On the Cross Sections of Cl_2 and N_2 for Slow Electrons

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Measurements of total cross section for collision of slow electrons between 2 and 40 volts have been carried out in N_2 and Cl_2 by use of a Brode type apparatus. The results for N_2 compare well with those of previous investigators and with the theory of elastic scattering. The cross section of Cl_2 is of order 2000 sq. atomic units with a maximum at 2.65 $\sqrt{V}$, the curve being similar to those for Na, K, Cs and Rb. Application of the theory of elastic scattering indicates that only a small portion of these collisions can be elastic.

1. INTRODUCTION

A NUMBER of researches have been made during the past few years by a variety of methods to determine the "effective cross section for collisions" of atoms and molecules when subject to electron bombardment.[1] This paper concerns itself chiefly with measurements of the total cross section for slow electrons in chlorine. The purpose in undertaking this experiment was several-fold: (i) for completeness, as no cross-sectional measurements for halogen molecules have been reported; (ii) to put the theory of elastic collisions for diatomic molecules[2] to further test, inasmuch as Cl_2 is one of the few molecules for which calculations can be carried through; (iii) to discover whether or not any correlation could be made between the cross sections of H_2 and Cl_2, and that of HCl, as suggested by Brüche;[3] (iv) and, finally, to obtain any further insight into the nature of molecular fields, and the habits of Cl_2, which the experiment might choose to reveal.

2. APPARATUS AND METHOD OF MEASUREMENT

The method adopted was essentially that developed by Brode[4] and used subsequently by Normand[5] and others. The scattering chamber consisted of a cylindrical box constructed of tantalum in which a number of slits on the circumference of a 3.0 cm diameter circle served to define a narrow beam of electrons, focused by means of Helmholtz coils, from the source to the collector (Fig. 1). The source was a 3 mil tungsten filament parallel to the axis of a long 7.0 mm diameter cylinder in which a 0.1 mm slit was made, 5 mm in height. The return lead for the filament came back through this cylinder as close as possible to the filament in order to minimize the magnetic field of the straight wire. The current to the collector, I, was measured by means of a sensitive galvanometer. This current then passed through a second galvanometer which measured the total current from the source slit, assumed to be equal to some constant times I_0. That is

$$I = I_0 e^{-\alpha p x},$$

p being the pressure, x the path length. The absorption coefficient, α, is then related to Q, the total cross section for collision, by $Q = 1.02\ \alpha$ where Q is in square atomic units.

The scattering chamber was mounted in a Pyrex tube, in which precaution was taken against electrical leakage. Provision was made for the gas, first N_2, and later Cl_2, to flow continuously through the tube from a large reservoir.

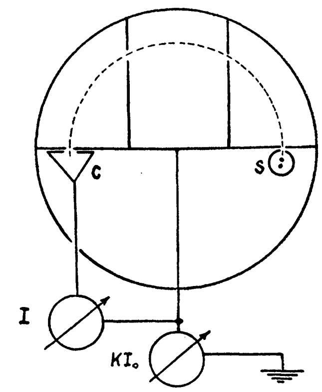

FIG. 1. Schematic diagram of apparatus.

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[1] Ramsauer and Kollath, *Handbuch der Physik*, XXII/2, 243 *et seq.*; R. B. Brode, Rev. Mod. Phys. **5**, 257 (1933).
[2] J. B. Fisk, Phys. Rev. **49**, 167 (1936).
[3] E. Brüche, Ann. d. Physik **82**, 25 (1927).
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[5] C. E. Normand, Phys. Rev. **35**, 1217 (1930).

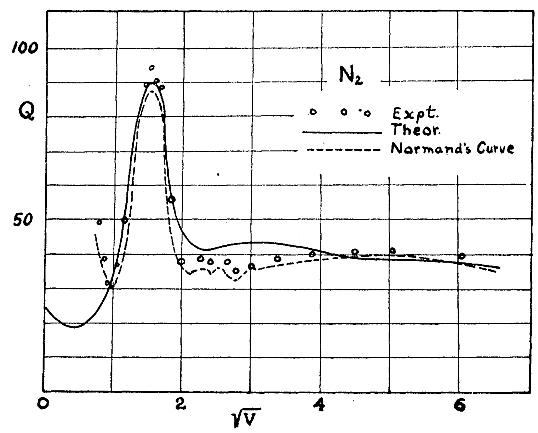

FIG. 2. Total cross section for scattering, Q, as a function of electron velocity in $\sqrt{V}$ for N_2. Circles are expt. points. Solid line is elastic cross section calculated. Dotted line is experimental curve of Normand.

