular limitations imposed by the tip of the second collimating channel, the lower edge of the detector mask, and the edge of the thermopile. This is done by dividing the scattering path into three sections, each characterized by a range of angle, θ_1 , θ_2 , or

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

² L. Harris, *J. Opt. Soc. Am.* **36**, 597 (1946).

TABLE I. Summary of collision cross-section results.

Voltage	\bar{S} A ²	S A ²	\bar{L} cm	Percent error (\pm)
300	10.10	10.52	0.0280	2.7
400	9.91	9.38	0.0286	2.2
500	8.39	8.50	0.0377	2.4
600	7.78	7.78	0.0364	1.7
700	7.39	7.19	0.0383	1.8
800	7.58	6.72	0.0373	1.8
900	7.18	6.37	0.0394	1.8
1000	6.31	6.10	0.0448	1.3
1100	5.85	5.86	0.0484	2.7

θ_3 , through which a beam particle may be scattered and still strike the detector.

Total collision cross sections were computed, as heretofore, from ratios of beam intensities after traversing the scattering path containing argon at two different pressures. A total of 139 determinations were made, from 8 to 24 at each voltage, and the usual tests were applied for the absence of multiple scattering, namely, constancy, at a given voltage, of cross sections computed from runs in which widely different scattering pressures were used. The final results of the present experiments are summarized in Table I which includes 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 curve which eliminates the maximum near 800 volts as shown in Fig. 2, and \bar{L} , the average mean free path at 1 mm of Hg and 0°C computed from the relation

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

where n is the number of scattering molecules at 1 mm of Hg and 0°C. The percentage errors are the probable errors of the tabulated \bar{S} and \bar{L} values. The purity of the argon used in the experiments was better than 99.6 percent.

DISCUSSION

A. Inelastic Scattering

The relative maximum at 800 volts in Fig. 2 is assumed to be due to ionization of the argon scattering gas by the argon beam for the following reasons:

1. In the absence of diffraction effects (a condition which is met in the present experiments since the de Broglie wave-length of the scattering system is extremely small compared to the collision radius), the collision cross section should everywhere decrease with increasing voltage if the repulsive potential between two argon atoms depends only upon the separation distance.

2. Rostagni³ and Berry⁴ have measured ionization cross sections for argon atoms in argon in the energy ranges 0–1000 and 1000–5000 volts, respectively. The absolute values of their cross sections are somewhat

uncertain due to experimental difficulties, but both investigators agree on a value of the order of 1A². Although Rostagni's results do not show the effect, Berry states that the correct ionization curve would exhibit a maximum between 700 and 1000 volts. The smooth curve in Fig. 2 which is taken to represent elastic collision cross sections indicates that the increment in cross section due to ionization at 800 volts is about 0.9A² in agreement with the order of magnitude value of the ionization cross section as determined by Rostagni and by Berry.

Although it is possible that a slight maximum exists near 400 volts, it has not been shown in Fig. 2 since the deviations of the 300- and 400-volt points from the smooth curve are not sufficiently greater than the probable errors shown in Table I.

B. Calculation of Repulsive Potential

Since the angular aperture of the present detecting system is sufficiently large to eliminate diffraction effects, the total elastic cross sections of Table I may be used to calculate the repulsive potential for the A–A system using classical scattering theory. As shown recently in connection with the recalculation of the repulsive potentials for the He–He and H–H₂ systems,⁵ it is necessary to take account of the variation of scattering intensity with angle by averaging the theoretical expression for the total elastic cross section over the entire scattering path, 7.738 cm, in the present case. A procedure for carrying out this averaging process when the potential function, $V(r)$, can be represented by K/r^n , where r is the separation distance, was originally