The reservoir pressure, and that in the tube itself, was adjusted by means of ungreased, sealed L stopcocks on which long grooves were filed. Auxiliary pressure control was had by use of a mercury cutoff near the diffusion pump whose inner sleeve was punctured by a series of holes of decreasing diameter ordered vertically.

Pressure was measured by means of a MacLeod gauge. While Boyle's law does not hold accurately to within a few percent for Cl_2, this method of measurement seemed, nevertheless, to be the best available. Great care must be taken, however, that the entire system is free from water vapor. When this is done the reaction of Cl_2 with the Hg of the gauge is only noticeable after several weeks of use, and consistent readings can be made. In the preliminary measurements with N_2, the capillary leaks were calibrated against the MacLeod gauge, thereby offering an auxiliary test of consistency of pressure readings when Cl_2 was used.

Before any measurements were made the tube was thoroughly baked at 450°C. The filament was aged at 2600° for 24 hours. At the end of this aging process a copious emission of electrons was obtained, and reproducible measurements could be made.

The earth's magnetic field was balanced out by a second Helmholtz coil, the electron velocities then calculated directly in terms of the current through the focusing coils and the geometry of the apparatus. This current would be set to focus a particular velocity electron beam, the accelerating potential between filament and source slit then increased until a very sharp maximum was observed from the collector galvanometer. Measurements were taken at several pressures, then plots made of $\ln (KI_0/I)$ *vs.* pressure to determine the validity of the assumption concerning I_0. The slope of the resulting line is $-\alpha x$, from which Q is immediately obtainable.

3. Results of Measurements

The aggressive nature of Cl_2, and the uncertainty occasioned thereby concerning the life of the filament, made it desirable to carry through measurements first with some relatively inert gas. Nitrogen was used for this purpose. The results for N_2 compare very favorably with those of previous investigators, and with the theory of elastic scattering, as will be discussed later. These results are shown in Fig. 2.

Chlorine was then introduced into the system. The procedure followed in filament aging and in measurement was exactly that used for N_2. The

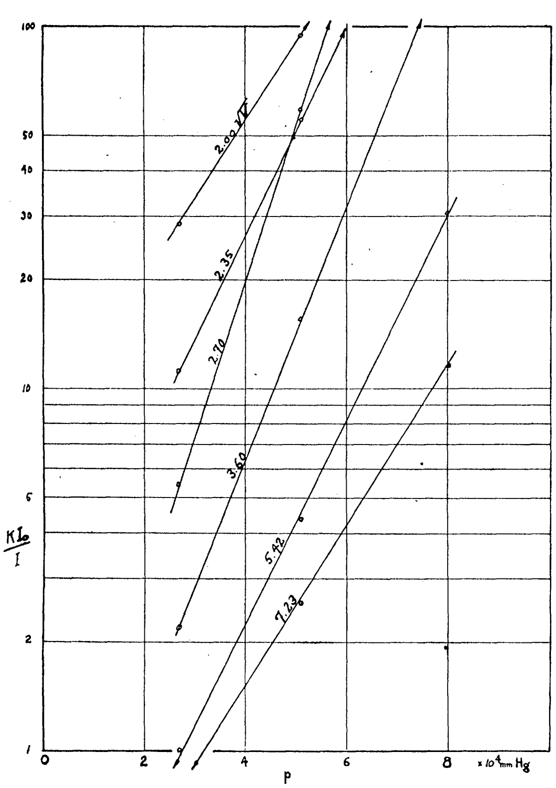

FIG. 3. Logarithmic plot of (KI_0/I) against pressure for Cl_2.

filament evaporated somewhat more rapidly in an atmosphere of Cl_2 than in N_2. It was immediately obvious that the cross sections were very large thereby necessitating the use of a much smaller pressure range for the measurements.

The assumption that the total current leaving the source slit was proportional to I_0 (the current which would be collected at zero pressure or with zero path length) was then put to test. Fig. 2 shows that the assumption is justified inasmuch as the plot of ln (KI_0/I) against pressure results in straight lines. With Cl_2 it was found very difficult to obtain any results below 1.5 $\sqrt{V}$. Fig. 4 shows the total cross section calculated directly from such plots as Fig. 3. The crosses and circle represent two entirely independent sets of data.

4. Interpretation of Results

A. Theory of elastic scattering

The theory of elastic scattering of slow electrons by diatomic molecules has been developed previously[2] and has been applied with considerable success to N_2, O_2 and H_2. The molecular field is assumed to be confined within a spheroid. Solutions of the wave equation inside and outside the molecule are then joined at the boundary, these boundary conditions determining the "phase-defects," δ_{ml}, from which the cross section Q may be calculated:

$$Q=4\pi(d/2)^2\sum_{m,\,l} q_{ml}=(4\pi/k^2)\sum_{m,\,l}(2-\delta_{0m})\sin^2\delta_{ml},$$

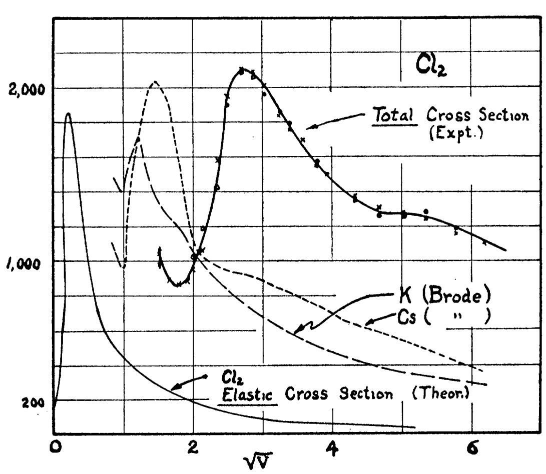

FIG. 4. Total cross section for scattering in Cl_2; with the experimental results of Brode for K and Cs for comparison. The solid line is the theoretical elastic cross section for Cl_2.

where $\delta_{0m}=0$ if $m\neq 0$; d is the internuclear distance; and $k=2\pi/\lambda$. The "phase-defects," δ_{ml}, are given by

$$\tan\delta_{ml} =(-1)^m\left[\frac{R'e^{(1)}{}_{m,\,l}(c,\,\xi_0)-g_{ml}\cdot Re^{(1)}{}_{m,\,l}(c,\,\xi_0)}{g_{ml}Re^{(2)}{}_{m,\,l}(c,\,\xi_0)-R'e^{(2)}{}_{m,\,l}(c,\,\xi_0)}\right],$$

where the $Re_{m,\,l}{}^{(1)\text{ or }(2)}(c,\,\xi_0)$ are spheroidal functions, solutions of the wave equation for $V=0$; and

$$g_{ml}=f'(\xi_0)/f(\xi_0)-(\alpha-c^2)^{\frac{1}{2}},$$

$f(\xi_0)$ being the "radial" part of the solution for $\xi<\xi_0$, i.e., $V\neq 0$, α being $2Zd\xi_0/(\xi_0-1)^2$, ξ_0 the spheroidal boundary and c being $\pi d/\lambda$.

The cross sections may be obtained in terms of a parameter $\beta^2=Z^*\cdot d\cdot\xi_0/4$ where Z^* is an "effective" charge number determined for a given molecule from Slater's rules on shielding constants. For each symmetrical diatomic molecule there is then a unique value of β to determine its elastic cross section. For N_2 the value of β is 1.32, for Cl_2 it is 2.10. Referring to previous calculations of "partial cross sections" as functions of β, the total cross sections for elastic scattering may be obtained as a sum of partial cross sections.

B. Relation of theory to experiment

The solid line of Fig. 2 is the theoretical cross section calculated as above for N_2. The agreement here is excellent. It seems that up to electron velocities of 50 volts nearly all of the scattering is elastic. The experimental curve of Normand[5] is given for comparison.