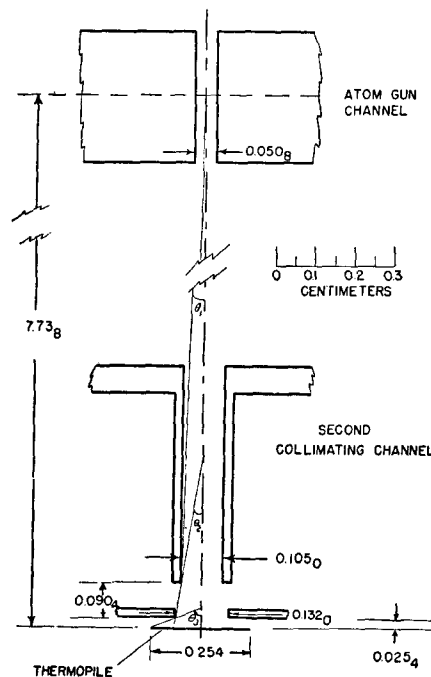


FIG. 1. Details of scattering path.

³ A. Rostagni, Nature 134, 626 (1934); Nuovo Cimento 12, 134 (1935); 13, 389 (1936).

⁴ H. W. Berry, Phys. Rev. 62, 378 (1942).

⁵ I. Amdur, J. Chem. Phys. 17, 844 (1949).

suggested by Simons, Fontana, Muschlitz, and Jackson⁶ and by Simons, Muschlitz, and Unger⁷ and improved by Kells⁸ for the case of small angle scattering which is treated by Kennard.⁹ Kells' treatment is applicable in the present case and leads to the following relations

$$\begin{aligned} S &= (\pi/l) \int_0^l b^2 dx \\ &= (\pi/l) \int_0^l r_0^2 dx - [2K\pi/(\mu v^2)] \int_0^l r_0^{2-n} dx \\ &= (\pi/l) [KC/(\mu v^2)]^{2/n} (\phi - 2\psi/C), \end{aligned} \quad (2)$$

where

$$\begin{aligned} \phi &= \int_0^{7.271} [(7.622-x)/0.0515]^{2/n} dx \\ &+ \int_{7.271}^{7.698} [(7.713-x)/0.0660]^{2/n} dx \\ &+ \int_{7.698}^{7.738} [(7.738-x)/0.1796]^{2/n} dx \end{aligned} \quad (3)$$

and

$$\begin{aligned} \psi &= \int_0^{7.271} [(7.622-x)/0.0525]^{(2-n)/n} dx \\ &+ \int_{7.271}^{7.698} [(7.713-x)/0.0660]^{(2-n)/n} dx \\ &+ \int_{7.698}^{7.738} [(7.738-x)/0.1796]^{(2-n)/n} dx. \end{aligned} \quad (4)$$

Symbols in Eq. (2) which have not been defined previously are: l , length of scattering path, 7.738 cm; x , any point on the scattering path; b , impact parameter defined by $b^2 = [1 - 2V(r_0)/(\mu v^2)]r_0^2$; r_0 , distance of closest approach of centers of beam particle and scatterer; μ , reduced mass of scattering system; v , relative initial velocity of scattering system; and C , a constant, $\pi^{1/2}\Gamma(n/2 + \frac{1}{2})/\Gamma(n/2)$. The separate integrals which appear in Eqs. (3) and (4) arise from the necessity, previously referred to, of dividing the scattering path into three sections as follows: 7.271 cm in which the scattering is limited by the tip of the second collimating channel, 0.427 cm (from $x=7.271$ to $x=7.698$) in which the scattering is limited by the lower edge of the detector mask, and the remaining 0.040 cm of path in which the thermopile surface itself is the limiting factor. For simplicity, it has been assumed that this surface may be approximated by the area of a circle, 0.1796 cm in radius, which can be circumscribed about the actual

square receiver. Since this approximation enters into only 0.040 cm of the scattering path, the error introduced is negligible, less than 0.1 percent.

The potential function is obtained by taking logarithms of both sides of Eq. (2), whereupon a straight line relation should result between $\log S$ and $\log(\mu v^2)$ in which the slope, $-2/n$, gives the index of r , and the intercept, $(\pi/l)(KC)^{2/n}(\phi - 2\psi/C)$, gives the constant, K , in the expression $V(r) = K/r^n$. The extent to which the straight line relation is valid is a direct measure of the ability of the expression K/r^n to represent the variation of potential energy with separation distance. The method of least squares was used to obtain the equation

$$\log S = -0.462 \log(\mu v^2) - 19.2780 \quad (\mu v^2 \text{ in ergs; } S \text{ in cm}^2) \quad (6)$$

whose calculated S values show a maximum deviation of 1.2 percent and an average absolute deviation of 0.6 percent from the values of Table I. Accordingly, the assumed potential form is valid and the required function is

$$V(r) = 1.08 \times 10^{-45}/r^{4.33} \text{ ergs (} r \text{ in cm)} \quad (7)$$

or

$$V(r) = 4.61 \times 10^{-11}/r^{4.33} \text{ ergs (} r \text{ in A)}, \quad (8)$$

for values of r in the range 1.37–1.84 Å. Equation (8) is equivalent, within 0.9 percent, to

$$V(r) = 3.66 \times 10^{-8} \exp(-6.88r) \text{ ergs (} r \text{ in A)}, \quad (9)$$

which is shown in graphical form in Fig. 3.

The potential calculated from Eqs. (8) or (9) is 0.33 that obtained by assuming that the average relative angular deflection of a beam particle which just misses the detector is 5.76° , twice the geometric average angular aperture of the detecting system. This illustrates the importance of calculating potentials by taking account of the distribution of scattered intensity with angle along the scattering path, since the *effective* relative angular aperture for scattering is, in the present case, only one-third of the geometric average relative angular aperture.

After the present experiments had been completed, results on the scattering of 500–3500 electron volt argon

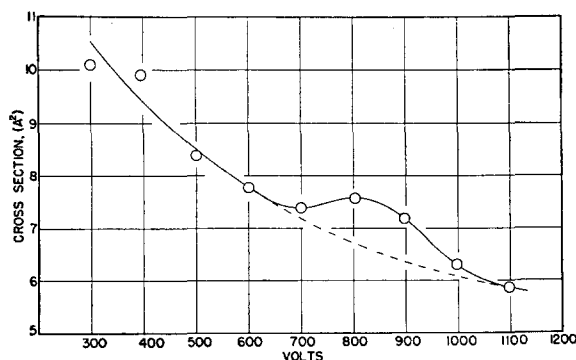


FIG. 2. Total collision cross sections.

⁶ Simons, Fontana, Muschlitz, and Jackson, J. Chem. Phys. 11, 307 (1943).

⁷ Simons, Muschlitz, and Unger, J. Chem. Phys. 11, 332 (1943).

⁸ M. C. Kells, J. Chem. Phys. 16, 1174 (1948).

⁹ E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), pp. 115 ff.

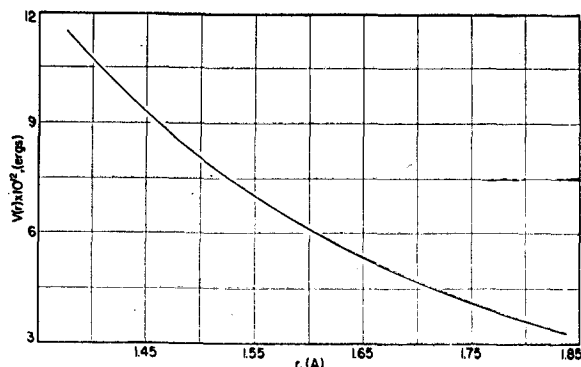


FIG. 3. Repulsive potential between two argon atoms.