For Cl_2, however, it is quite a different matter. Theory predicts a very high maximum below 0.5 $\sqrt{V}$, falling rapidly as the velocity approaches zero. This peak is contributed by the $q_{m=0,\,l=1}$ "partial cross section." For fluorine theory gives a similar result. This result is not unlike that obtained for scattering in Na, K, Cs, Rb by Allis and Morse[6] and experimentally by Brode.[1] It is obvious then that either the theory breaks down for Cl_2, or the extremely large cross section ($Q=2100$ at 2.65 $\sqrt{V}$) is due chiefly to several possible types of inelastic collisions. The theory for Na, etc., gives no account for the extremely high maxima observed. Similarity between the cross sections of those elements with one electron

[6] Allis and Morse, Zeits. f. Physik **70**, 567 (1931).

outside a closed shell, the alkali metals, and those with an almost completed shell, the halogens, is not surprising. The fields of both of these groups of elements must spread out much farther than those of any of the other elements. The ratio of the energies at which the high maxima occur in K and in Cl_2 corresponds roughly to the ratio of their ionization potentials. Here, however, any conclusion is difficult inasmuch as the process in Cl_2 is much more complicated than in K.

Even at very low velocities one would hardly expect to check with the theory of elastic scattering for here the probability of capture to form a negative ion would be large. The remainder of the cross section curve must be accounted for by a number of probable events: dissociation (the energy required being but 2.47 V) with the formation of negative ions, ionization, excitation, and excitation of vibration and rotation. It would be interesting to explain by a direct calculation these high and unexplained peaks in the Na, K, Cs, Rb and Cl_2 curves. These involved calculations require approximate wave functions, which at present are not available.

Comparison of the cross section curves of H_2, HCl, and Cl_2 is interesting. H_2 has a maximum of about 60 of these atomic units at 1.5 $\sqrt{V}$, whereas Cl_2 has the value of $Q=2100$ at 2.65 $\sqrt{V}$. HCl, on the other hand, has a peak at 3.5 $\sqrt{V}$ of some 80 sq. atomic units. This comparison only lends weight to the previous conclusion of Brüche[3] that the cross section is determined by the nature of the external shell of electrons; HCl being very like argon.

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Probe Measurements on High Pressure Arcs

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The introduction of a probe in a carbon arc in air at atmospheric pressuie has been found to increase the arc voltage by several volts, the increase being almost independent of the velocity with which the probe is moved, but being a function of probe perimeter. Observation showed that the probe was surrounded by a dark space, with a fairly definite boundary several times the diameter of the probe, which was uninfluenced by the potential applied to the probe. The gas temperature fell from several thousand degrees at the outer boundary of the dark space to a few hundred degrees at the probe surface. The rate of flow of energy to the probe was measured to be about 50 watts per cm length of probe, for a 0.03 cm diameter probe at the center of a 6-amp. arc; calculations show about half the energy was carried by thermal conduction across the dark space, and about half came from recombination of dissociated molecules upon the probe surface.

The interpretation of the probe current voltage characteristic, valid at low pressures, does not apply at high pressures because ions reaching the probe must travel from the arc through the dark space. An insulated probe must have a potential several volts negative with respect to the cathode side of the dark space boundary; from this interpretation, the cathode fall of the arc lies above 10 volts, and the anode fall is about 20 volts. In a 6-amp. arc, the current density in the positive column is about 20 amp. per cm^2; the gradient, 33 volts per cm; and the ion density, above 10^{14}.

Knowledge of low pressure gas discharges has been greatly advanced by numerous investigations in the dozen years since Langmuir showed how the current voltage characteristics of probes could be made to yield information about the distribution of potential, ion density, and electron temperature in such discharges. In attempting to apply the Langmuir probe methods, however, to the study of high pressure positive columns (pressure of a few millimeters or greater) one encounters experimental difficulties at once: the melting of the probe used, or the attainment of a temperature sufficient for thermionic emission. Nottingham overcame these by moving a probe through the arc at a speed so great that the probe never attained a high temperature. Meas-