atoms in argon were published by Berry.¹⁰ His method involved the measurement of the intensity of scattered beam particles, in terms of the number of secondary electrons ejected from a tantalum detector, as a function of angle over as wide a range as possible. Collision cross sections were calculated from the relation $S = \int_0^\pi f(\theta_r) d\theta_r$, where $f(\theta_r)$ is the polar scattering coefficient for the relative angle of scattering, θ_r , and may be defined by the condition that $f(\theta_r) d\theta_r$ shall represent the fraction of the beam molecules incident on unit area which are scattered by one scattering molecule in all directions making an angle between θ_r and $\theta_r + d\theta_r$ with the direction of the incident beam. Berry deduced a repulsive potential in graphical form for separation distances between 0.6 and 1.2A. Although the potential derived from the present experiments is valid only between 1.37 and 1.84A, comparison of numerical values of the respective potentials at 1.2A and 1.37A indicates that, if the energy range had been extended in the two investigations so as to obtain repulsive potentials covering the same range of separation distance, Berry's potential would be considerably larger than that shown in Fig. 3, but that order of magnitude agreement would exist. It is not possible to account for the disparity without more detailed information than that given in Berry's paper, but the following factors might be responsible for the disagreement: (1) the use of approximate methods to obtain $f(\theta_r)$ for θ_r greater than 90° due to low accuracy in measurement of intensity and angular position at the larger angles; and (2) the effect of the presence of scattering gas upon the efficiency of secondary electron emission from the tantalum detector. The authors feel that, in view of the much greater difficulty in obtaining accurate cross sections by measuring scattered intensities as a function of angle at all angles, as compared with the measurement of axis intensities at two scattering pressures, the probable order of magnitude agreement between the two potentials should not be considered unsatisfactory.

A word of caution seems in order with respect to the danger of extrapolating potential energy functions, derived for separation distances near the minimum, to

¹⁰ H. W. Berry, Phys. Rev. 75, 913 (1949).

the very small distances involved in the scattering of atoms with energies of the order of hundreds or thousands of electron volts. For example, Berry finds that the repulsive portion of a potential function deduced from experimental values of the second virial coefficient by Buckingham,¹¹

$$V(r) = 1.69 \times 10^{-8} \exp(-r/0.273) \text{ ergs } (r \text{ in A}), \quad (10)$$

when extrapolated to $r=0.6$ to $1.2A$, agrees well with his potential. Yet, the repulsive portion of the potential function deduced from the lattice constant and heat of sublimation of solid argon by Herzfeld and Goeppert-Mayer,¹²

$$V(r) = 1.34 \times 10^{-9} \exp(-r/0.345) \text{ ergs } (r \text{ in A}), \quad (11)$$

when similarly extrapolated, gives $V(r)$ values which are eightfold smaller at $0.6A$ and fivefold smaller at $1.2A$ than those of Buckingham. Finally, the repulsive portion of a potential function also deduced from the lattice constant and heat of sublimation of solid argon by Kane,¹³

$$V(r) = 8.30 \times 10^{-7} \exp(-r/0.2091) \text{ ergs } (r \text{ in A}), \quad (12)$$

gives $V(r)$ values which are twenty-six fold greater at $0.6A$ and thirteen-fold greater at $1.2A$ than those of Buckingham. At $3.6A$, which is the approximate distance of closest approach of two argon atoms at room temperature, the energies of repulsion as calculated from Eqs. (10)–(12) agree quite well, the values being 3.2×10^{-14} , 3.8×10^{-14} , and 2.8×10^{-14} ergs, respectively. Since at this distance, the repulsive potential is a minor fraction of the net potential, which is attractive, the agreement among the net potentials is even better due to compensation of the slightly different attractive terms for the discrepancies in the repulsive terms. Because of this compensation, and the fact that the experimental information upon which the potential functions are based are not likely to involve interaction distances much smaller than that at which $V(r)$ is zero, or much larger than that at which $V(r)$ is a minimum (about $3.4A$ and $3.8A$, respectively for argon), the repulsive portion of the potential taken by itself is not of much significance, particularly when extrapolated far beyond the original range of validity. Even in the case of helium, where satisfactory theoretical calculations of the repulsive potential alone have been made for r as small as $1A$, and where the calculated potential and that derived from scattering experiments agree well at $1A$, extrapolation to $0.52A$ results in a discrepancy of over 100 percent.⁵

ACKNOWLEDGMENT

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¹¹ R. A. Buckingham, Proc. Roy. Soc. 168, 264 (1938).

¹² K. F. Herzfeld and M. Goeppert-Mayer, Phys. Rev. 46, 995 (1934).

¹³ G. Kane, J. Chem. Phys. 7, 603 (1939).